

EMAC276 Polymer Properties & Design

Time:

MWF, 10:35P.M. - 11:25P.M., spring semester 2023

Location:

Kent Hale Smith 119

Instructor:

Dr. Lei Zhu, Professor of Macromolecular Science and Engineering
Office: Kent Hale Smith (KHS), Room 312, Tel. (216)368-5861
Office hours: Mon. - Fri. 9:00A.M. - 5:30P.M. or by appointment
Email: lxz121@case.edu
Website: <https://case.edu/engineering/groups/leizhu/>

Co-Instructors:

Dr. Andrew Olah, Adjunct Professor
Office: Kent Hale Smith (KHS), Room 423
Tel. O: 216-368-0606, C: 216-272-0505, Email: amo5@case.edu
Office Hours: M-W-F (preferably by appointment)

Teaching Assistants:

Nathan Maslowski: Email: nam139@case.edu

Course Description (3 credits): The course reviews chemical and physical structures of a wide range of applications for synthetic and natural polymers, and addresses “Which polymer do we choose for a specific application and why?” We examine the polymer properties, the way that these depend on the chemical and physical structures, and reviews how they are processed. We aim to understand the advantages and disadvantages of the different chemical options and why the actual polymers that are used commercially are the best available in terms of properties, processability and cost. The requirements include several written assignments and one oral presentation.

Prerequisite: ENGR 145 and EMAC 270.

Course Objectives:

This course serves as an introduction to the synthesis, properties, design and applications of industrially relevant synthetic polymers, which include polyolefins (e.g., polyethylene and polypropylene), vinyl polymers [e.g., polystyrene, poly(vinyl chloride)], diene polymers (e.g., rubbers), polyesters, polyamides, polyimides, silicone polymers, polyurethanes, epoxy polymers, etc. We aim to achieve the following objectives:

- i) Understand industrial scale synthesis of certain important polymers; *← Taught, not tested*
- ii) Understand the basic structure and properties of these polymers. These properties include thermal, mechanical, melt viscosity, and electrical properties;
- iii) Know the design of polymeric materials and their applications. In particular, know how polymer products work.
- iv) Be able to design a component (structural or otherwise) to be made from polymers, reflecting a practical understanding of ultimate thermal and mechanical properties of relevance to an application.

Optional Textbook:

D. Feldman and A. Barbalata, *Synthetic Polymers: Technology, Properties, Applications*; Chapman & Hall: London, 1996.

This book can be used as a general reading, and you are not required to purchase it. Some closely related chapters will be posted on Canvas. If you need the book, you can borrow through Case library (only one copy) or Ohiolink.

Study Groups:

Study groups will consist of ~5 students. The purpose of the study groups is to provide peer-support from the homework and to work as a team on a project related to materials specification and selection.

Grades:

Homework: 15%

In-class quizzes: 10%

Final design project: 15% (oral 7% + report 8%)

Mid-term and final exams: 30% + 30%

Homework Assignment and In-class Quizzes:

Given the nature of this course, which is qualitative and information-based, we do not intend to give conventional homework assignment. Instead, take-home reading materials or online searching will be used. Short essay and in-class quizzes will be used to assess the reading and searching results.

Homework will be collected one week after being assigned. Although the homework will be graded, the homework/quiz grades will represent only a small part (25%) of your final grade. The homework you turn in should be your work alone; however, you are encouraged to discuss the homework in study groups. Generally, we will not answer questions concerning the homework. We expect that you will learn the material better by working through the homework on your own or with the study group. **Late homework will be penalized 4% per weekday or weekend (Saturday + Sunday). No homework will be accepted after May 1st, 2023.**

Exams:

There will be two exams at the end of each teaching period by Prof. Olah and Prof. Zhu. These exams will not be cumulative.

Final Project:

Each study group is responsible for a project involving materials specification and selection. An oral presentation (10 min) will be given at the end of the class. Details will be announced in class.

Emphasis on Ethical Considerations:

Cheating in any formats in exams, quizzes, and homework assignment is strictly forbidden throughout the course. Whoever commits cheating will be fully responsible for the consequences.

EMAC 276 Polymer Properties & Design - 2023

Dates in 2023	Subjects	Homework
Jan. 17 – 27 (Dr. Olah)	<u>Introduction to Polymer Industry</u> <u>Hierarchical Structures</u> <u>Mechanical Properties of Polymers</u> <u>Styrenic Polymers</u>	Assignment #1 Due on Feb. 3
Jan. 30 – Mar. 10 (Dr. Olah) (Prof. Zhu will cover Feb. 3-10)	<u>Polyolefin Polymers</u> <u>Vinyl Polymers</u> <u>Diene Polymers</u> <u>Silicone Polymers</u>	Assignment #2 Due on Mar. 3
Mar. 10	<u>Exam #1</u>	
Mar. 13 - 17	Spring Break	
Mar. 20 – May 1 (Dr. Zhu)	<u>Polyesters: Thermal Plastic and Thermosets</u>	Assignment #3 Due on Mar. 31
Mar. 6 – May 1 (Dr. Zhu)	<u>Polyamides and Polyimides</u> <u>Polyurethanes</u> <u>Epoxy Polymers</u>	Assignment #4 Due on Apr. 14 Assignment #5 Due on Apr. 28
Apr. 28 and May 1	<u>Final Project Presentation:</u> Please use what you have learned in this course to design a polymer project that can replace wood, metals or ceramics	Final project report Due on May 1
May 4-11	<u>Exam #2</u>	
May 13	<u>Final Grades</u>	

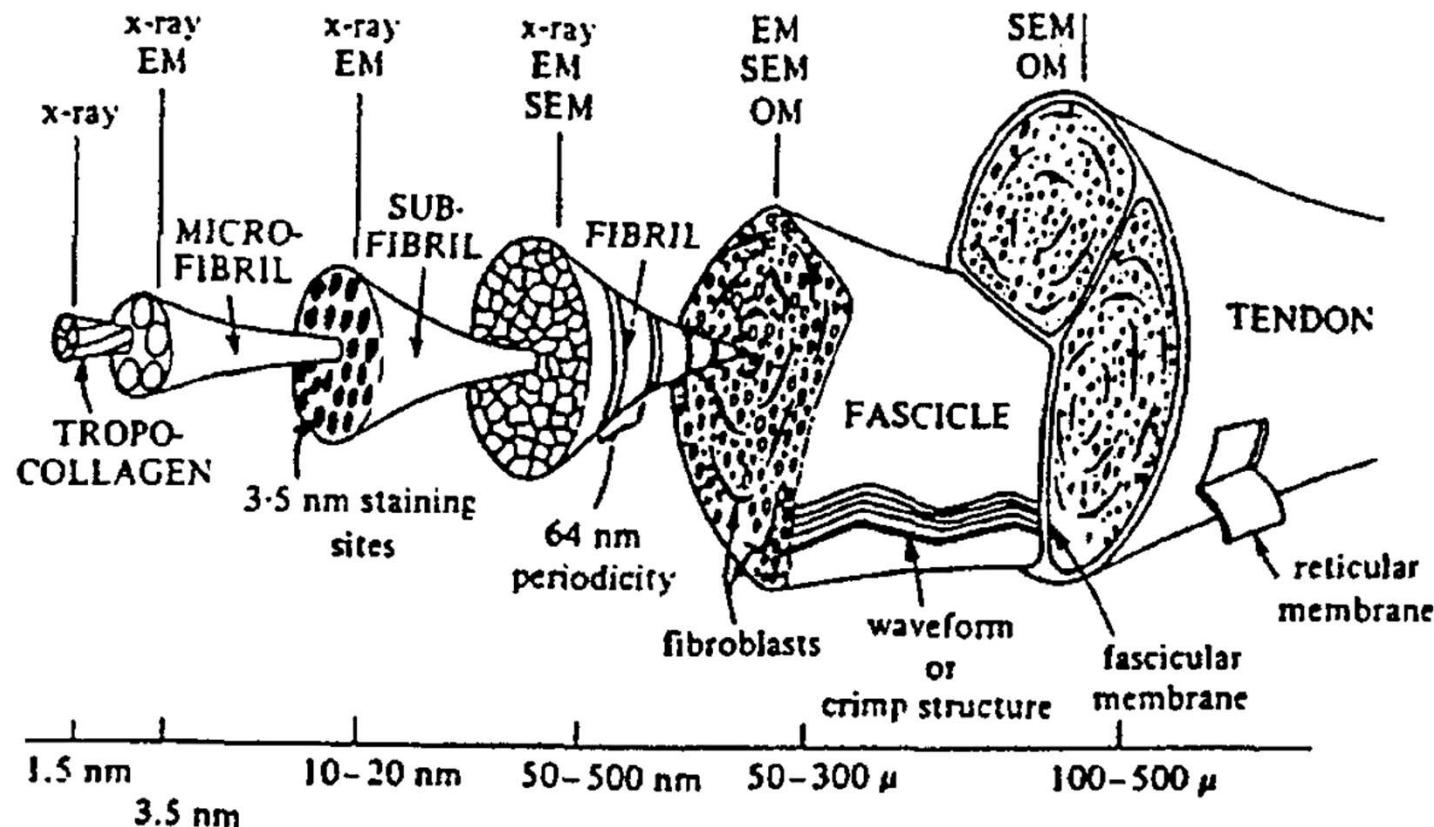
Note: If possible, we will arrange two lab observations for: i) multilayer coextrusion of polymer films (Kent Hale Smith Bldg.) and ii) 3D printing of polymers (Thinkbox). These will help you understand some of the course content and broaden your knowledge.

EMAC 276

Lesson 1 & 2: Lessons From Biology: Hierarchical Structures

**Prof. Eric Baer, Dr. Andy Olah, Prof. Lei Zhu
January 10 & 12, 2022**

Example of a Biological Hierarchical Structure: Tendon (1978)



- Tendons operate reversibly at uniaxial tension.
- The hierarchical structure absorbs energy and protects the tendon as a whole from catastrophic failure.

Diamant, J., Keller, A., Baer, E. L. H. M., Litt, M., & Arridge, R. G. C. (1972). Proceedings of the Royal Society of London 180(1060), 293-315.

Dale, W. C., Baer, E., Keller, A., & Kohn, R. R. (1972). Cellular and Molecular Life Sciences, 28(11), 1293-1295.

Niven H., Baer E., Hiltner A. (1982). Collagen Rel. Res., 2, 131-142.

Kastelic, J., Galeski, A., Baer, E. (1978). Connective tissue research, 6(1), 11-23.

Lakes R. Nature. (1993), 361(6412):511-5.

What is Meant by Hierarchical Structure



Q:z

- Hierarchical structures are assemblages of molecular units or their aggregates that are embedded or intertwined with other phases, which in turn are similarly organized at increasing size levels
- Such multilevel architectures are capable of conferring unique properties to the structure. Hierarchical structures can be prepared from metals, ceramics, or polymers, or from hybrids of various classes of these materials.
- The unifying theme for all types of materials is the pervasiveness of hierarchical structures in practically all complex systems, particularly naturally occurring ones.

Design Principle in Biological Materials: Rules for Complex Assemblies (1994)

Know

1. Scale

- The structure is organized in discrete levels or scales.

2. Interaction

- The levels of structural organization are held together by specific interactions between components.

3. Architecture

- Highly interacting levels are organized into an oriented hierarchical composite system that is designed to meet a complex spectrum of functional requirements.
- The more complex the structure, the more functions it has.

Outline

- 1. Hierarchical Structures in Animals**
 - a. Mammalian Hierarchical Systems
 - b. Photonic Layered Systems — Butterfly Wings
 - c. Inorganic/Organic Layered System — Nacre Shells and Bone
- 2. Hierarchical Structures in Plants**
- 3. Polymeric Hierarchical Structures and Others**
- 4. Complex Assembly in Biological Materials**

Outline

1. Hierarchical Structures in Animals

a. Mammalian Hierarchical Systems

- i. Tendon
- ii. Human Hair

b. Photonic Layered Systems

c. Inorganic/Organic Layered Systems

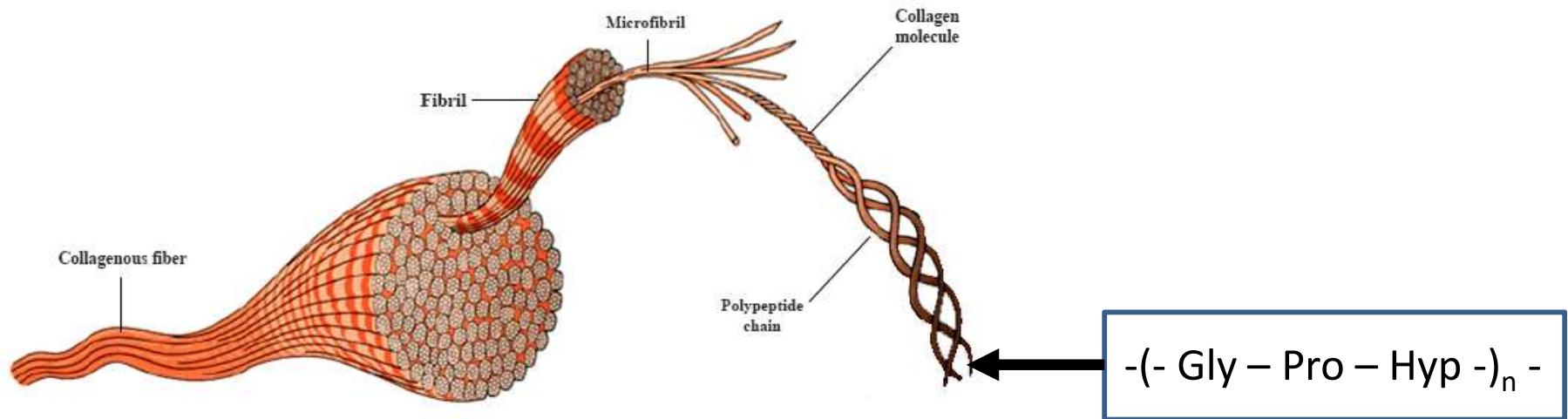
2. Hierarchical Structures in Plants

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Uniaxial Mechanical System: Tendon

Structure of collagen

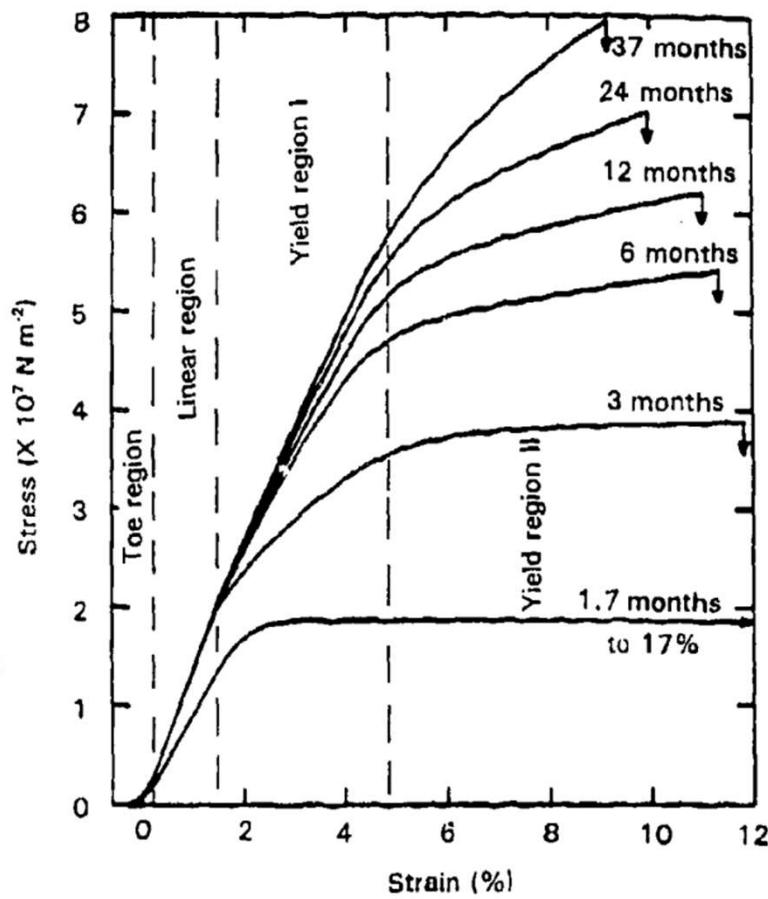
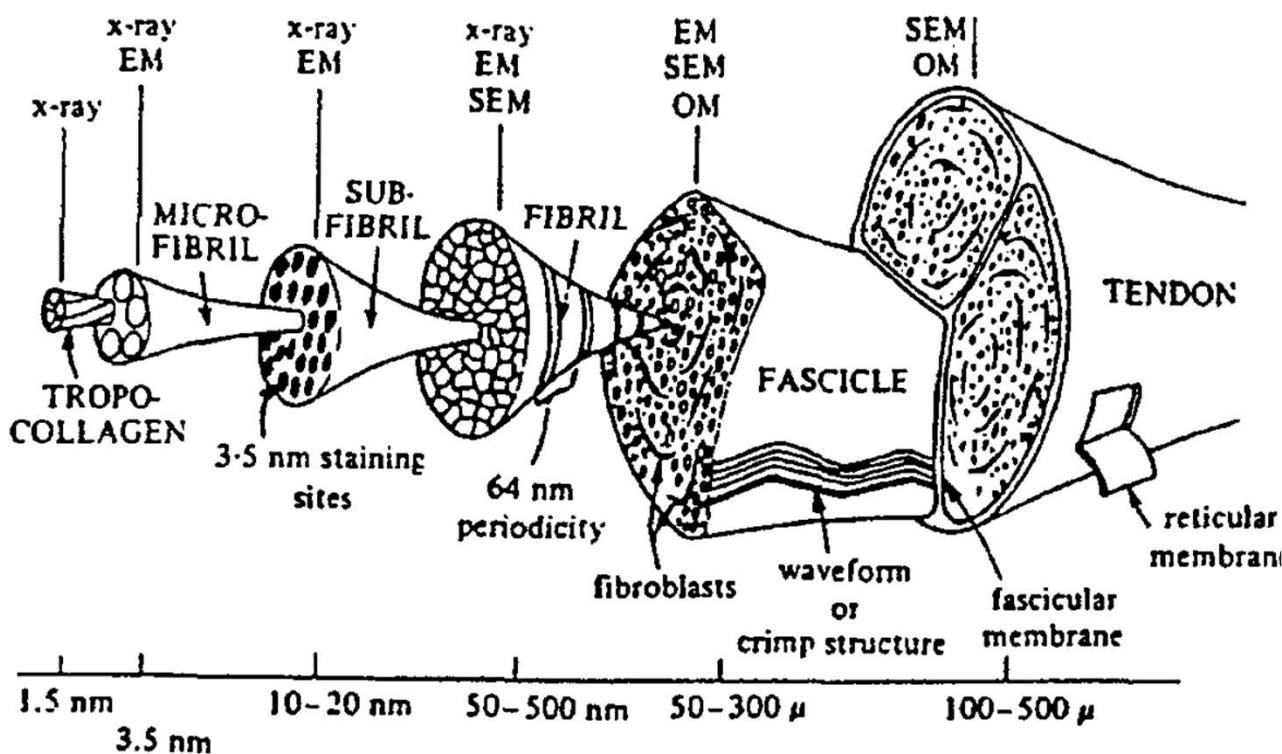


Collagen consists of three polypeptide chains. These so-called α -chains are wrapped around each other to form triple-helical macromolecules: a unique structure, size and amino acid sequence.

In collagenous sequences, glycine (Gly) is present as every third residue. This enables the formation of the three chains into a triple-helical structure. Thus, the common feature for all collagens is a sequence that can be expressed as $(\text{Gly}-\text{X}-\text{Y})^n$, where X and Y are frequently represented by proline (Pro) and hydroxyproline (Hyp), respectively.

This sequence is necessary for the collagen to assemble the fibrils that subsequently form fibers, providing unmatched structural integrity for the extracellular matrix of conjunctive tissues.

Uniaxial Mechanical System: Tendon (1978)

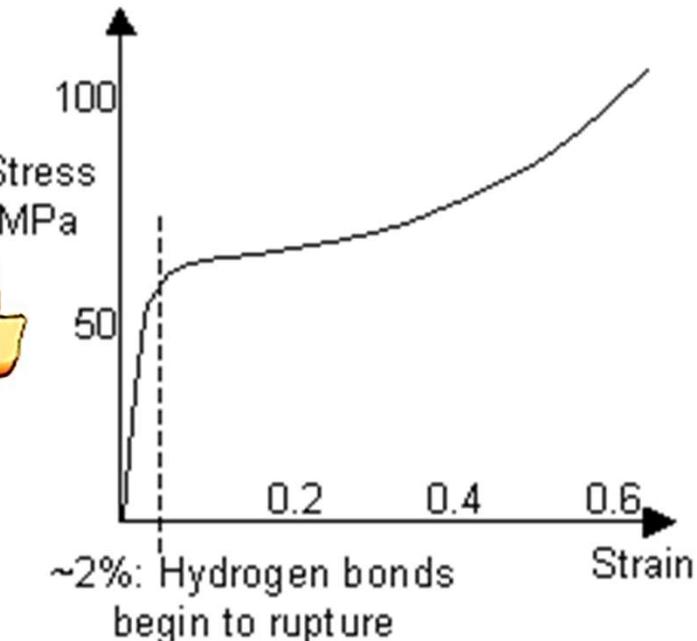
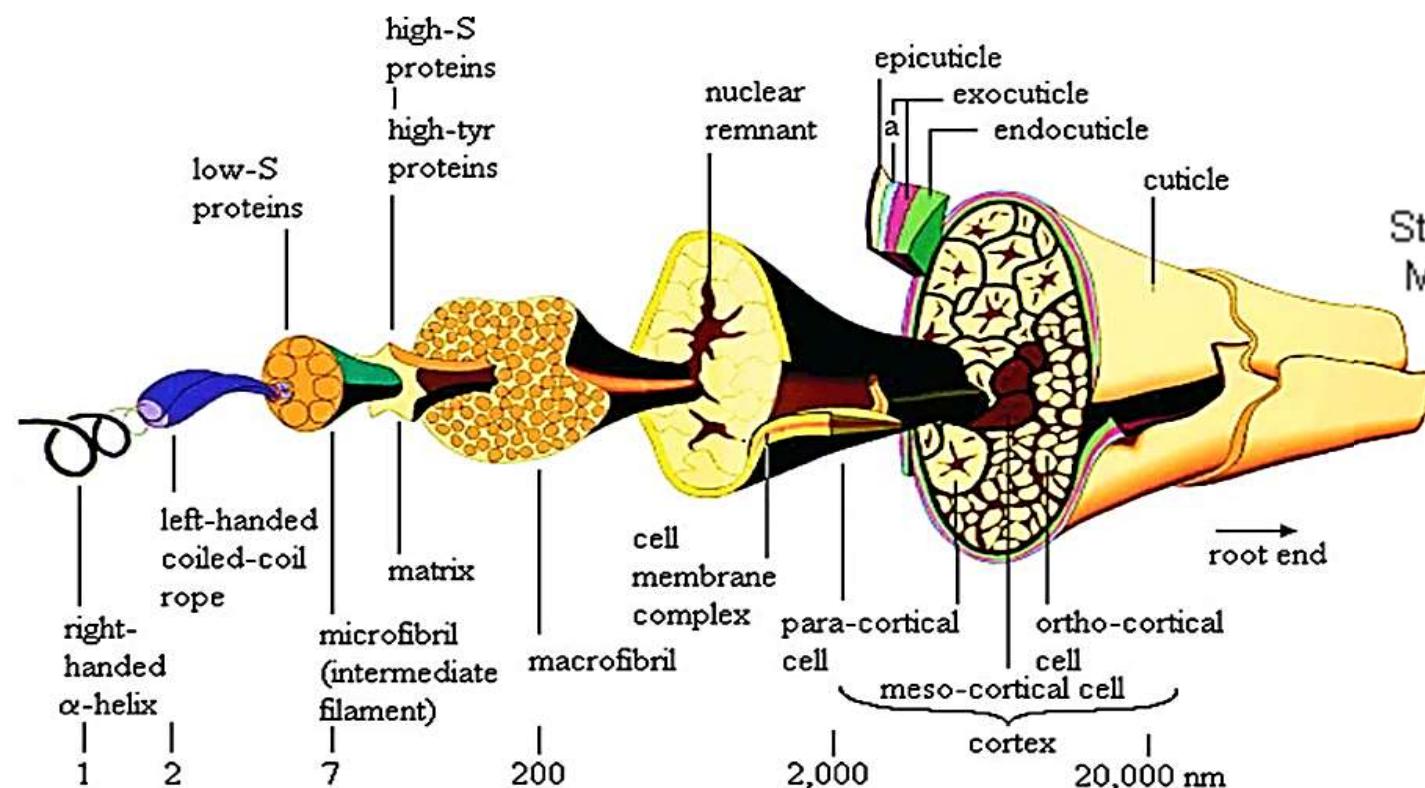


Stress-strain behavior of rat tail tendon as a function of age

- Tendons operate reversibly at uniaxial tension.
- The hierarchical structure absorbs energy and protects the tendon as a whole from catastrophic failure.

Diamant, J., Keller, A., Baer, E. L. H. M., Litt, M., & Arridge, R. G. C. (1972). Proceedings of the Royal Society of London 180(1060), 293-315.
 Dale, W. C., Baer, E., Keller, A., & Kohn, R. R. (1972). Cellular and Molecular Life Sciences, 28(11), 1293-1295.
 Niven H., Baer E., Hiltner A. (1982). Collagen Rel. Res., 2, 131-142.
 Kastelic, J., Galeski, A., Baer, E. (1978). Connective tissue research, 6(1), 11-23.
 Lakes R. Nature. (1993), 361(6412):511-5.

Uniaxial Mechanical System: Human Hair (2002)



- Hair is a proteinaceous fiber with a strongly hierarchical organization of subunits, from the α -keratin chains, via intermediate filaments, to the fiber.
- Human hair is stronger than Nylon 6 fiber.

Astbury, W., Street, A., (1931). General. Phil. Trans. Roy. Soc. A 230, 75–101.
Popescu, C., Höcker, H. (2007). Chemical Society Reviews, 36(8), 1282-1291.
Feughelman, M. (2002). Journal of Applied Polymer Science, 83(3), 489-507.

Outline

1. Hierarchical Structures in Animals

- a. Mammalian Hierarchical Systems
- b. **Photonic Layered Systems**
 - i. Butterfly wings
 - ii. Beetle elytra
 - iii. Inorganic/Organic Layered Systems

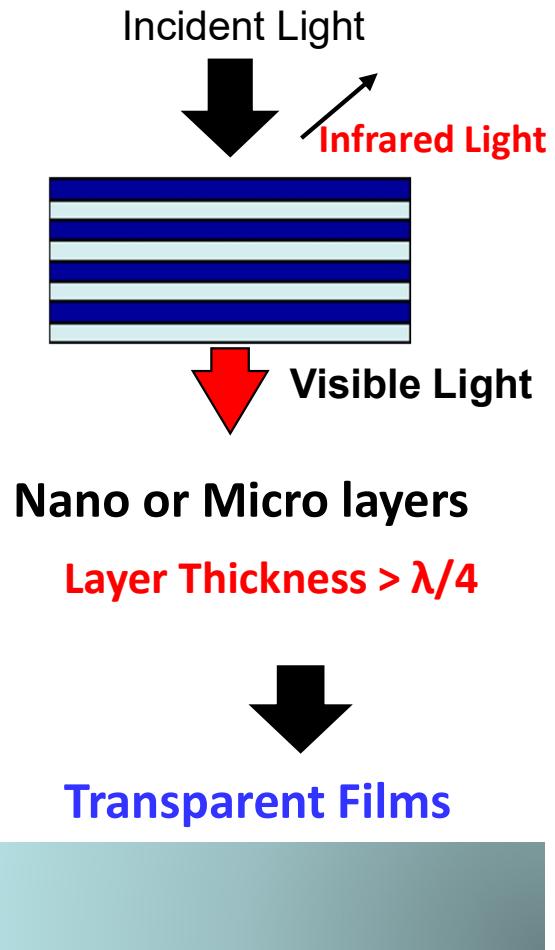
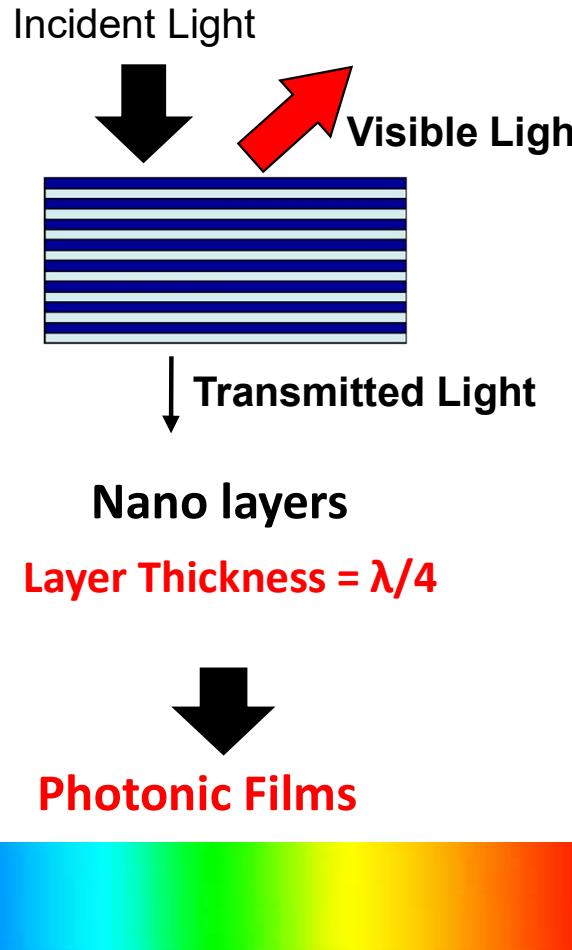
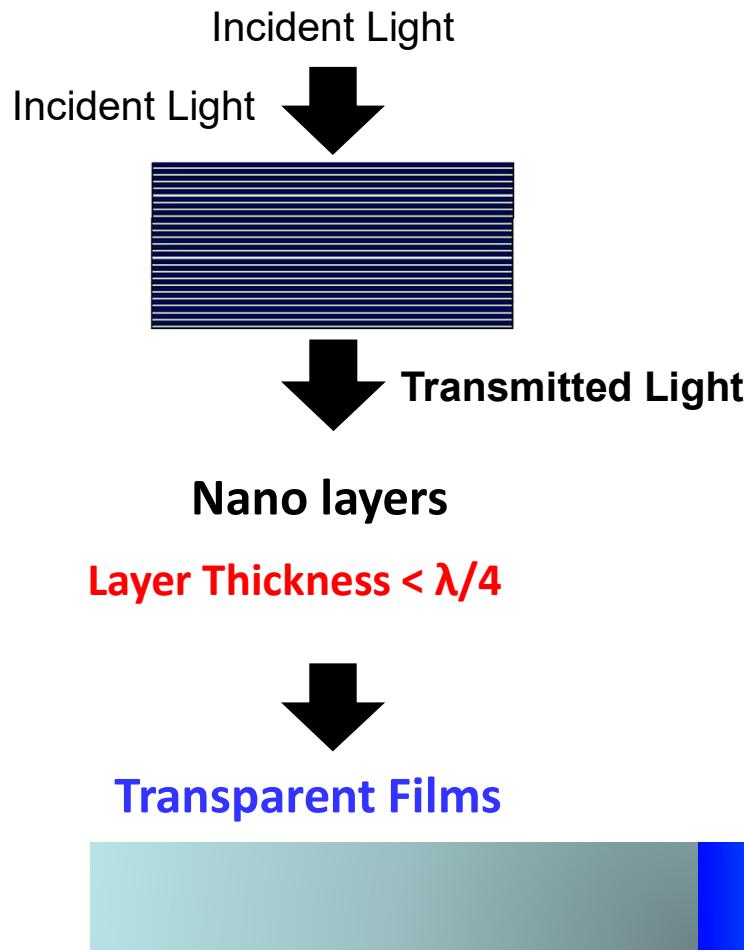
2. Hierarchical Structures in Plants

3. Complex Assembly in Biological Materials

4. Polymeric Hierarchical Structures and Others

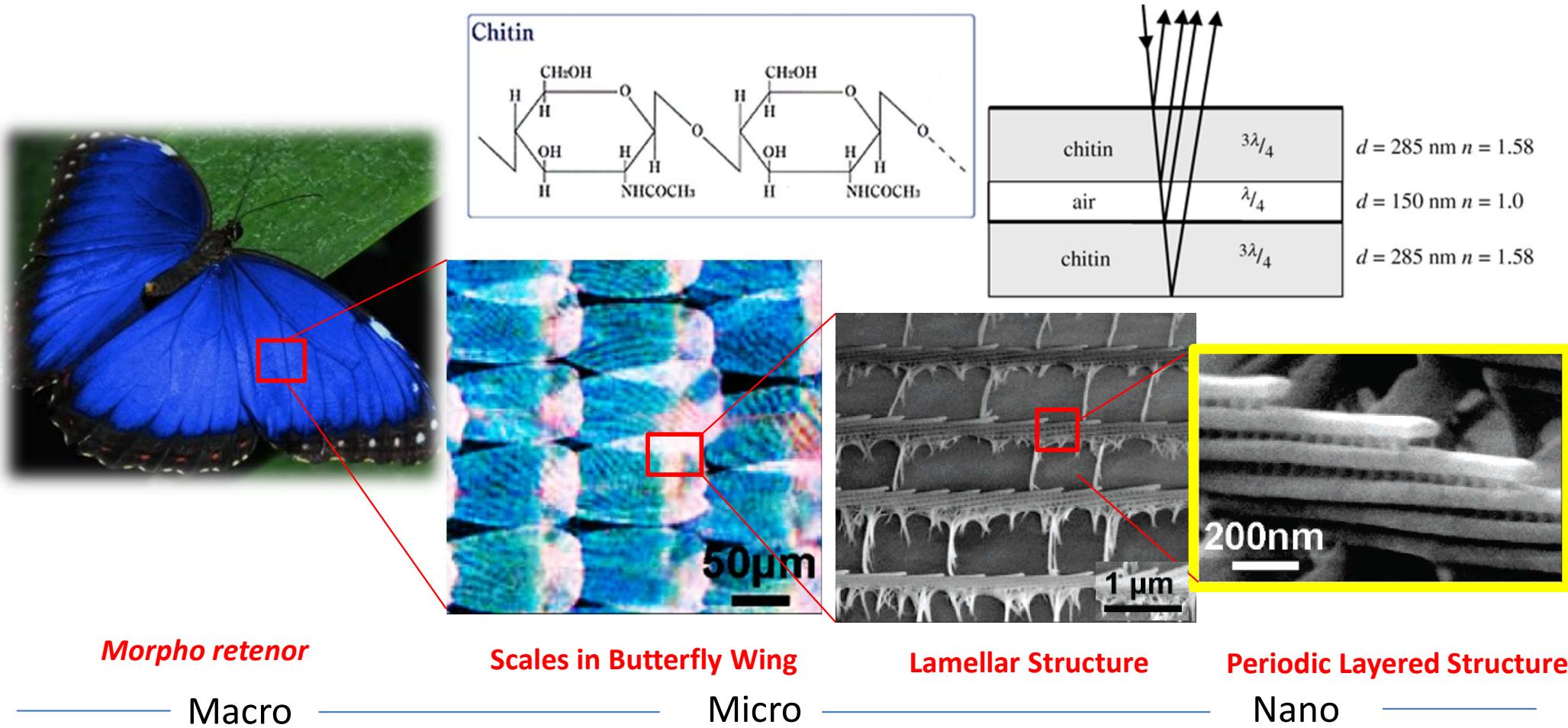
Optical Effects in Multilayer Structures

$$n_A - n_B \geq 0.05, \lambda = \text{visible light}$$



- The optical effects of multilayered structures change with layer thickness.

Photonic Layered Systems: Butterfly Wings

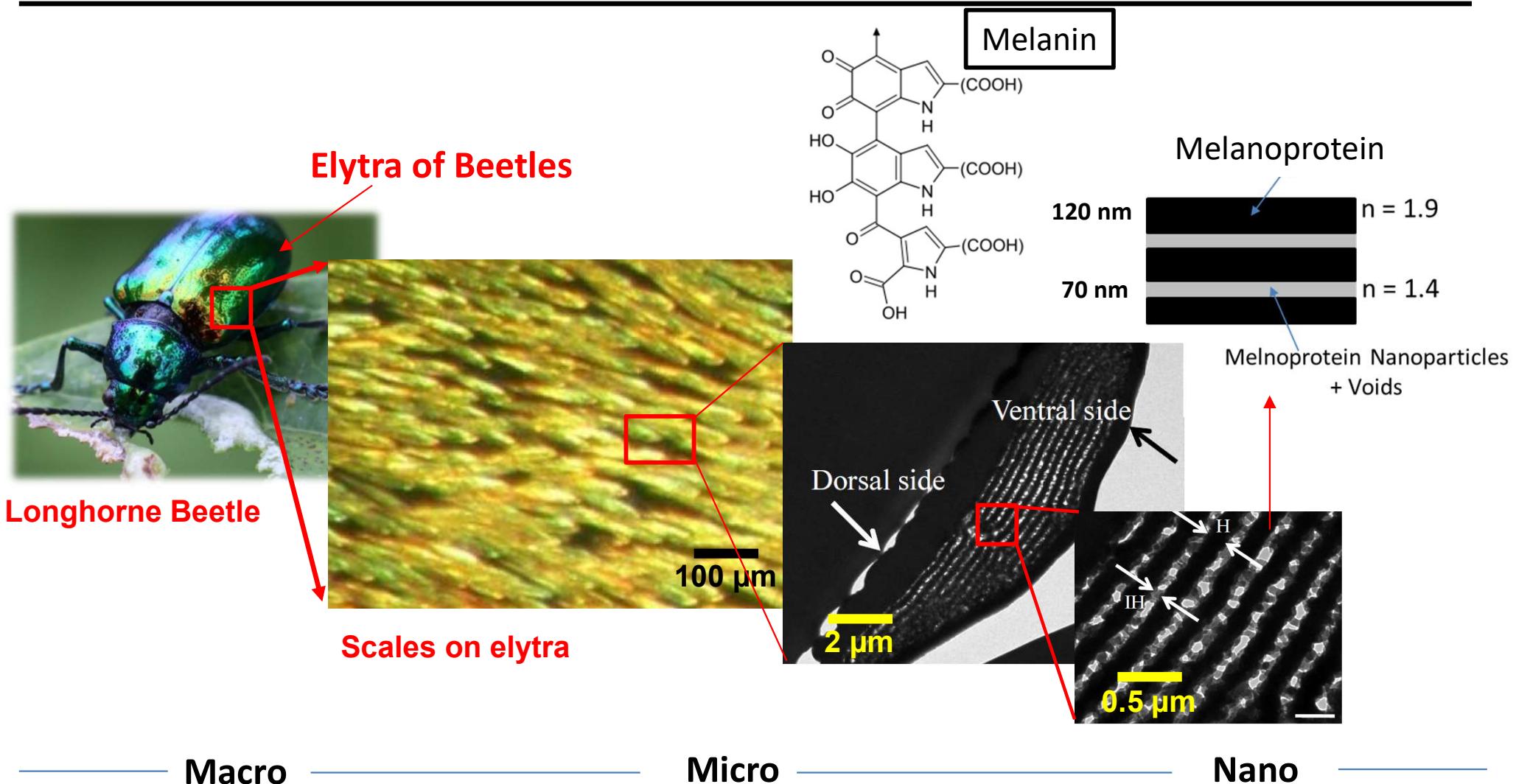


- Periodic structure creates photonic band gap that gives brilliant blue color.
- Periodicity is different in different butterflies, thus giving different color to their wings.

Liu, X., Zhang, S., Zhang, H. (2016). Optik, 127(4), 1729-1733.

Huang, J., Wang, X., Wang, Z. (2006). Nano letters, 6(10), 2325-2331.

Photonic Layered Systems: Elytra of Beetles



- The iridescent coloration of scales originates from a multilayer structure.
- Scales, being hydrophilic, change color upon swelling in wet state.
- The elytra changes color under stress condition, e.g. presence of prey.

Liu, F., Dong, B., Liu, X., Zheng, Y., Zi, J. (2009). Optics express, 17(18), 16183-16191.

Gebeshuber, I., Lee, D. (2012). Nanostructures for coloration

Outline

1. Hierarchical Structures in Animals

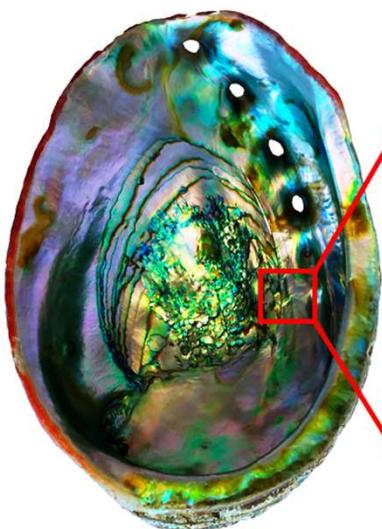
- a. Mammalian Hierarchical Systems
- b. Fibrillar System
- c. Photonic Layered Systems
- d. Inorganic/Organic Layered Systems
 - i. Nacre Shell
 - ii. Bone

2. Hierarchical Structures in Plants

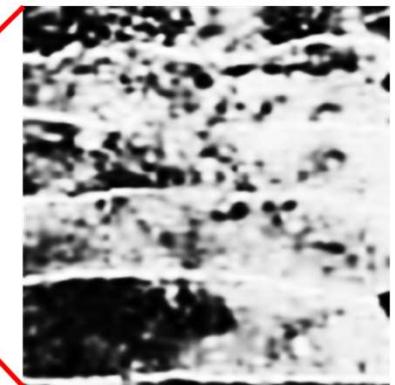
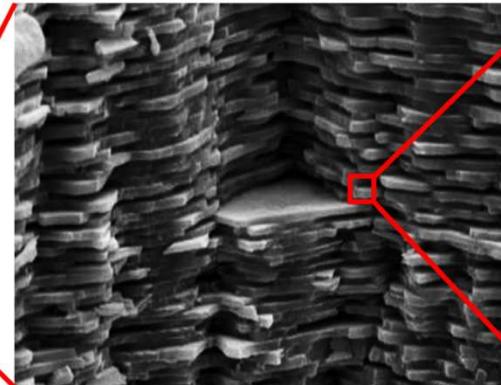
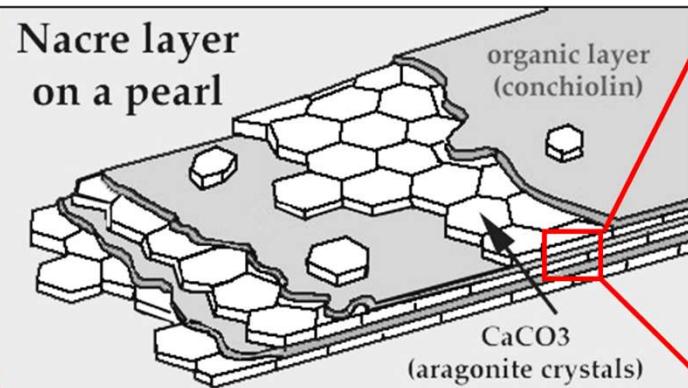
3. Polymeric Hierarchical Structures and Others

4. Complex Assembly in Biological Materials

Organic/Inorganic Layered System: Nacre Shell



$$n(\text{CaCO}_3) = 1.66, n(\text{conchiolin}) = 1.53, \Delta n = 0.13$$



Abalone Shell

'Brick & Mortar Structure'
of Nacre Sheet

Aragonite Platelets

Layers of Aragonite
Tablets

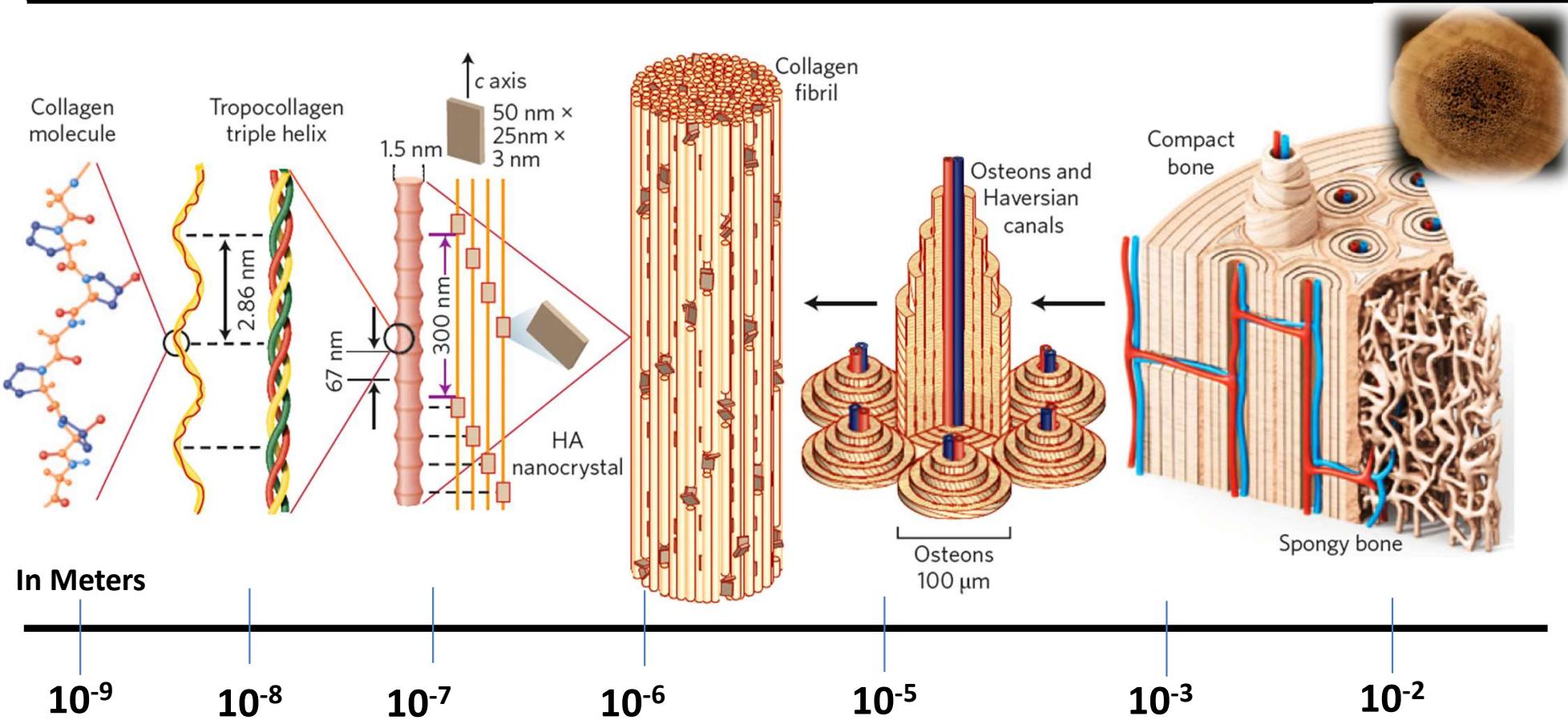
- The organic content act as the ductile fraction preventing crack growth
- Elastic moduli at dry and wet state are 70 and 60 GPa, respectively.
- Tensile strength at dry and wet states are 170 and 130 MPa, respectively.
- The flexural strength of nacre, between 100 and 200 MPa, is comparable to that of many common ceramics.

Barthelat F. Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences. 2007 Dec 15;365(1861):2907-19.

Barthelat F, Tang H, Zavattieri PD, Li CM, Espinosa HD. Journal of the Mechanics and Physics of Solids. 2007 Feb 28;55(2):306-37.

Sun J, Bhushan B. Hierarchical structure and mechanical properties of nacre: a review. Rsc Advances. 2012;2(20):7617-32.

Organic/Inorganic Layered Systems: Bone



- Bone is highly fracture resistant due to its complex hierarchical structure both at the exterior and interior.
- The Young's modulus of cortical bone varies from 8 to 24 GPa.

Meyers, M., Chen, P., Lin, A. Y., Seki, Y. (2008). Prog. in Mat. Sci., 53(1), 1-206.

Wegst, U., Bai, H., Saiz, E., Tomsia, A., Ritchie, R. (2015). Nature materials, 14(1), 23-36.

Outline

1. Hierarchical Structures in Animals

- a. Mammalian Hierarchical Systems
- b. Photonic Layered Systems
- c. Inorganic/Organic Layered Systems

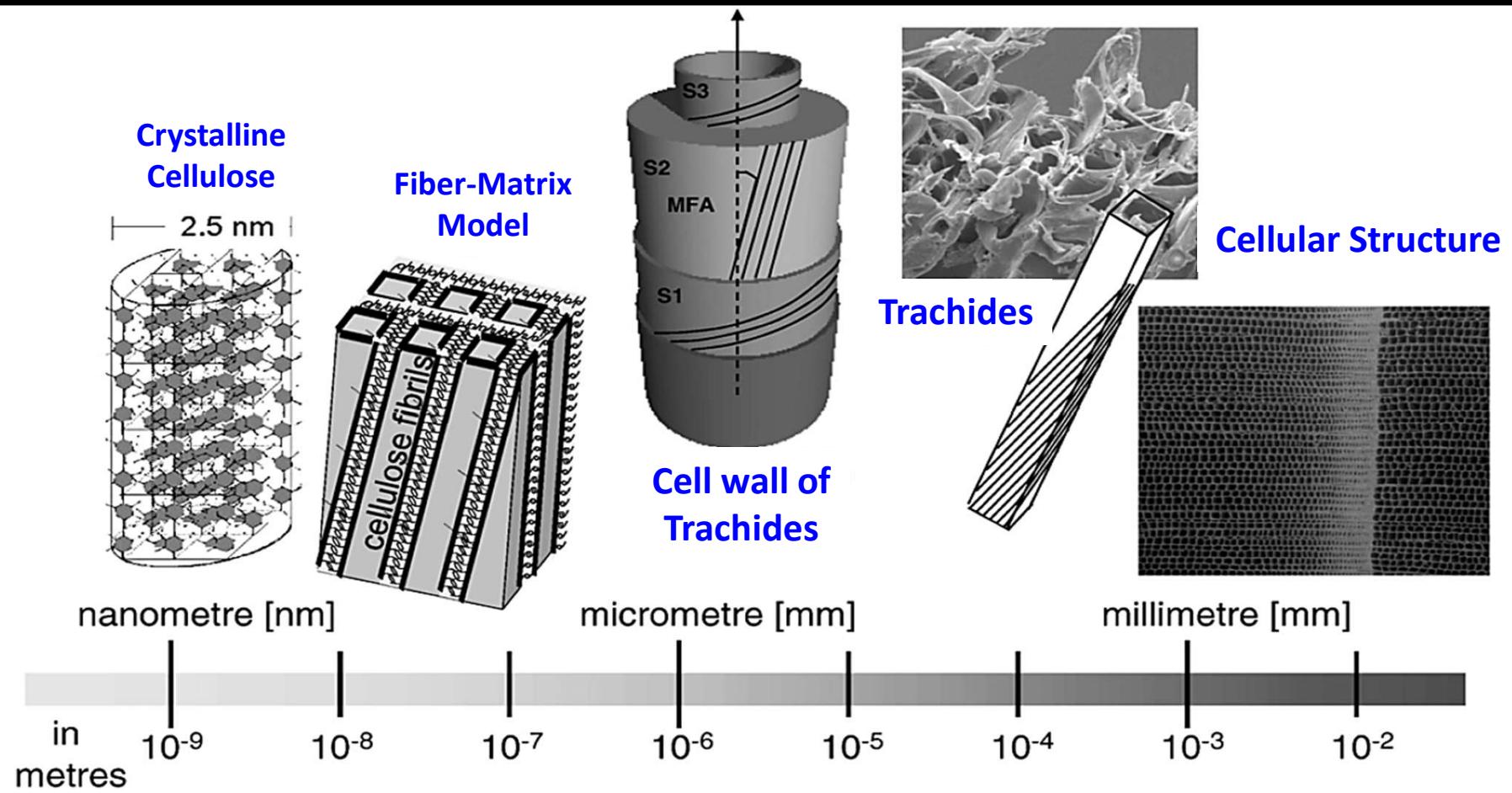
2. Hierarchical Structures in Plants

- i. Wood Cellulose
- ii. Bamboo

3. Polymeric Hierarchical Structures and Others

4. Complex Assembly in Biological Materials

Hierarchical Structures in Plants: Wood Cellulose



- The mechanical properties of wood are highly anisotropic due to the preferred orientation of cellulose fibrils (parallel to the trunk).
- The stiffness and strength are greatest in the axial direction by a factor of 2–20 than that in the radial and tangential directions, depending on the species.

Gibson, L., Ashby, M. (1999). Cellular solids: structure and properties.

Meyers, M., Chen, P., Lin, A. Y., Seki, Y. (2008). Prog. in Mat. Sci., 53(1), 1-206.

Hierarchical Structures in Plants: Wood Cellulose

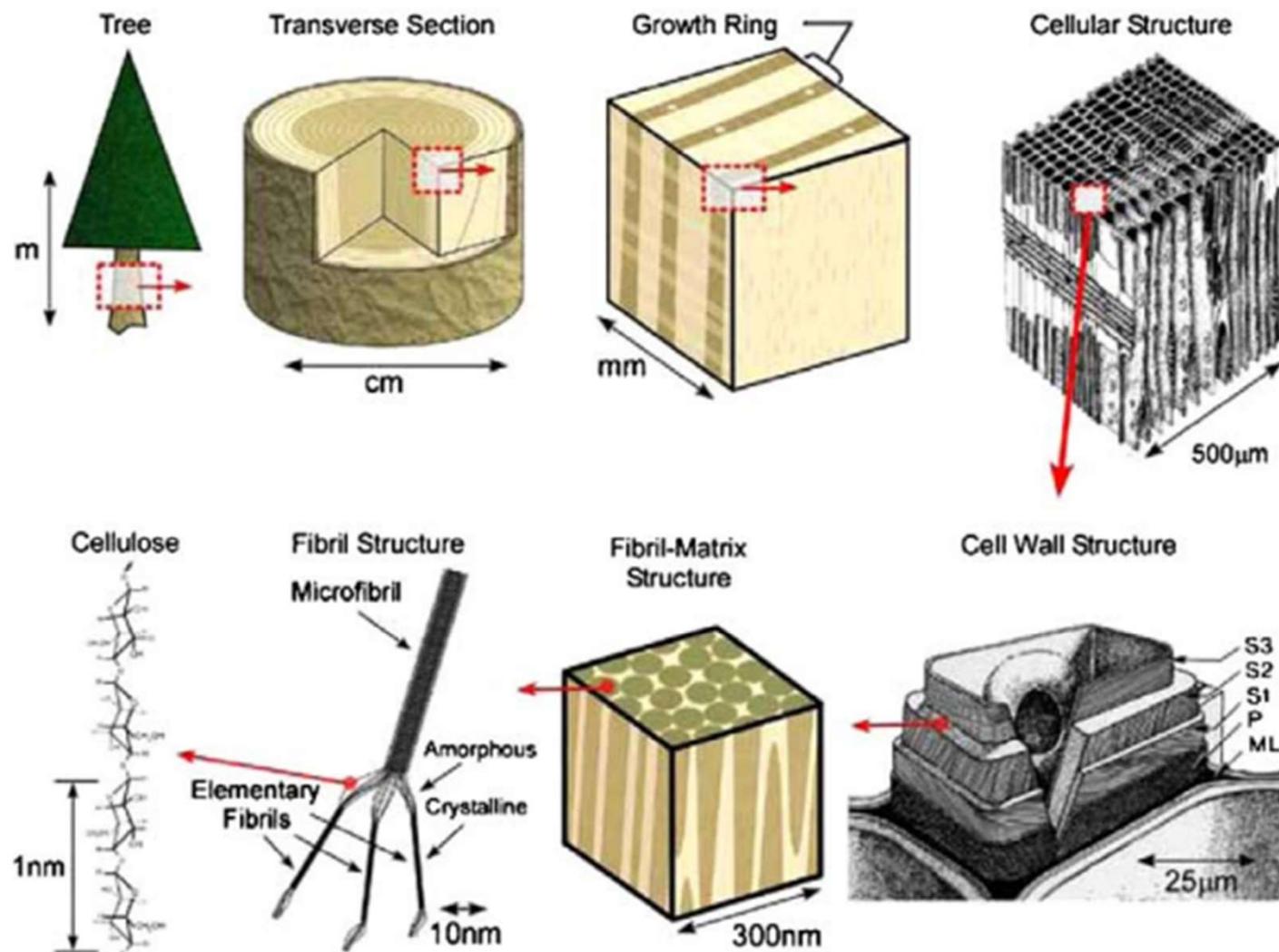


Figure 1. Structure of wood from the tree to the CNCs (after [2]). ML = middle lamellae between tracheids, P = primary cell wall, S1, S2, S3 = cell wall layers.

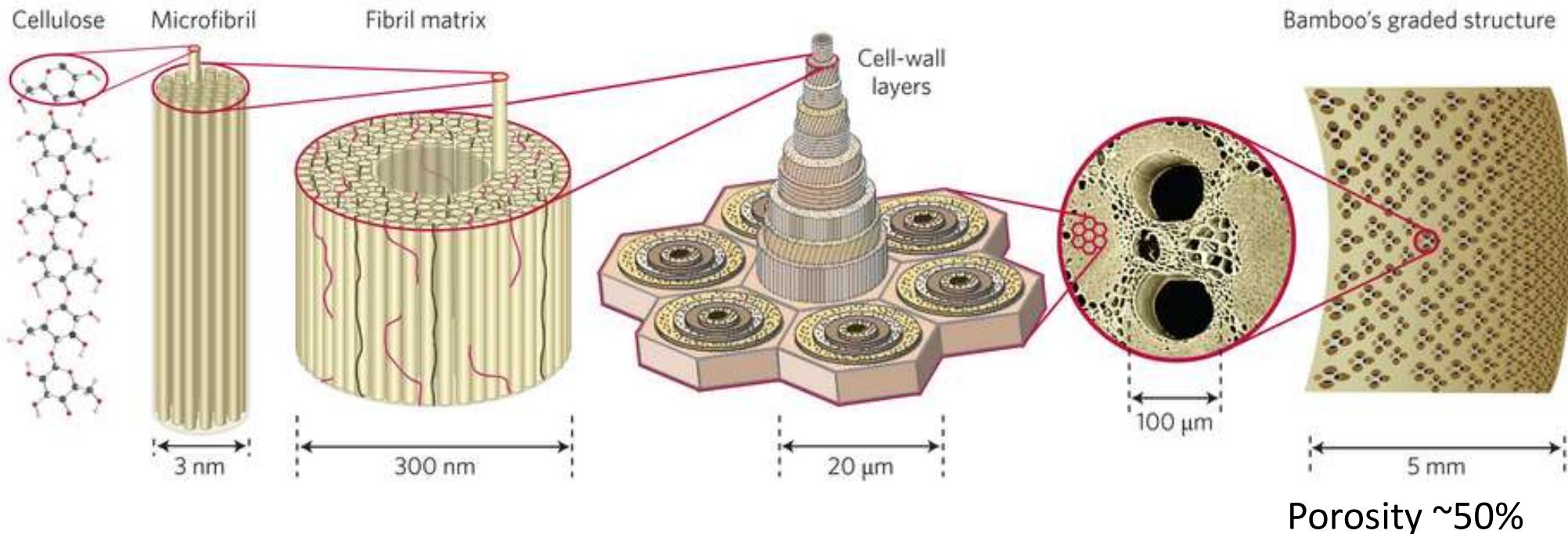
Meas. Sci. Technol. 22 (2011) 024005 (10pp)

doi:10.1088/0957-0233/22/2/024005

Development of the metrology and imaging of cellulose nanocrystals

Michael T Postek^{1,4}, András Vladár¹, John Dagata¹, Natalia Farkas¹, Bin Ming¹, Ryan Wagner², Arvind Raman², Robert J Moon^{2,3}, Ronald Sabo³, Theodore H Wegner³ and James Beecher³

Hierarchical Structures in Plants: Bamboo



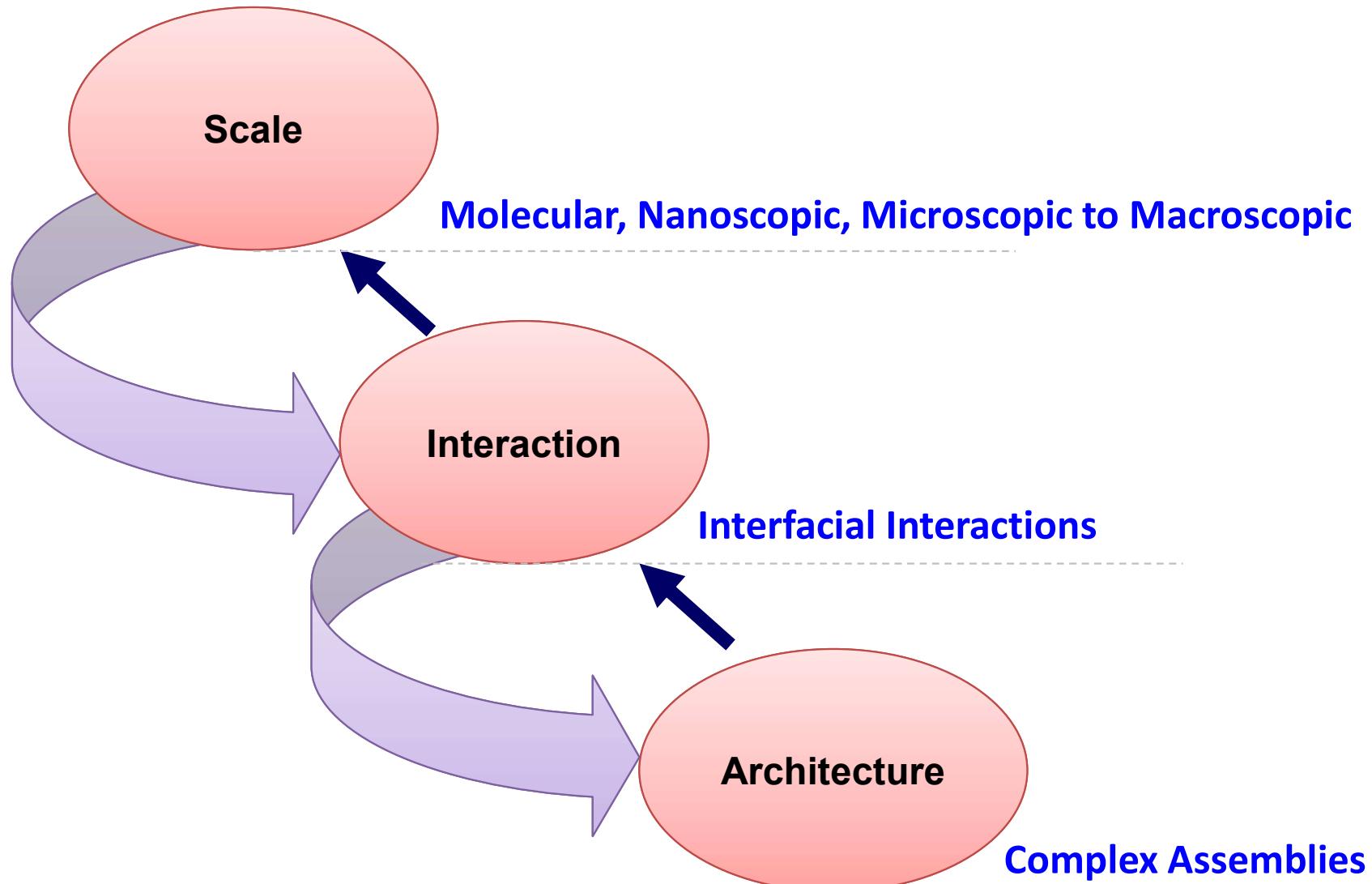
- The hierarchical structure of bamboo comprises three fundamental tissues named epidermis, vascular bundles and parenchyma ground.
- Graded cellular structure can be observed in bamboo culm. The size of cellular vascular bundles is bigger (~400 μm) near the core and smaller (150 μm) near the epidermis .
- Each vascular bundle can be identified as subcellular structure. The diameter of cells is ~100 μm .

Habibi, M. , Lu, Y. (2014). Scientific reports, 4.

Wang, X., Ren, H., Zhang, B., Fei, B., Burgert, I. (2011). Journal of the Royal Society Interface, 0462.

Wegst, U., Bai, H., Saiz, E., Tomsia, A., Ritchie, R. (2015). Nature materials, 14(1), 23-36.

Important Components of Hierarchical Structures



Outline

1. Hierarchical Structures in Animals

- a. Mammalian Hierarchical Systems
- b. Photonic Layered Systems — Butterfly Wings
- c. Inorganic/Organic Layered System — Nacre Shells and Bone

2. Hierarchical Structures in Plants

3. Hierarchical Structures in Polymers and Elsewhere

4. Complex Assembly in Biological Materials

Polymeric Hierarchical Structure: Spherulites

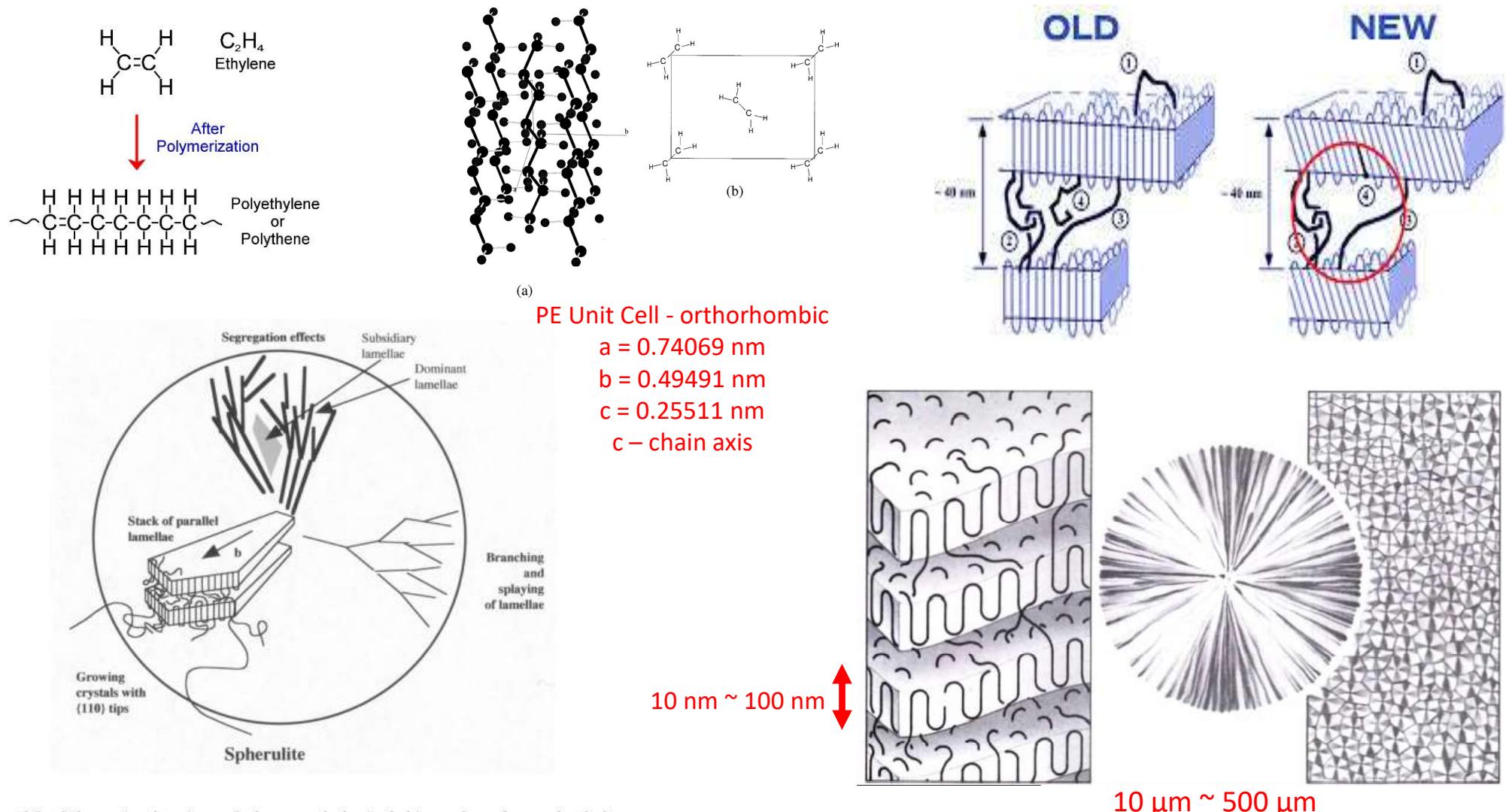
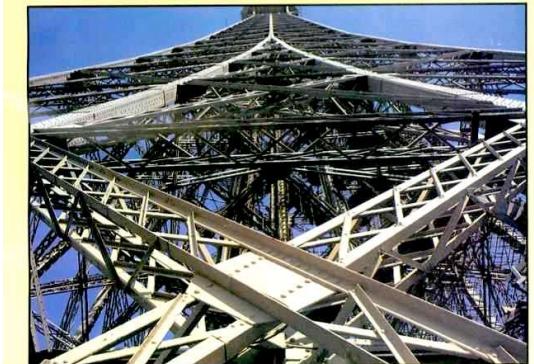
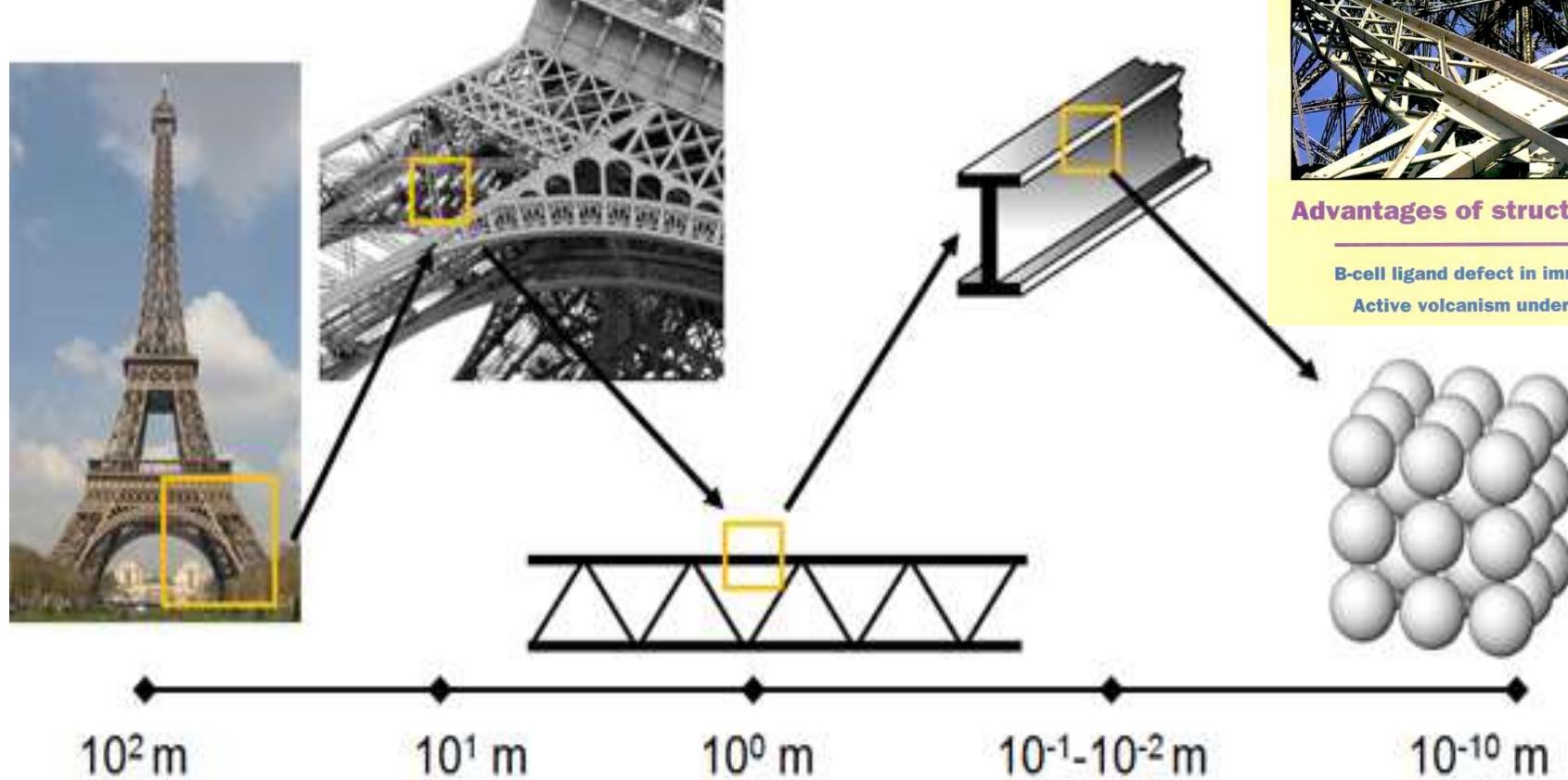


Fig. 6.8. Schematic drawing of the morphological hierarchy of a polyethylene spherulite.

Spherulitic Structure of Semi-crystalline Materials

Sunburst-like structures formed as the polymer solidified and crystal growth began at nucleation points and radiated outward.

Hierarchical Structure of Eiffel Tower



Advantages of structural hierarchy

B-cell ligand defect in immunodeficiency

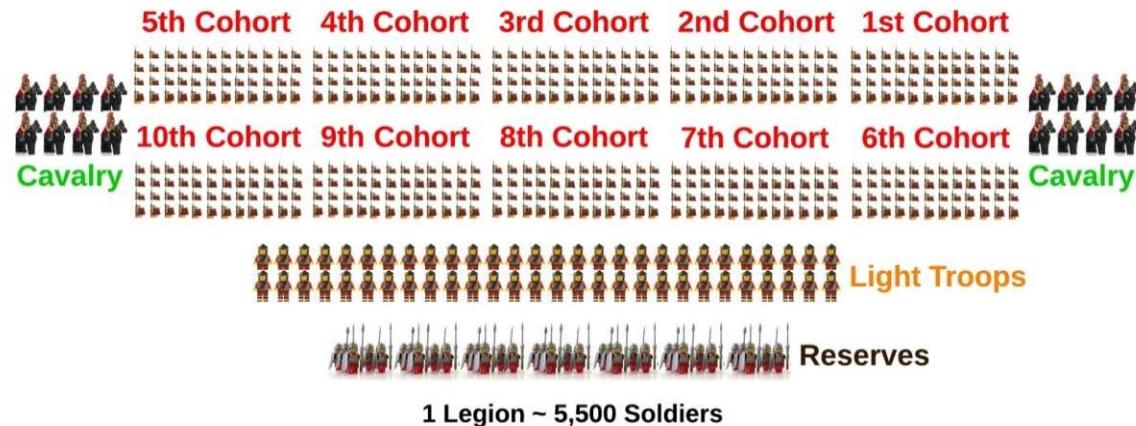
Active volcanism under Antarctic ice

technology
review

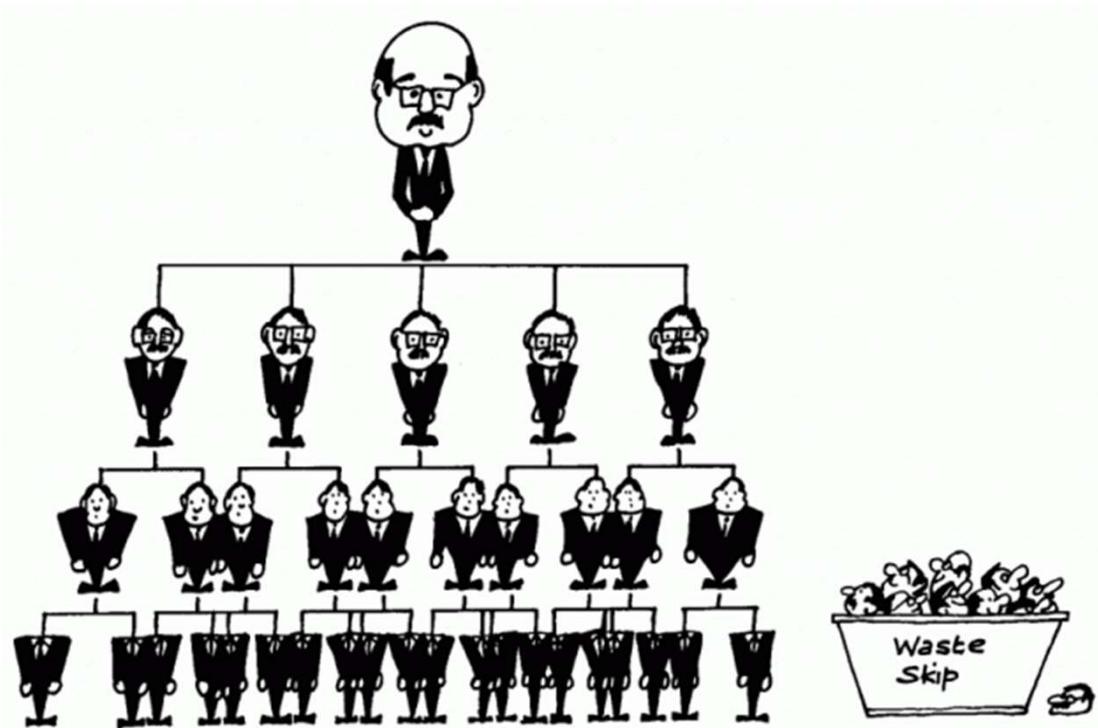
Hierarchical Structure in Management

Formation of Roman Army
(200 BC)

1 Century = 80 Soldiers
1 Cohort = 6 Centuries



Hierarchy of Modern Enterprises



Outline

1. Hierarchical Structures in Animals

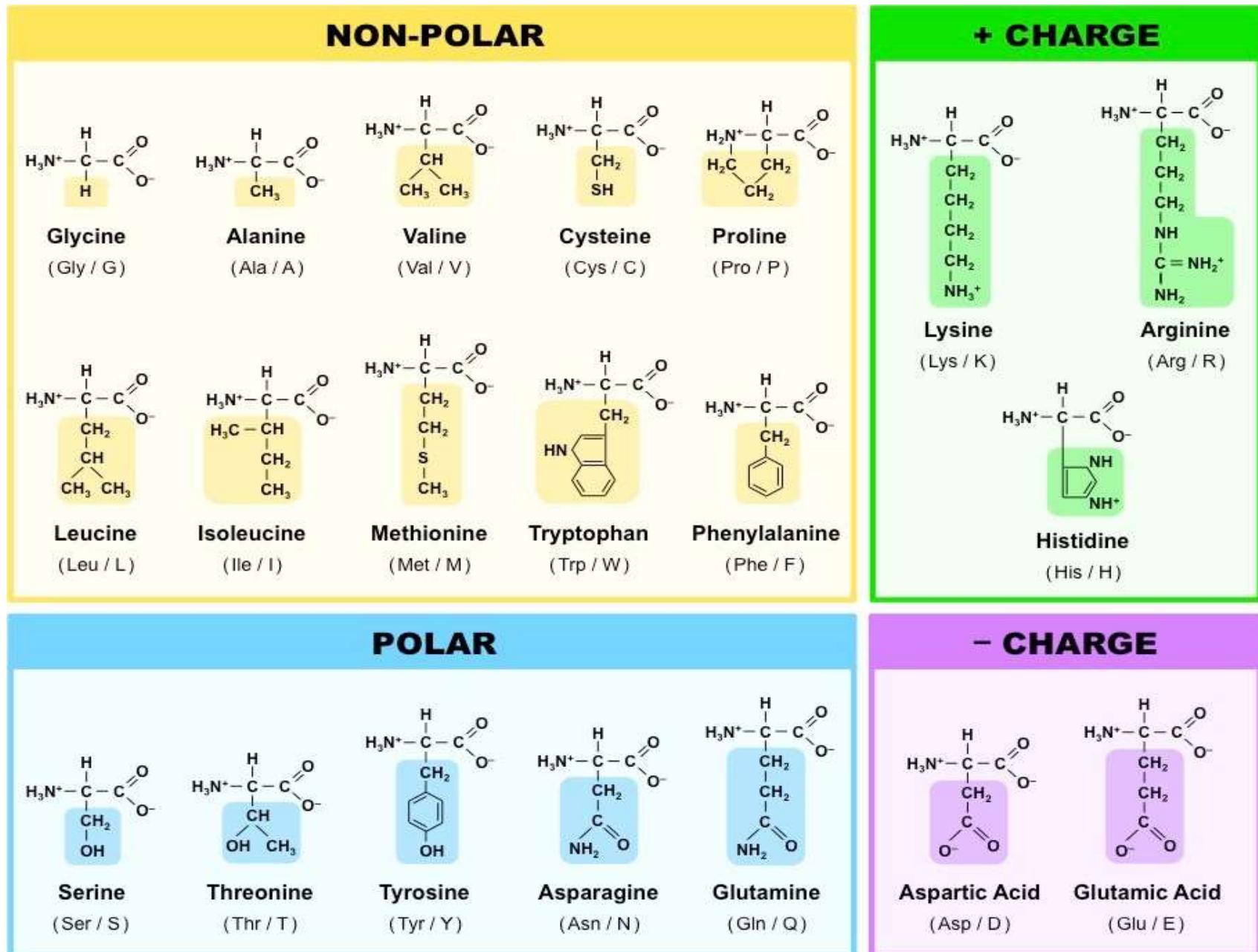
- a. Mammalian Hierarchical Systems
- b. Photonic Layered Systems
- c. Inorganic/Organic Layered Systems

2. Hierarchical Structures in Plants

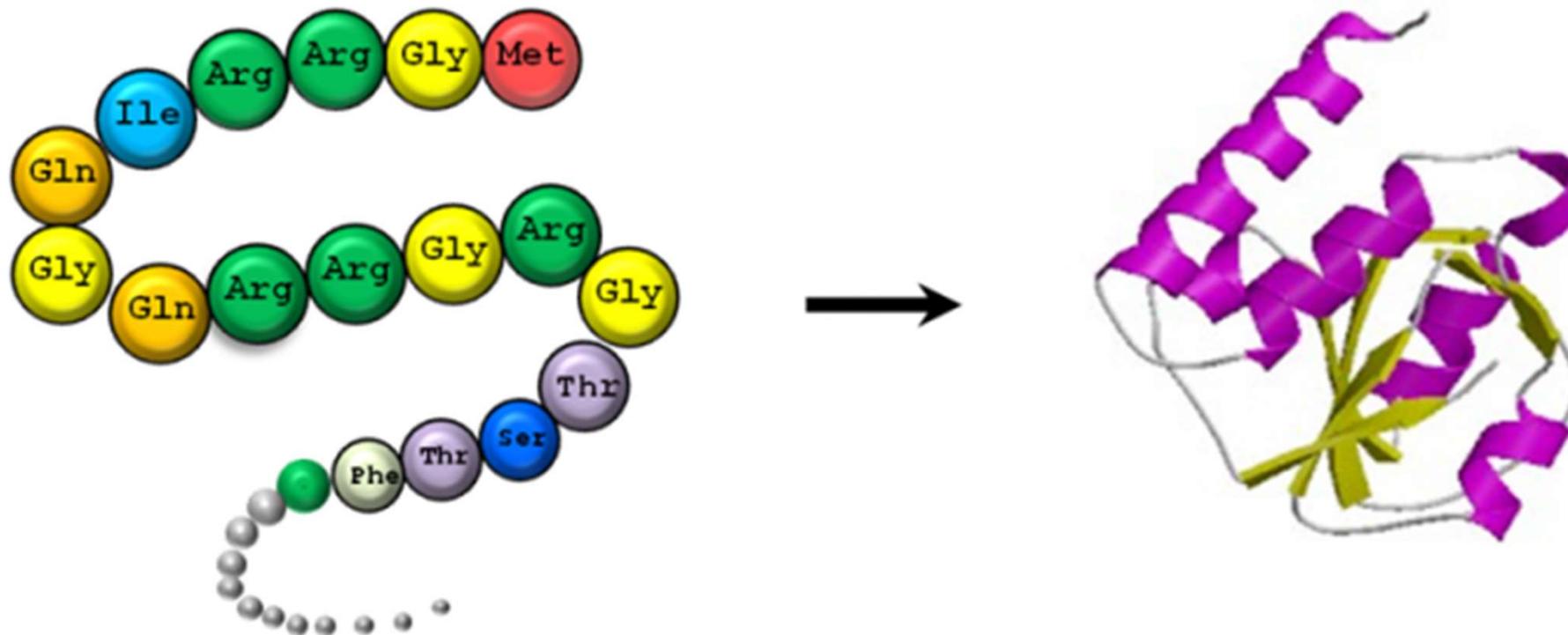
3. Polymeric Hierarchical Structures and Others

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Protein Hierarchical Structures are Based on Amino Acid Sequence

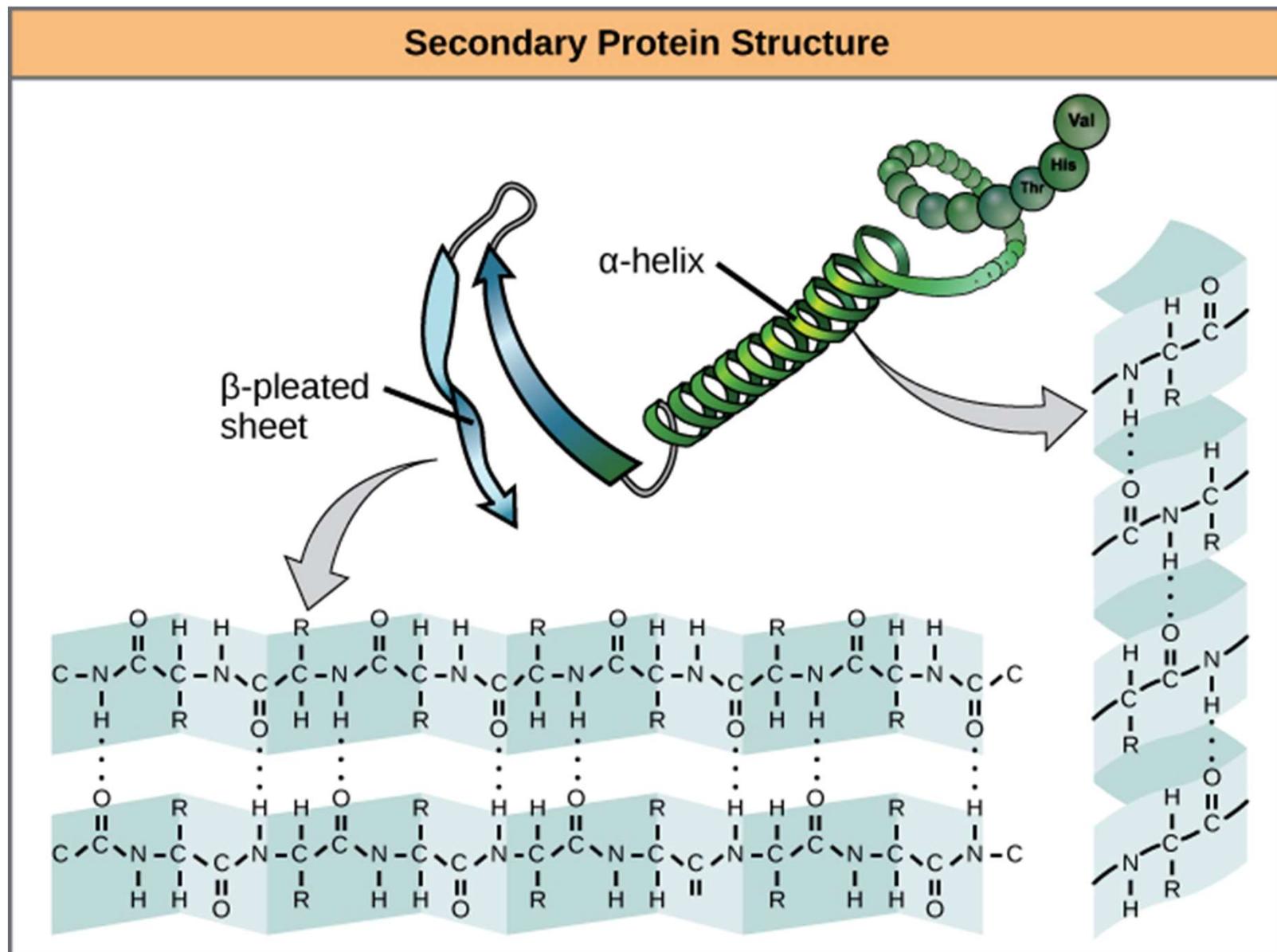


A Linear Sequence of a Large Number of Amino Acids Forms the Primary Protein Structure

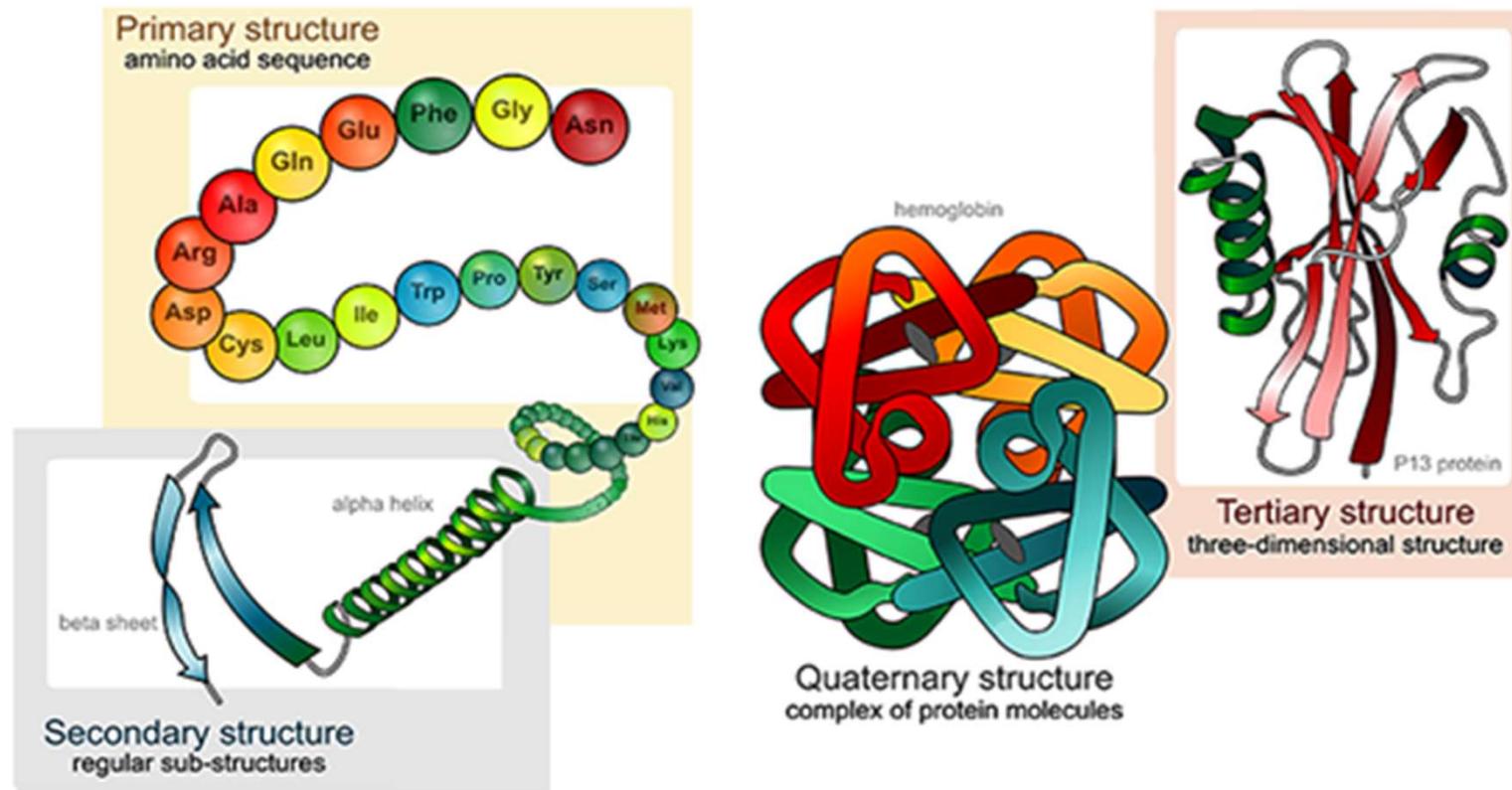


The Intramolecular Interactions Among Specific
Segments of the Amino Acids in the Primary Structure
Forms the Secondary Structure

Intramolecular Bonding Details of the Alpha Helix and Beta Sheet Imparting Protein Semi-Rigidity and Structure



Tertiary and Quaternary Protein Hierarchical Structure Based on Amino Acid Sequence

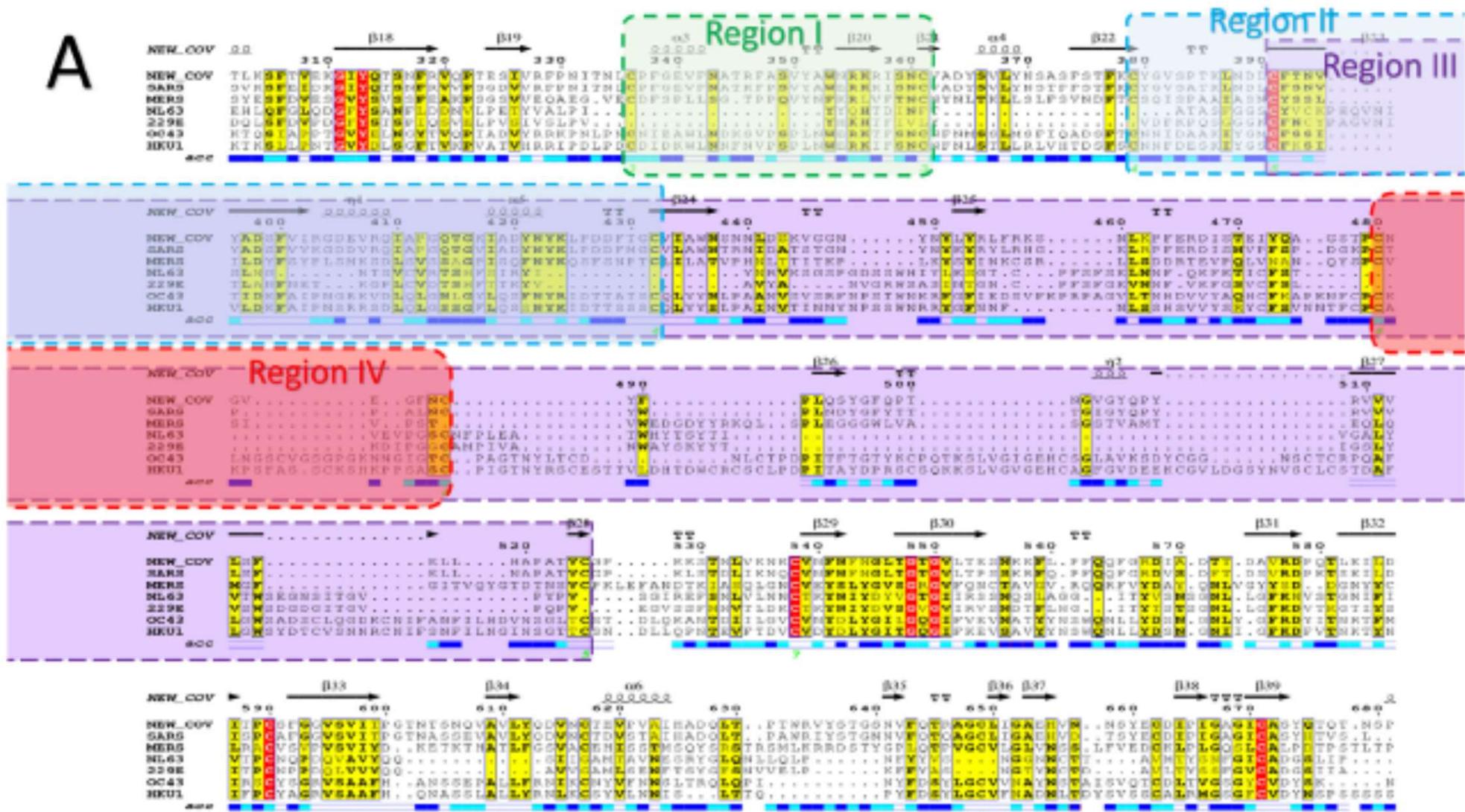


Tertiary Structure – Three Dimensional Spatial Configuration of a Single Protein

Quaternary Structure – Complexing of Two or More Proteins into a Semi-Rigid Structure; i.e., Hemoglobin (above)

Common Virus Spike Protein Hierarchical Structure Based on Amino Acid Sequence

A



Journal of Infection 80 (2020) 554–562

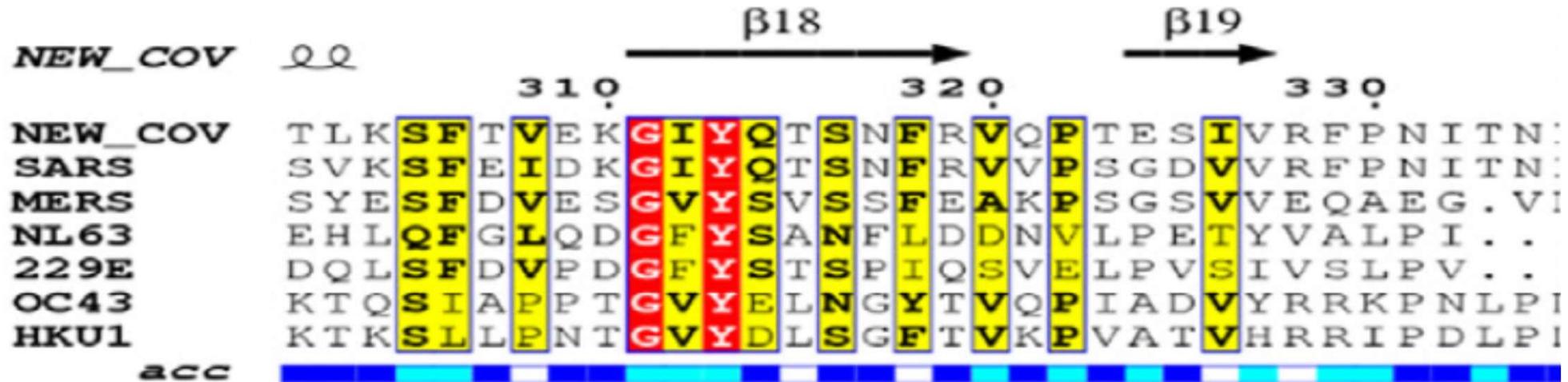
COVID-19 spike-host cell receptor GRP78 binding site prediction

Ibrahim M. Ibrahim^a, Doaa H. Abdelmalek^a, Mohammed E. Elshahat^a, Abdo A. Elfiky^{a,b,*}

^a Biophysics Department, Faculty of Sciences, Cairo University, Giza, Egypt

^b College of Applied Medical Sciences, University of Al-Jouf, Saudi Arabia

Section of the Common Viruses Spike Protein Amino Acid Sequence Mutations



Common human coronaviruses

1. 229E (alpha coronavirus)
2. NL63 (alpha coronavirus)
3. OC43 (beta coronavirus)
4. HKU1 (beta coronavirus)

Common human coronaviruses, including types 229E, NL63, OC43, and HKU1, usually cause mild to moderate upper-respiratory tract illnesses, like the common cold. Most people get infected with one or more of these viruses at some point in their lives. This information applies to common human coronaviruses and **should not be confused with [coronavirus disease 2019](#)** (formerly referred to as 2019 Novel Coronavirus).

Eg., T-L-K-S-F-T . . . = Threonine - Leucine - Lysine – Serine – Phenylalanine – Threonine - . . .

Virus Hierarchical Structure Based on Protein Association

Biophysical Reviews (2018) 10:659–665
<https://doi.org/10.1007/s12551-017-0375-2>

REVIEW

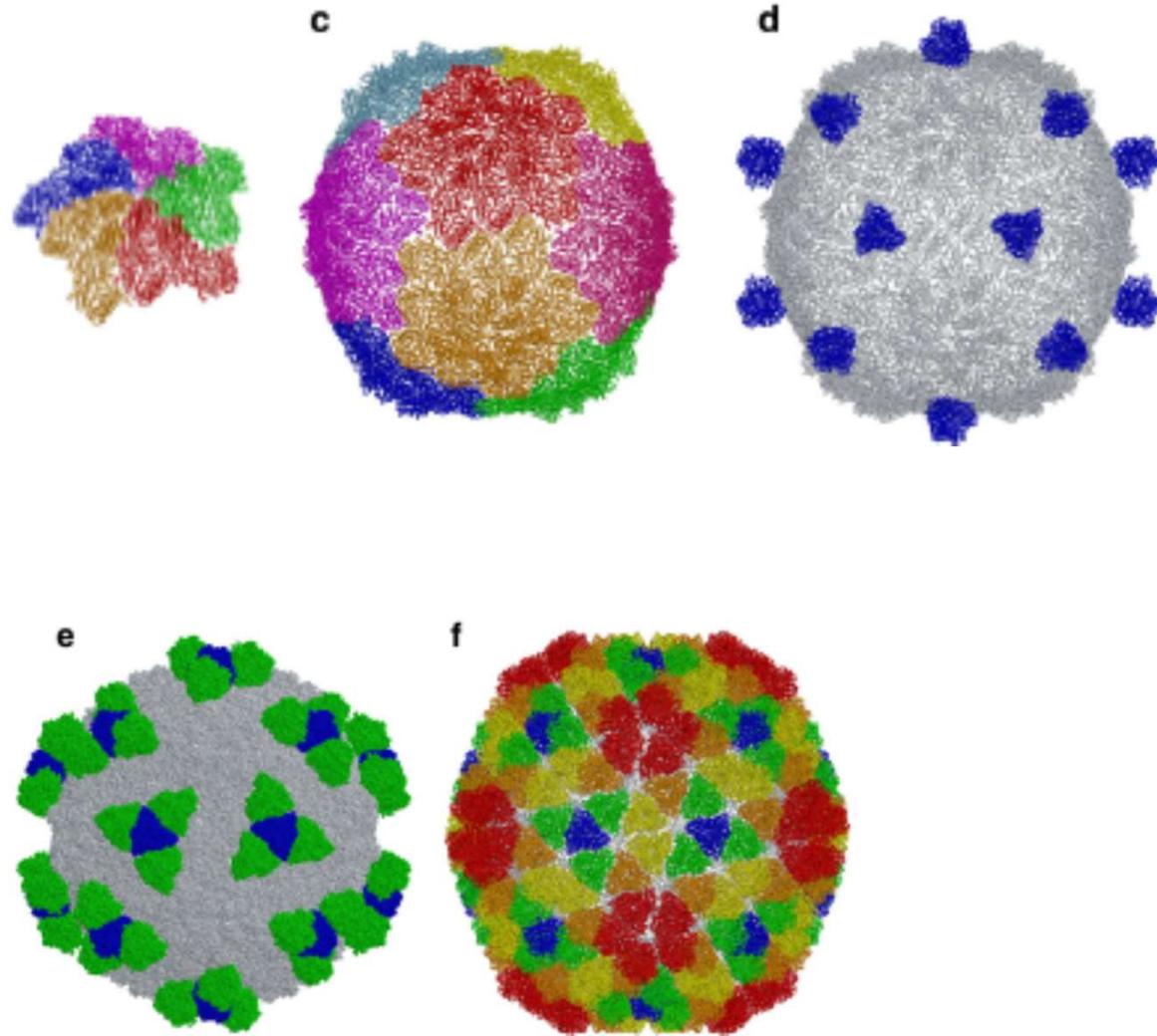


Hierarchical structure assembly model of rice dwarf virus particle formation

Atsushi Nakagawa¹ · Naoyuki Miyazaki¹ · Akifumi Higashiu¹

Proposed Rice Dward Virus (RDV) Model

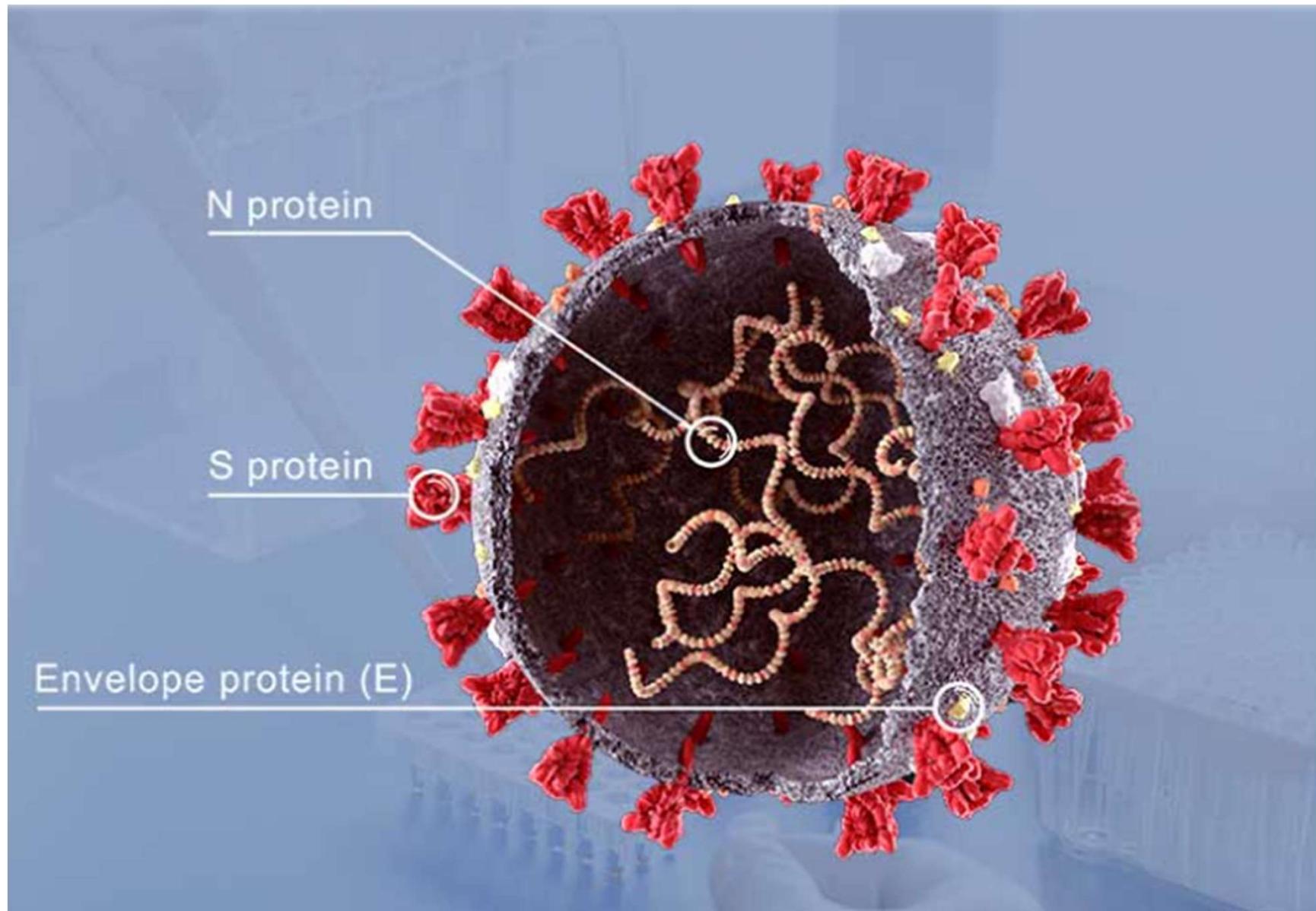
- a. Two protein chains associate into a dimer.
- b. Five dimers associate symmetrically around a 5-fold axis to form a decamer.
- c. Icosahedral symmetry forms an outer shell around a center core.
- d. PS trimers form at the 3-fold axis positions.
- e. Attachment of additional PS trimers.
- f. Completion of PS trimer attachment to surface forming final structure



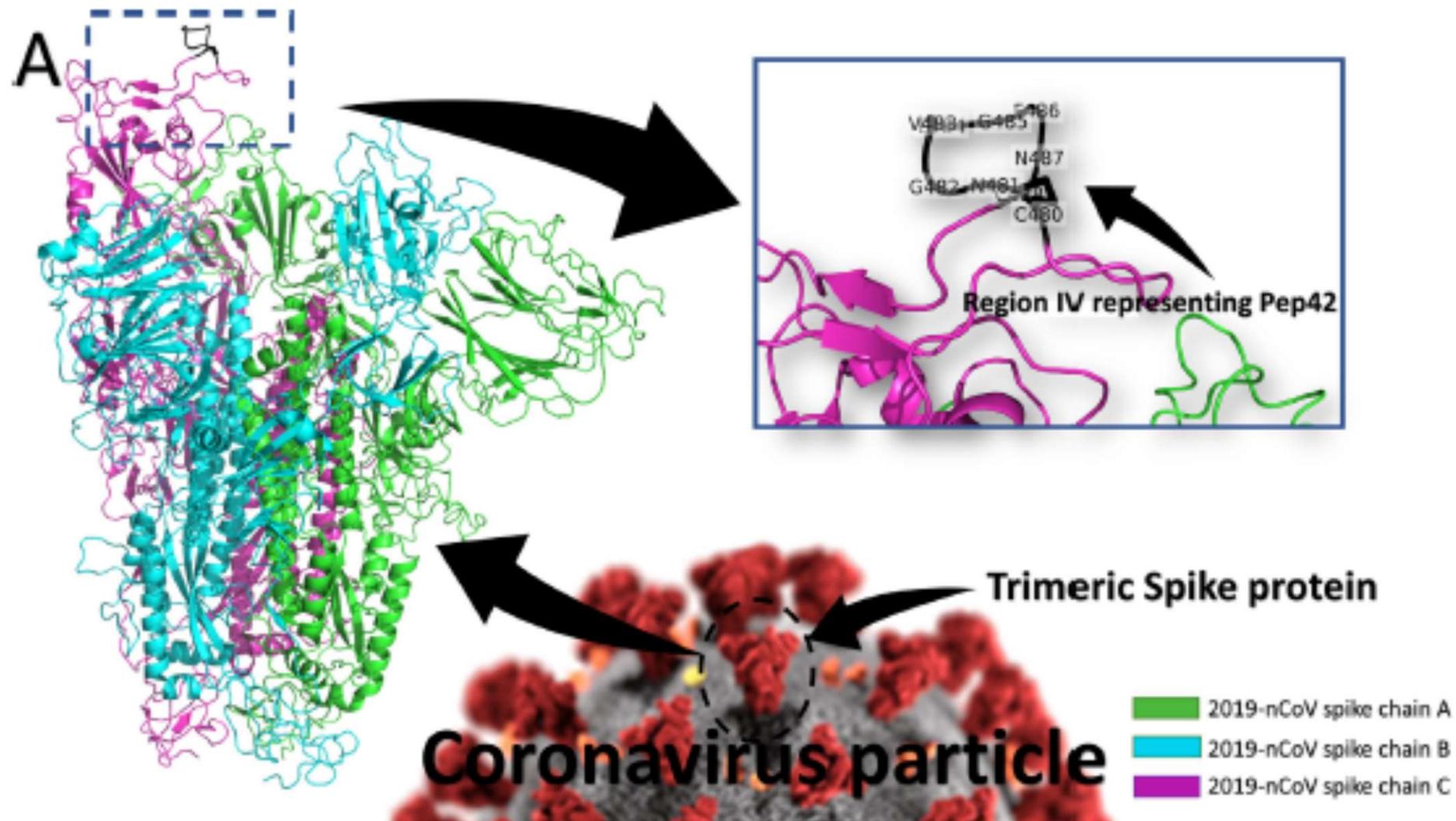
Rice Dwarf Virus

RDV causes severe disease in rice crops in South-East Asia, China, Japan and Korea, Nepal and the Philippines.

Three Major Protein Contributions to the Covid-19 Structure



Hierarchical Structure Covid-19 Spike is Based on Three Complexing Proteins

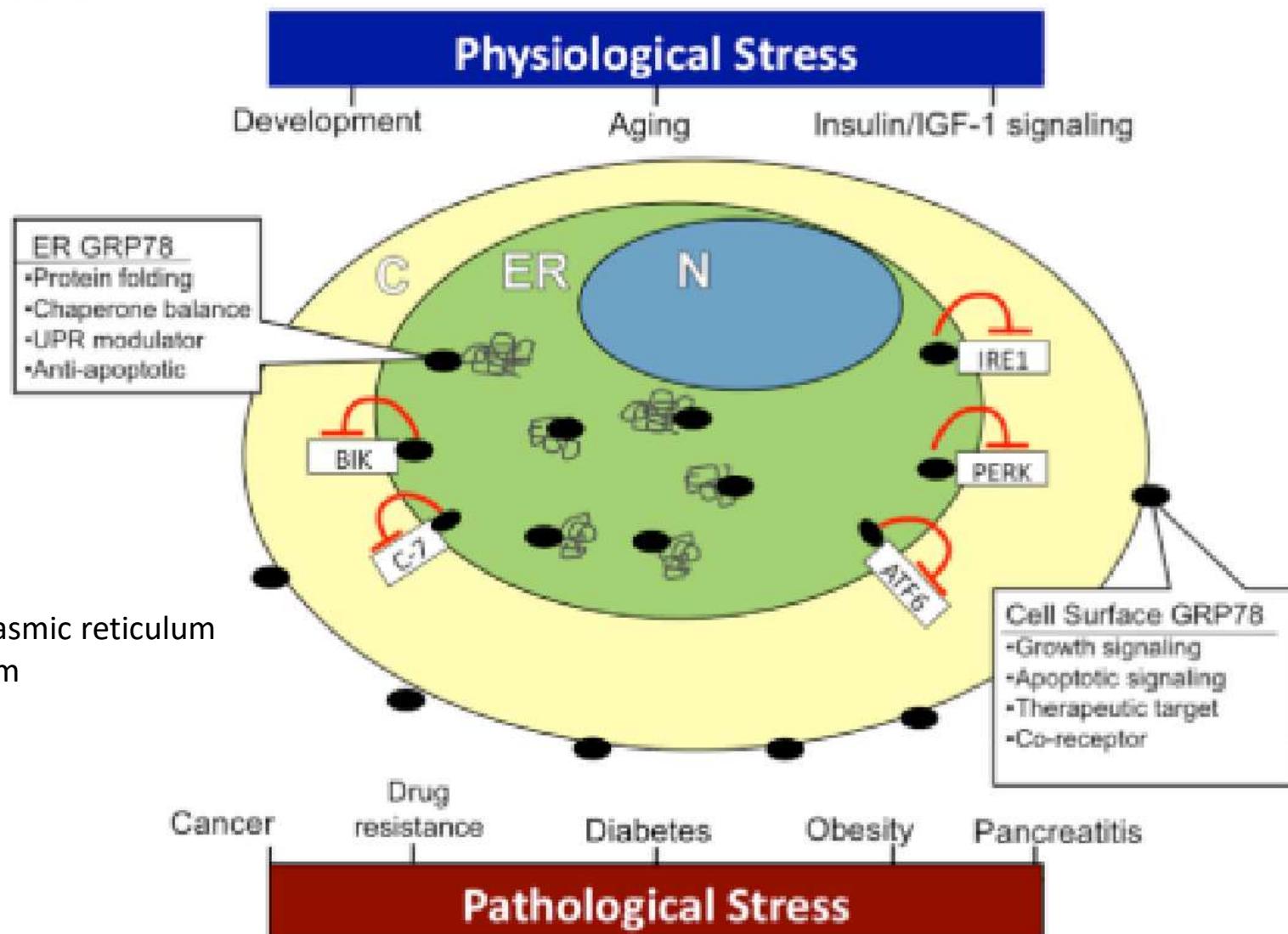


The critical role of GRP78 in physiologic and pathologic stress

Kyle T. Pfaffenbach and Amy S. Lee¹

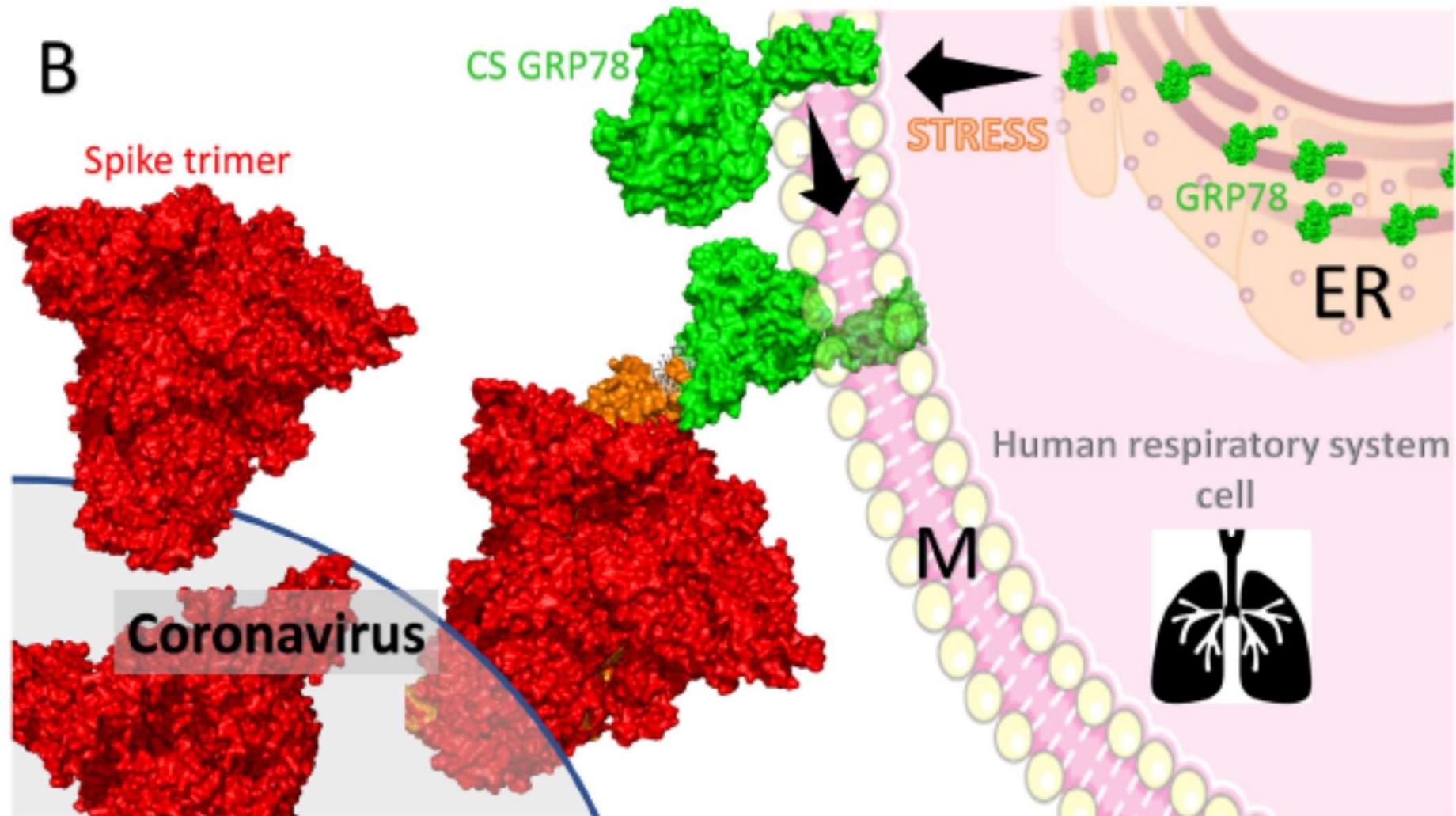
Department of Biochemistry and Molecular Biology, University of Southern California Keck School of Medicine, USC Norris Comprehensive Cancer Center, 1441 Eastlake Avenue, Los Angeles, California 90089-9176 USA

The Human respiratory system contains GRP78 = Glucose Regulated Protein 78 Released Under Physiological and Pathological Stress



Coronavirus Spike Protein Complexing with GRP78

The “handshake” between Coronavirus and the Human Respiratory System



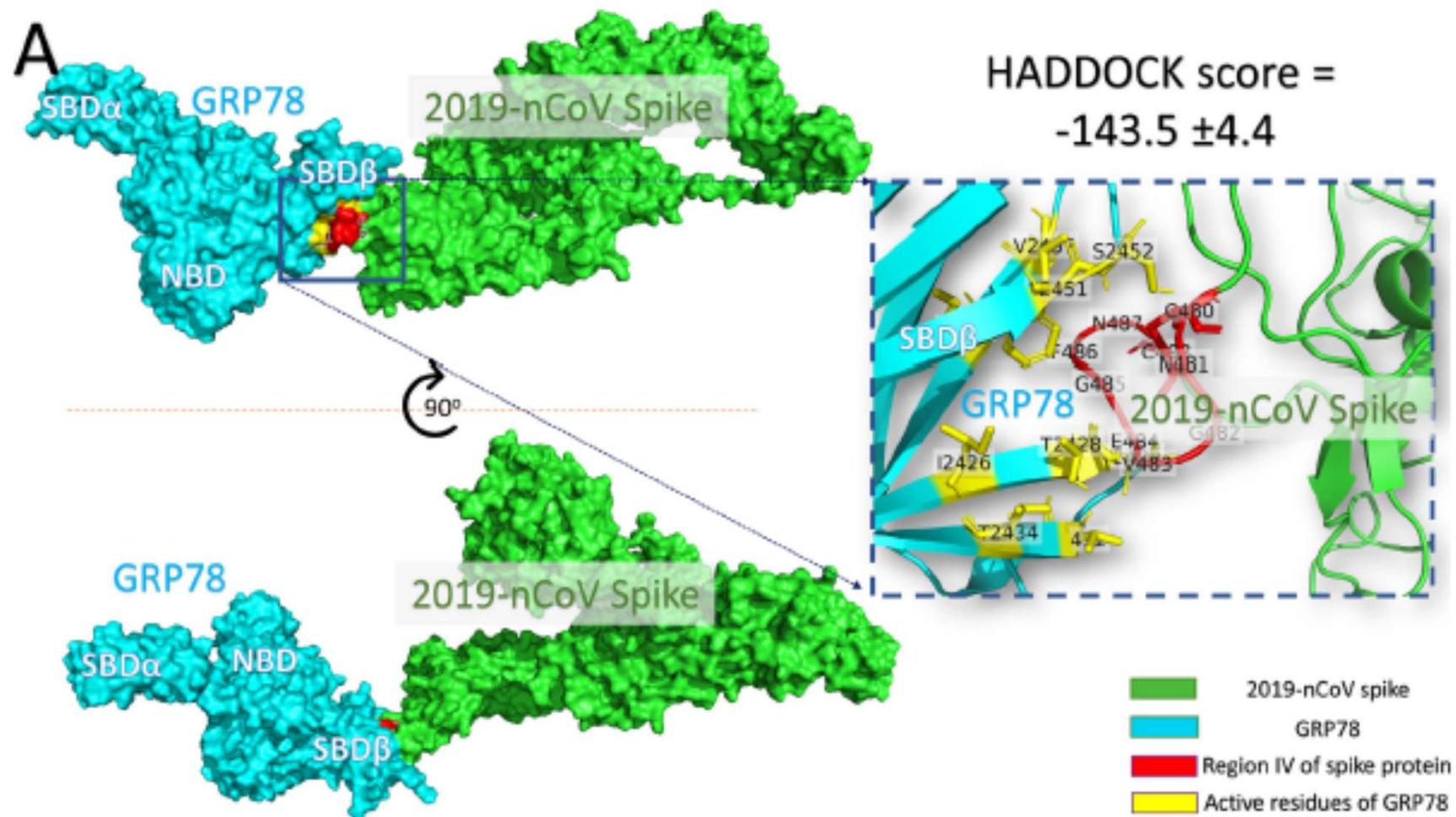
N = nucleus

ER = endoplasmic reticulum M = Cell Membrane

C = cytoplasm

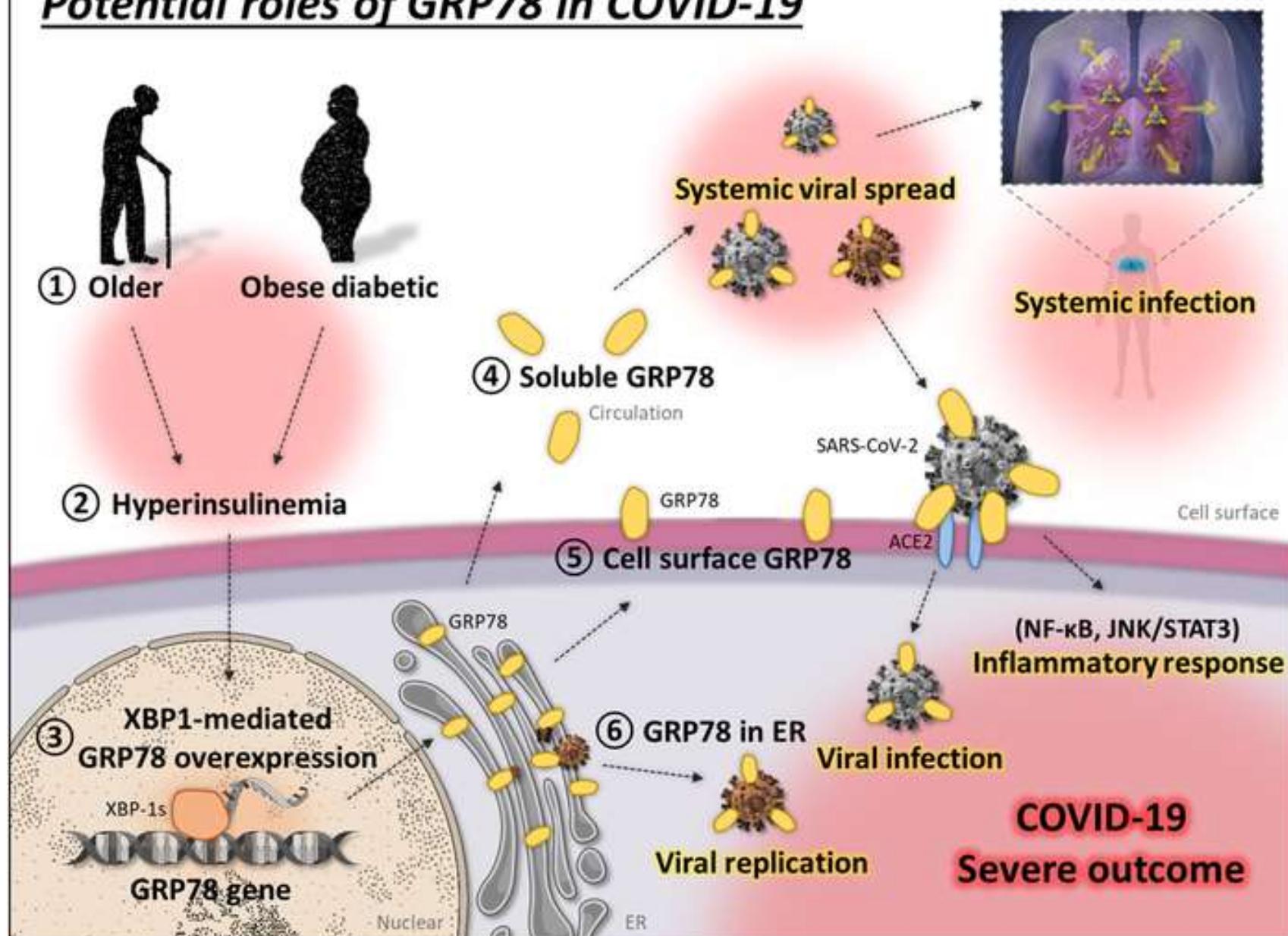
Detailed Complexing of the Covid-19 Spike to GRP78

The “handshake” Details of the Coronavirus Spike Reaction with the Human Respiratory System Protein GRP78



Simple Representation of Infection Pathway and Spread of Covid-19 via GRP78 and ACE2

Potential roles of GRP78 in COVID-19



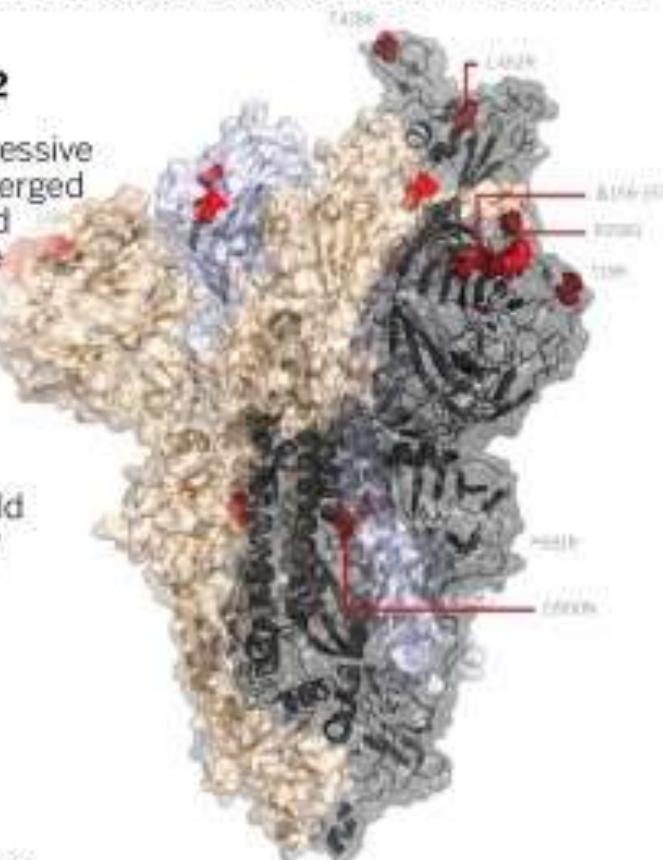
The Differences in the Covid-19 “Delta” and “Omicron” Variants are Primarily Reflected in the Amino Acid Sequence Mutations of the Three Spike Proteins

COVID-19 DELTA ANDOMICRON VARIANTS

The new omicron variant has more mutations than the rampant delta variant. Scientists worry that the mutations may make omicron more transmissible, more deadly or better able to evade vaccine protections. However, there is no proof yet that the omicron mutations have those effects.

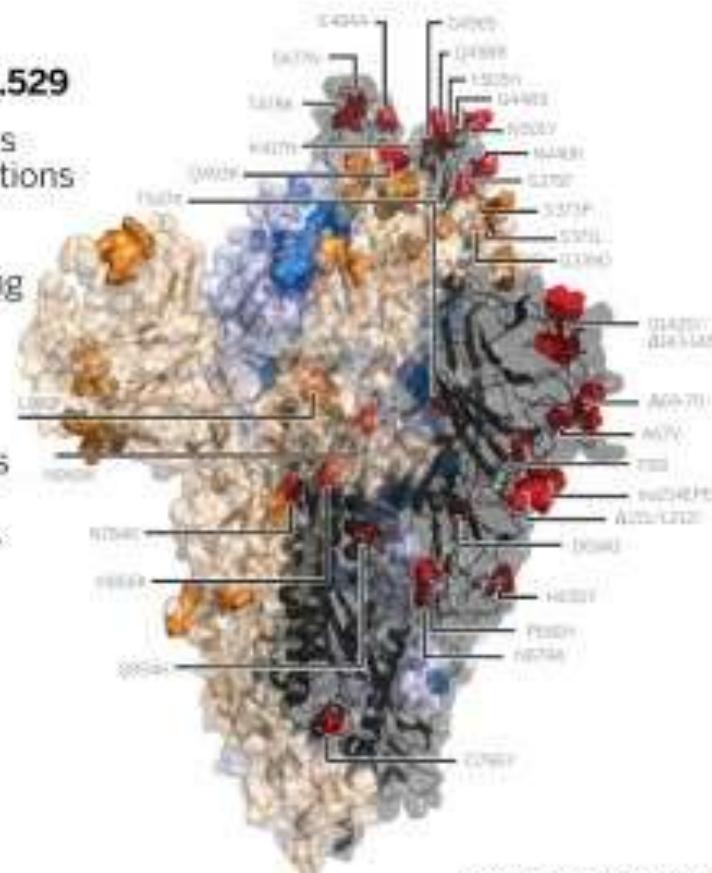
Delta: B.1.617.2

Delta is an aggressive variant that emerged in late 2020 and quickly became the most common variant in India. It continued spreading around the world and is currently the dominant variant.



Omicron: B.1.1.529

Omicron carries about 50 mutations not seen in combination before, including more than 30 mutations on the spike protein that the coronavirus uses to attach to human cells.



Source: New York Times,
COG-UK Mutation Explorer; <http://sars2.cvr.gla.ac.uk/coe-uk/>

BAY AREA NEWS GROUP

Alarming antibody evasion properties of rising SARS-CoV-2 BQ and XBB subvariants

Qian Wang,^{1,8} Sho Iketani,^{1,8} Zhiteng Li,^{1,8} Liyuan Liu,^{2,8} Yicheng Guo,^{1,8} Yiming Huang,² Anthony D. Bowen,^{1,3} Michael Liu,¹ Maple Wang,¹ Jian Yu,¹ Riccardo Valdez,⁴ Adam S. Lauring,⁵ Zizhang Sheng,¹ Harris H. Wang,² Aubree Gordon,⁴ Lihong Liu,^{1,*} and David D. Ho^{1,3,6,7,*}

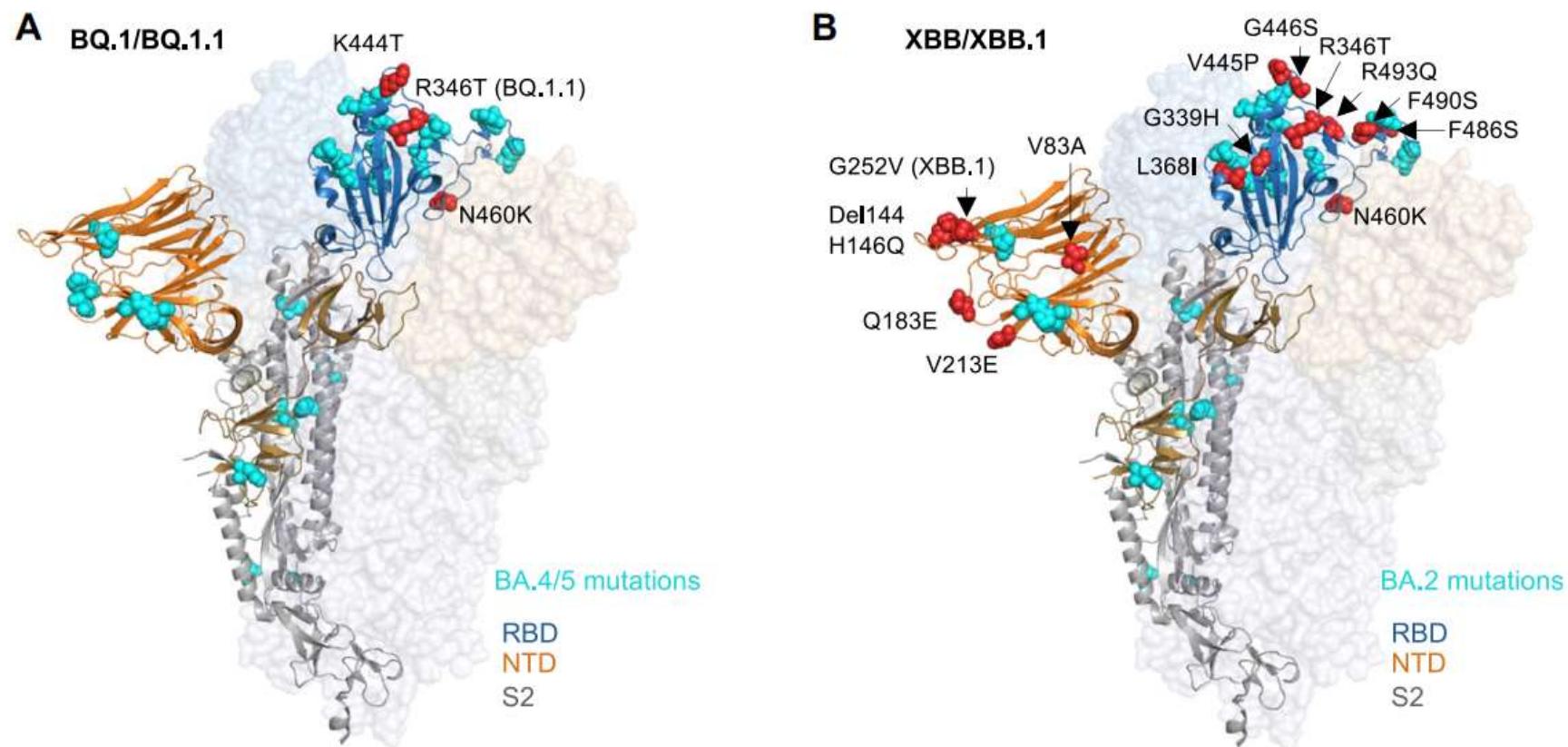
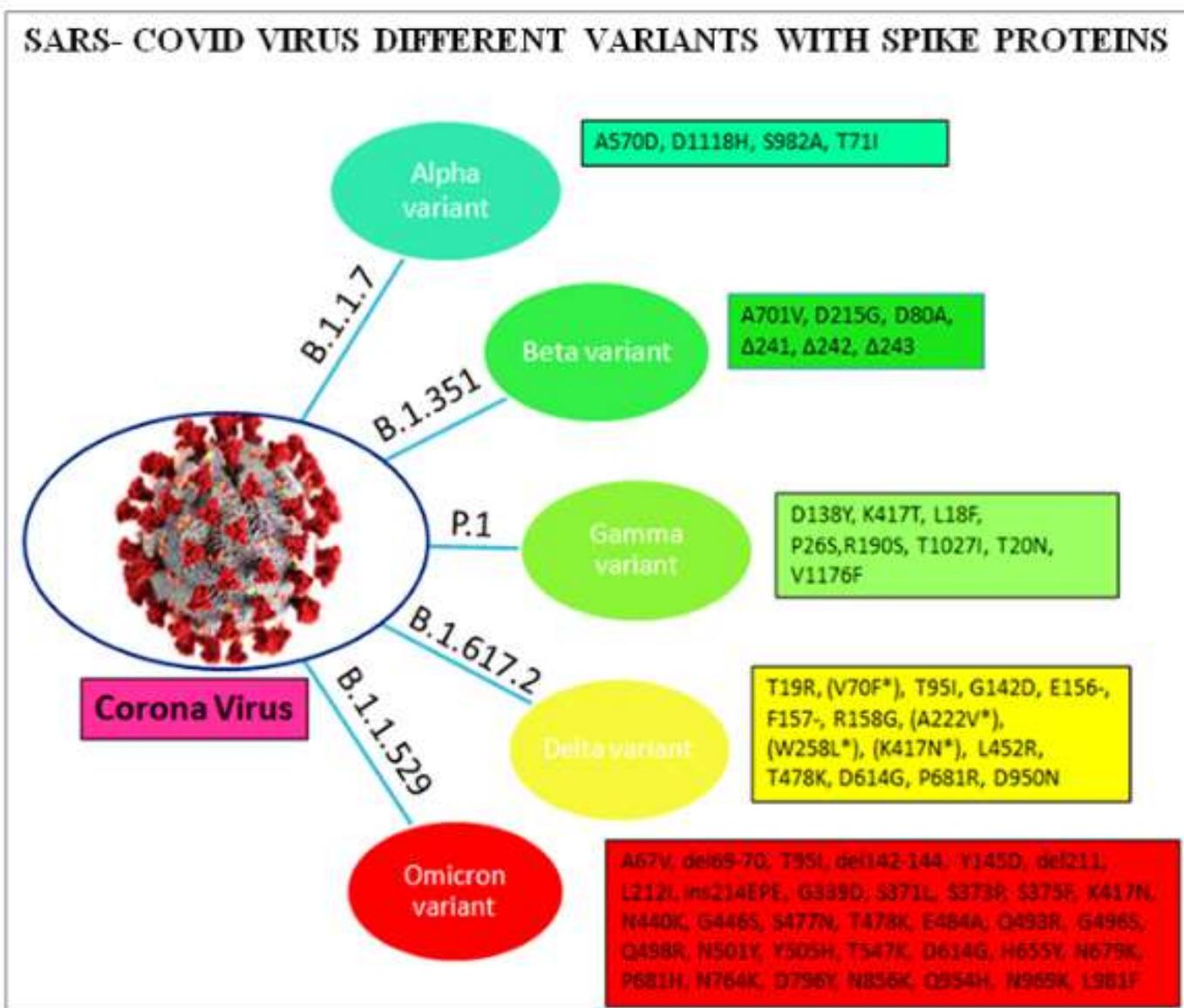


Figure S1. Key spike mutations of BQ and XBB subvariants, related to Figure 1

(A and B) Key mutations of BQ.1 and BQ.1.1 in the context of BA.4/5 (A), and key mutations of XBB and XBB.1 in the context of BA.2 (B). See also Figure 1.

A Mini Review on SARS-COVID-19-2 Omicron Variant (B.1.1.529)

Santhosh Kumar Etaboina, Komalatha Nakkala, K.S. Laddha



SciMedicine Journal

(ISSN: 2704-9833)

Vol. 3, No. 4, December, 2021

<http://dx.doi.org/10.28991/SciMedJ-2021-0304-10>

Figure 1. Different variants with their spike proteins

A Mini Review on SARS-COVID-19-2 Omicron Variant (B.1.1.529)

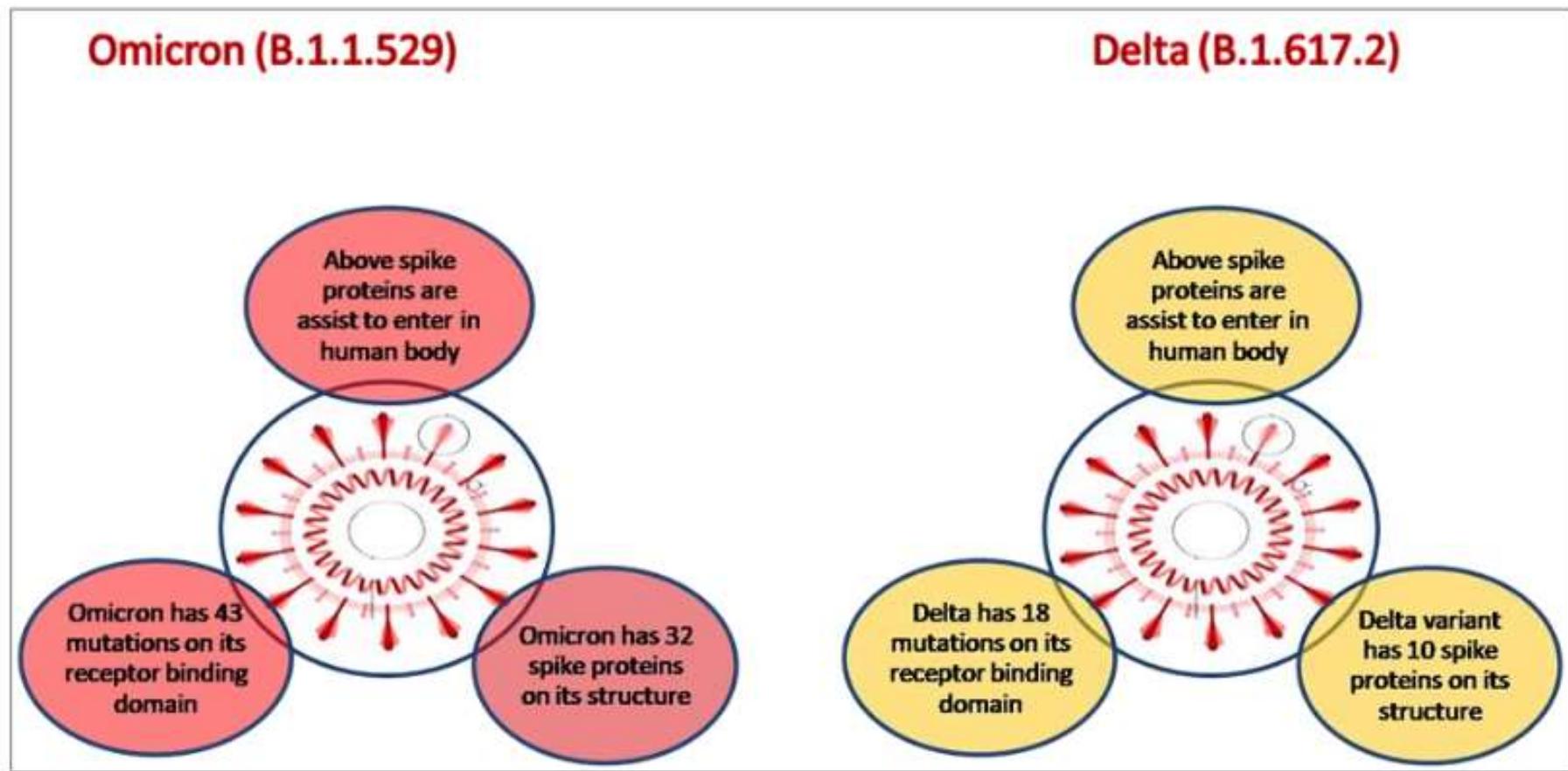


Figure 2. Different spike proteins between delta and omicron variants of SARS-COVID-19-2

SciMedicine Journal

(ISSN: 2704-9833)

Vol. 3, No. 4, December, 2021

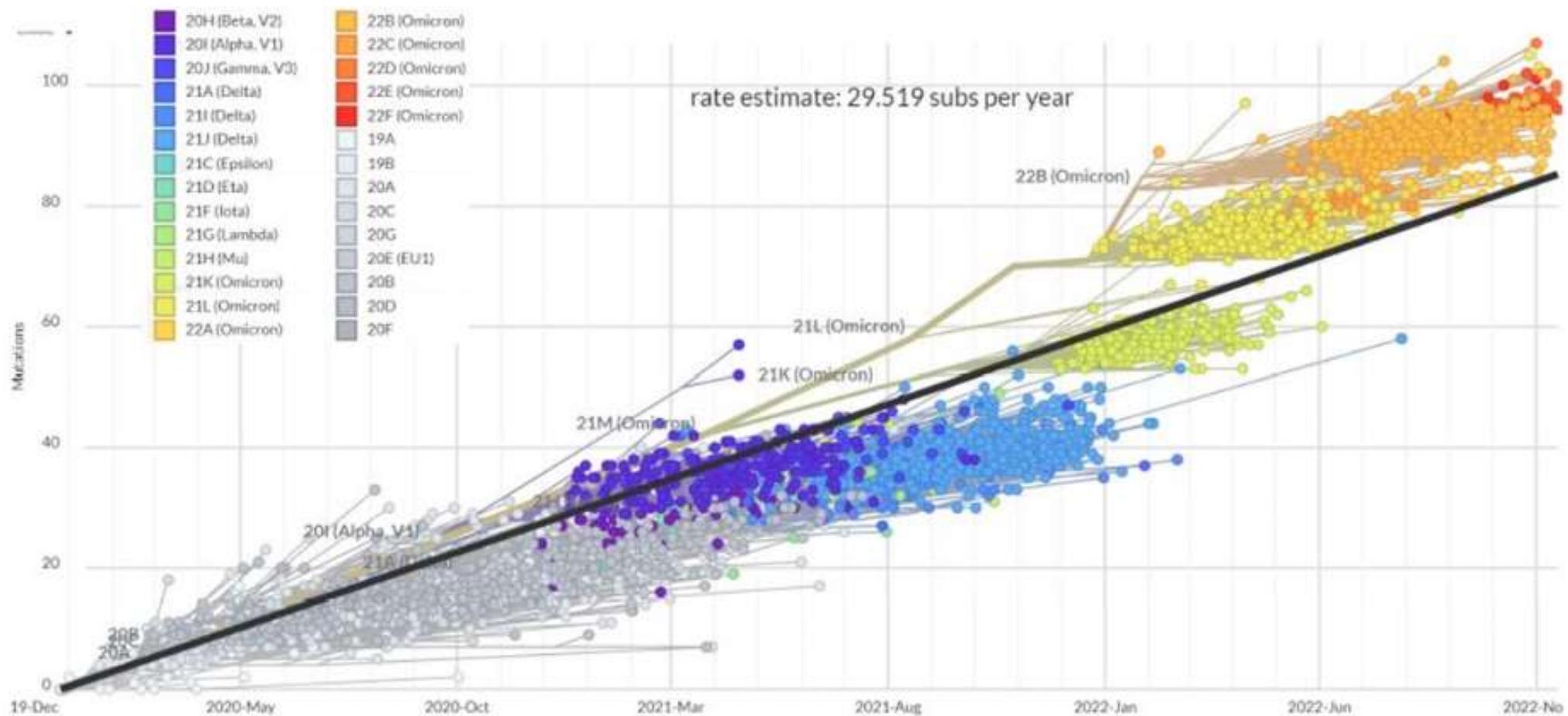
<http://dx.doi.org/10.28991/SciMedJ-2021-0304-10>

Convergent evolution in SARS-CoV-2 Spike creates a variant soup that causes new COVID-19 waves.

Daniele Focosi, Rodrigo Quiroga, Scott A. McConnell, Marc C. Johnson, Arturo Casadevall

Figure 2

Clock tree of SARS-CoV-2 evolution, with regression line showing an increase in the estimate rate of substitutions per year across 3045 genomes sampled between Dec 2019 and Nov 2022. Accessed online at <https://nextstrain.org/ncov/gisaid/global/all-time?l=clock&m=div> on November 26, 2022.



When is a COVID mutation a new variant, and when is it a subvariant? And what's a recombinant?

First, what are mutations?

When cells reproduce, they use a set of genetic instructions (made of DNA or RNA) to replicate. But given this is happening at such a rapid rate, sometimes errors can occur.

These errors, or changes in the genetic code, are also called mutations.

What are variants? Are they different to strains?

A variant is where the genetic code has changed due to a mutation, or a number of mutations.

A variant, while different genetically, does not necessarily differ in its behaviour from the parent virus.

The virus that causes COVID is a single species of coronavirus named SARS-CoV-2.

What are subvariants?

Omicron has been shown to be more infectious than its predecessors, hence has spread swiftly worldwide. Given the resulting abundant opportunities to reproduce,

Omicron has had the opportunity to acquire specific mutations of its own.

These have not been deemed significant enough to satisfy the definitions to call them new variants. However, they have had some slightly different properties. For this reason they have been referred to as "subvariants". Initially we saw BA.2 arise, which was found to be slightly more infectious than the original Omicron, BA.1

What are recombinants?

There are now a large number of Omicron subvariants. BA.4 was detected in January and is essentially a mixture of BA.1 and BA.3 with some new mutations, making it slightly more infectious than preceding subvariants.

When viruses reproduce inside host cells,
they can randomly collect pieces from multiple strains or variants when they reproduce,

Given this is basically forming a combination of both virus this process is called recombination. When this happens, the resulting "recombinant" can have properties of either or both viruses.

Variant Sequence

There are Ten Greek Letters between Delta and Omicron. Why Skip?

There have been Eight “*Variants of Interest*” between Delta and Omicron. Delta and Omicron are Both “*Variants of Concern*”.

There have been Two Skipped Greek Letters between Delta and Omicron.

COVID-19

How variants are named

The WHO has identified **five variants of concern (VOC)** and **eight variants of interest (VOI)**. They are named after the letters of the **Greek alphabet**.

A α	B β	Γ γ	Δ δ	E ε *
alpha United Kingdom September, 2020	beta South Africa May, 2020	gamma Brazil November, 2020	delta India October, 2020	epsilon India October, 2020
Z ζ *	H η *	Θ θ *	I ι *	K κ *
zeta Brazil April, 2020	eta Multiple countries December, 2020	theta Philippines January, 2021	lota United States November, 2020	kappa India October, 2020
Λ λ	M μ	N ν	Ξ ξ	O o
lambda Peru December, 2020	mu Colombia January, 2021	nu Skipped "Nu is too easily confounded with 'new' and Xi was not used because it is a common surname." - WHO	xi	omicron Multiple countries November, 2021
Π π	P ρ	Σ σ/ς	T τ	Y υ
pi	rho	sigma	tau	upsilon
Φ φ	X χ	Ψ ψ	Ω ω	
phi	chi	psi	omega	

variant of concern
Earliest documented samples

variant of interest
Earliest documented samples

* Formerly monitored variant of interest.

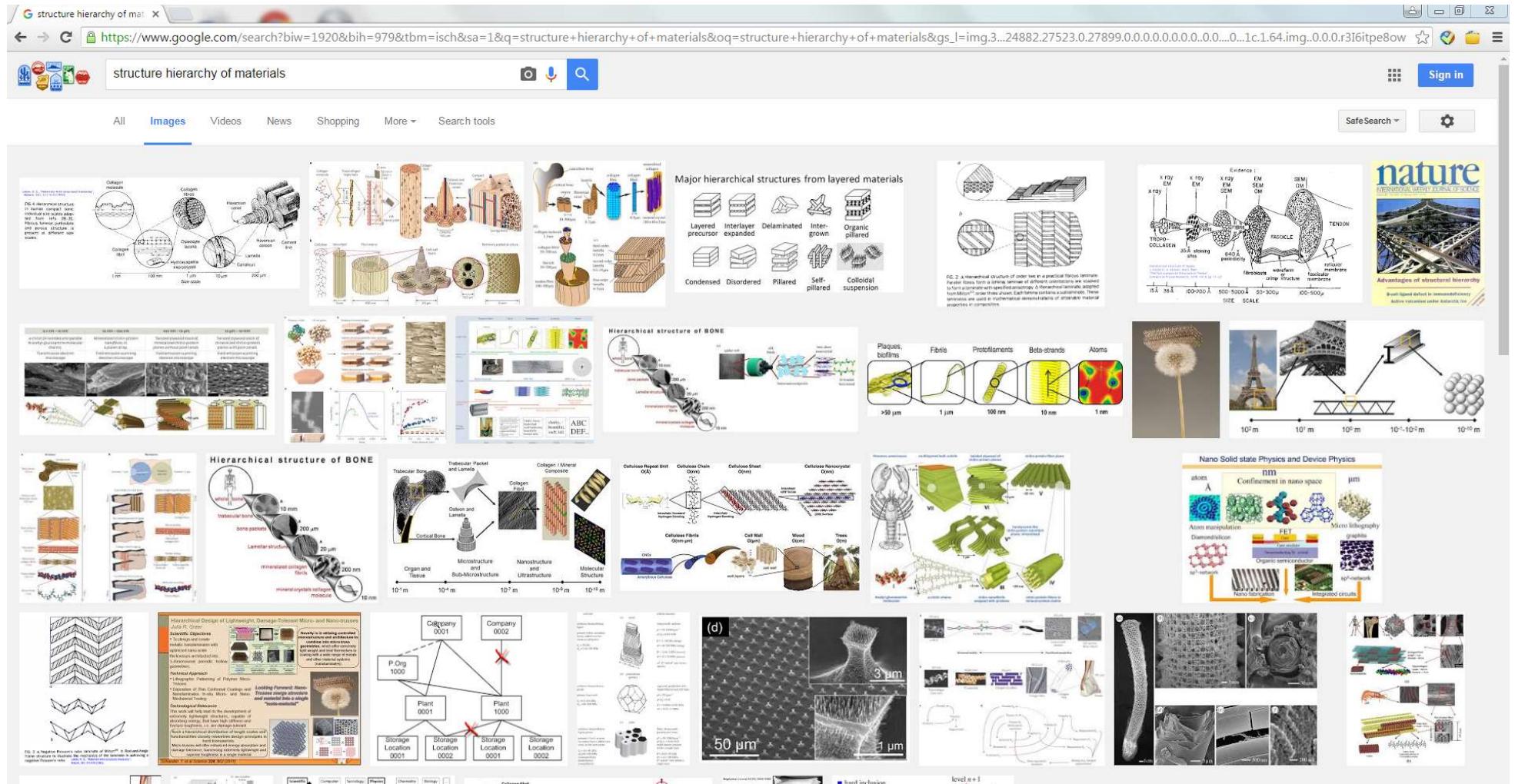


Source: WHO | November 29, 2021

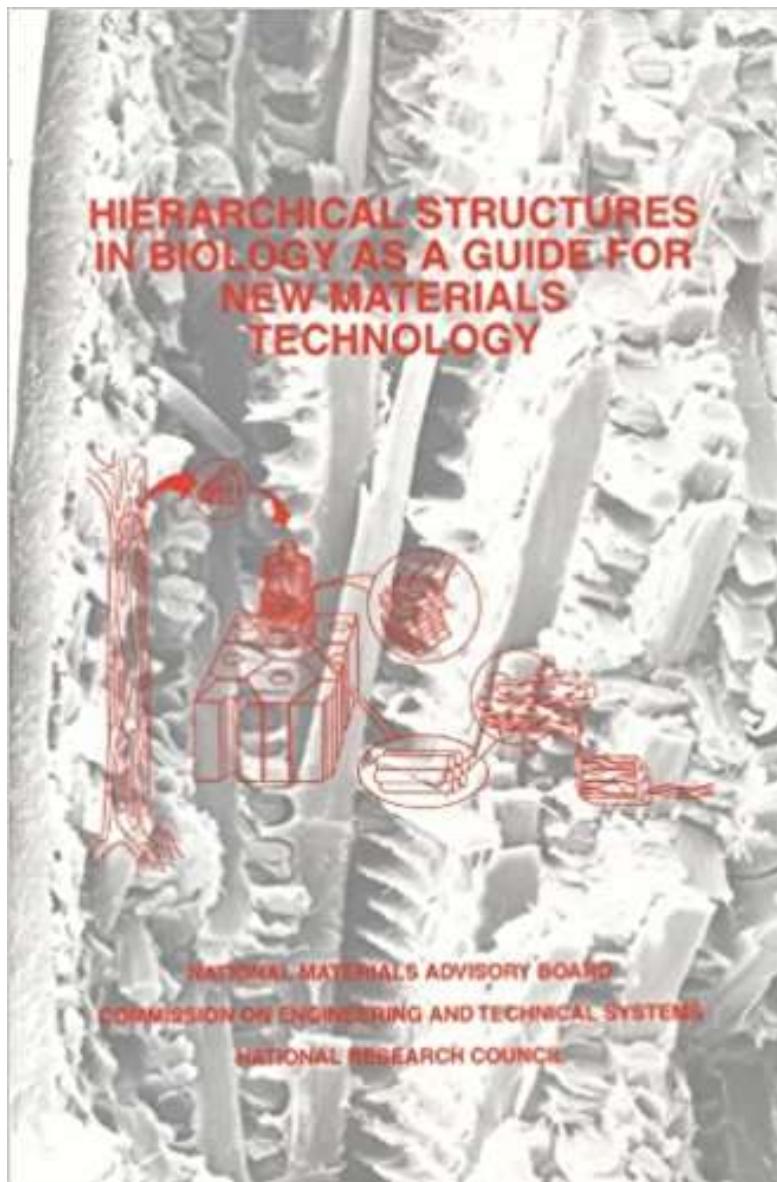


Hierarchical Structures Are Everywhere

Search results from Images.google.com



Recommended Reference



HIERARCHICAL STRUCTURES IN BIOLOGY AS A GUIDE FOR NEW MATERIALS TECHNOLOGY

COMMITTEE ON
SYNTHETIC HIERARCHICAL STRUCTURES

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STEPHEN A. WAINWRIGHT, Duke University, Durham, North Carolina

Hierarchical Structures

Questions?



Dr. Andy Olah, amo5@case.edu, O: 216-368-0606, C: 216-272-0505

“It’s probably my age that tricks people into thinking that I’m an adult.”

There will be a quiz on Friday

January 24, 2025



www/DesktopBackground.org

* From the Hitchhikers Guide to the Galaxy – Douglas Adams

EMAC 276 - Homework Assignment #1

Due: Friday January 24, 2024

Prof. Olah

We have spent some time on the Hierarchical Structure concept within several disciplines; i.e., biology, polymer science, mechanical engineering, management, etc.

Other than the examples we have provided in class, your assignment is to identify one additional example of the hierarchical structure concept.

In your description you must:

1. Identify the example and the discipline it involves.
2. Explain the number of hierarchical levels and the scale of each level.
3. Identify the relationship in your example of the three concepts of hierarchical structures:
 - a. Scale
 - b. Interaction
 - c. Architecture
4. Please keep your answer to one page.

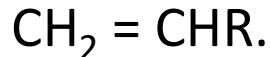
EMAC 276

Lesson 3: Polystyrene and Styrofoam

Andy Olah, Ph.D.
January 22, 2024

What is a “Vinyl” Type Polymer?

Vinyl polymers are the most common type of polymers derived from “vinyl-type” monomers having the general structure:



Where,

polystyrene – R = C₆H₅

polyvinyl chloride – R = Cl

polyvinyl acetate – R = O₂CCH₃

polyacrylonitrile - R = CN

Not to be confused with poly(vinyl chloride) (PVC) materials which have traditionally been identified as “vinyls”; i.e., vinyl siding, vinyl records, etc.

Olefin polymers are a subgroup of vinyl monomers produced from alkenes having a C_nH_{2n} monomer structure:

polyethylene – R = H => CH₂ = CH₂; (n = 2) => C₂H₄

polypropylene – R = CH₃ => CH₂ = CH-CH₃; (n = 3) => C₃H₆

polybutylene – R = CH₂-CH₃ => CH₂ = CH-CH₂-CH₃; (n=4) => C₄H₈

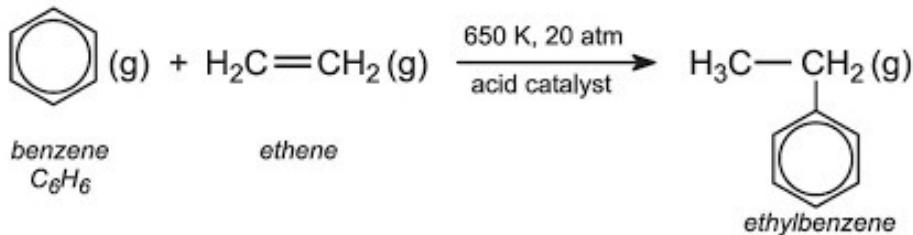
History of Polystyrene

- 1839 - Eduard Simon (Germany) – isolated styrene monomer (called Styrol) which developed into a thickened mass after several days.
- 1866 – Marcellin Berthelot (France) – recognized the formation of styrol to form a colloid-like material.
 - “One knows that styrene heated in a sealed vessel at 200°C, for several hours, it is changed into a resinous colloid (*polystyrene* ?), and that this colloid, [when] distilled abruptly, reproduces styrene.”
- 1926 – Hermann Staudinger (Germany) – identified a specific type of colloid as true macromolecules – i.e., polymers and in turn this materials was identified as polystyrene.
- 1931 – I.G. Farben/BASF (Germany) began manufacturing polystyrene.
- 1944 – Dow Chemical develops and patents a process to produce Styrofoam.
- 1952 – BASF produces and exhibits a process for expanded polystyrene beads.
- 1954 – Koppers Company and Dart Container develops a process for producing styrofoam cups.

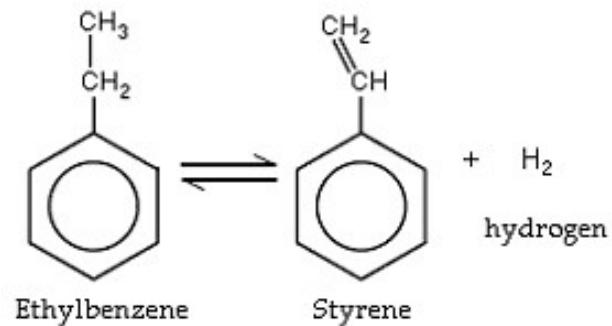
Synthesis of Styrene Monomer

Synthesis of Ethylbenzene with Aluminum Chloride

Reacts at ~380°C



Dehydrogenation to form Styrene



In current industrial practice **ethylbenzene dehydrogenation** is typically performed in a fixed-bed reactor in the **temperature** range 540–650 °C and uses potassium-promoted iron(III) oxide mixed with additional promoters to stabilize the morphology of the catalyst or avoid sintering.

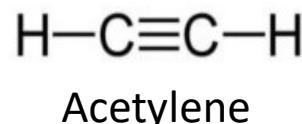
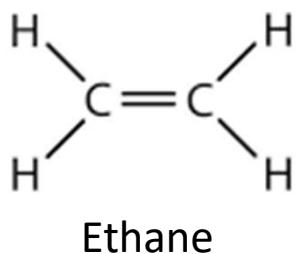
Does there exist a similar but alternative route without dehydrogenation?

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF
ROCHESTER.]

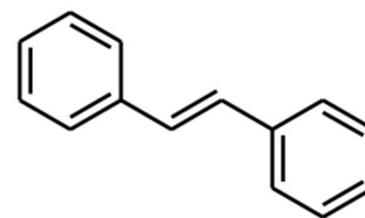
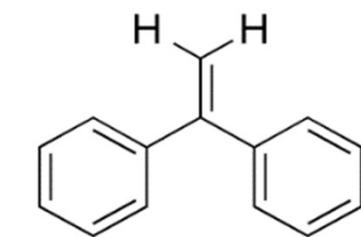
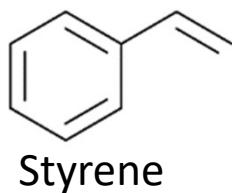
THE CONDENSATION OF ACETYLENE WITH BENZENE AND
ITS DERIVATIVES IN THE PRESENCE OF
ALUMINUM CHLORIDE.

By OTTO W. COOK AND VICTOR J. CHAMBERS.

Received August 23, 1920.



The first and most important work on this condensation was that of Varet and Vienne.¹ They passed acetylene through a mixture of benzene and aluminum chloride, and reported the formation of a product containing 80% phenyl ethylene (styrene), 15% *unsym.* diphenylethane and 5% *sym.* diphenylethane (dibenzyl). Neither the actual amounts obtained, referred to the reacting materials, nor the conditions under which the runs were made, were stated.



¹ Varet and Vienne, *Compt. Rend.*, **164**, 1375 (1886)

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF
ROCHESTER.]

THE CONDENSATION OF ACETYLENE WITH BENZENE AND
ITS DERIVATIVES IN THE PRESENCE OF
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By OTTO W. COOK AND VICTOR J. CHAMBERS.

Received August 23, 1920.

I. Condensation with Benzene.

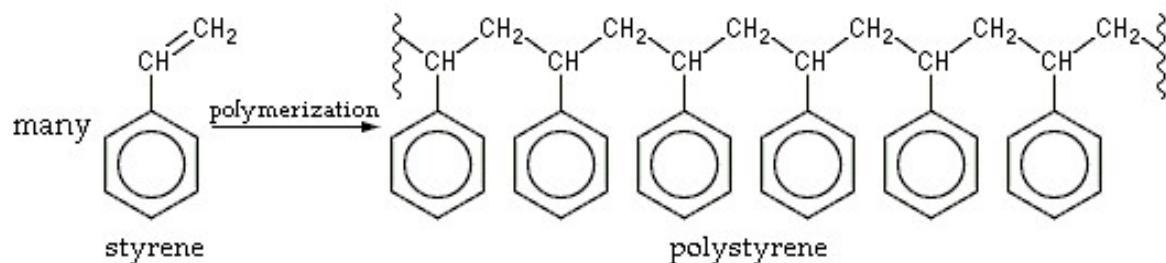
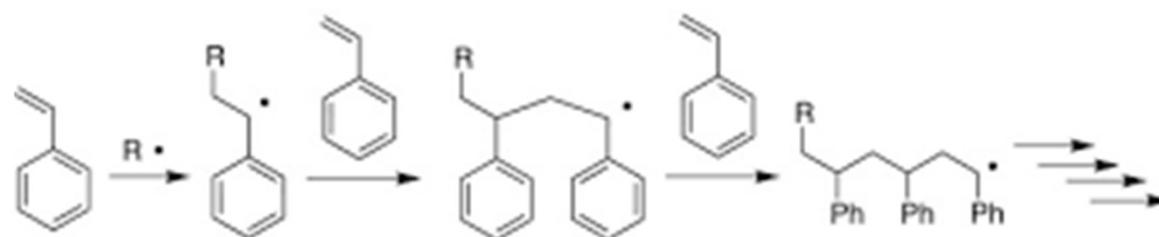
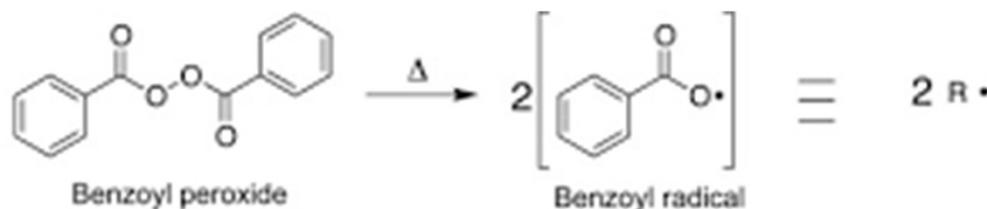
In the majority of these runs, the temperature was held within a few degrees' variation of a given point. When the mixture was left undisturbed, the temperature gradually rose to about 70° to 80° as the reaction proceeded, and, after about 3 hours, started to diminish. The condensation product consisted of a dirty yellow oil. When this oil was hydrolyzed and distilled with steam, it gave 2 volatile fractions and a black tarry residue.

The first fraction was unchanged benzene, together with some toluene and xylene, formed by the action of the aluminum chloride on benzene itself. A small portion of a material, b. p. 140–145°, was also obtained. This gave evidence of the presence of styrene, which, however, was not present in sufficient quantity to be isolated.

The second fraction, which came over very slowly (in from 4 to 6 hours), when dried, boiled at 280° to 290° and was identified as *unsym.* diphenylethane, b. p. 286°, by oxidation to benzophenone and the formation of benzophenone oxime, m. p. 140°.

The residue, dried and distilled, gave 2 principal fractions. One consisted of some diphenyl-ethane which had not come over with steam. The other fraction, which distilled above 360°, solidified, and, after several recrystallizations from alcohol, yielded long brown needles, m. p. 181°. On oxidation, it gave anthraquinone. It is therefore identified as the 9,10-dimethyl-anthracene hydride of Anschutz.¹ No dibenzyl could be found.

Free Radical Polymerization of Polystyrene



A **free radical** can be defined as any molecular species capable of independent existence that **contains an unpaired electron in an atomic orbital**. The presence of an unpaired electron results in certain common properties that are shared by most radicals. Many radicals are unstable and highly reactive. They can either donate an electron to or accept an electron from other molecules, therefore behaving as oxidants or reductants.

Peroxide Initiators for Free Radical Polymerization

Initiator	Radical Generated
Benzoyl peroxide (BPO)	
Di- <i>tert</i> -butyl peroxide (DTBP)	
Azobisisobutyronitrile (AIBN)	

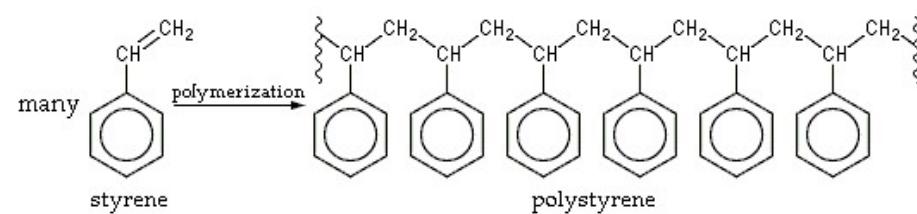


TABLE 3-12 Thermal Decomposition of Initiators^{a,b,c}

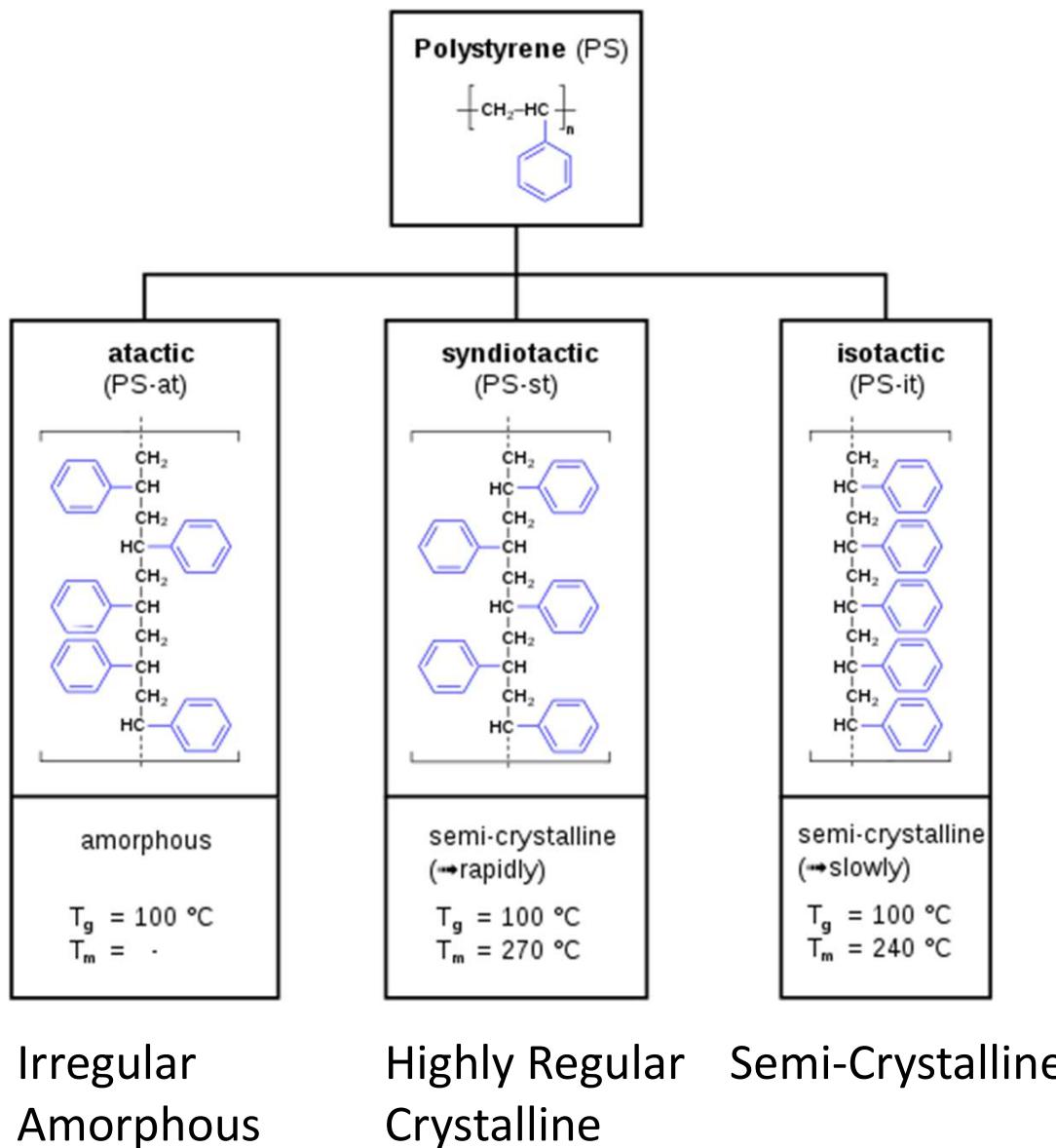
Initiator	$k_d \times 10^5$	T (°C)	E_d
2,2'-Azobisisobutyronitrile	0.845	60	123.4
Acetyl peroxide	2.39	70	136.0
Benzoyl peroxide	5.50	85	124.3
Cumyl peroxide	1.56	115	170.3
<i>t</i> -Butyl peroxide	3.00	130	146.9
<i>t</i> -Butyl hydroperoxide	0.429	155	170.7

^aAll data are for decompositions in benzene solution.

^bData from Brandrup and Immergut [1989].

^cThe units of k_d are sec⁻¹; the units of E_d are kJ/mole.

Atactic, Syndiotactic and Isotactic Polystyrene



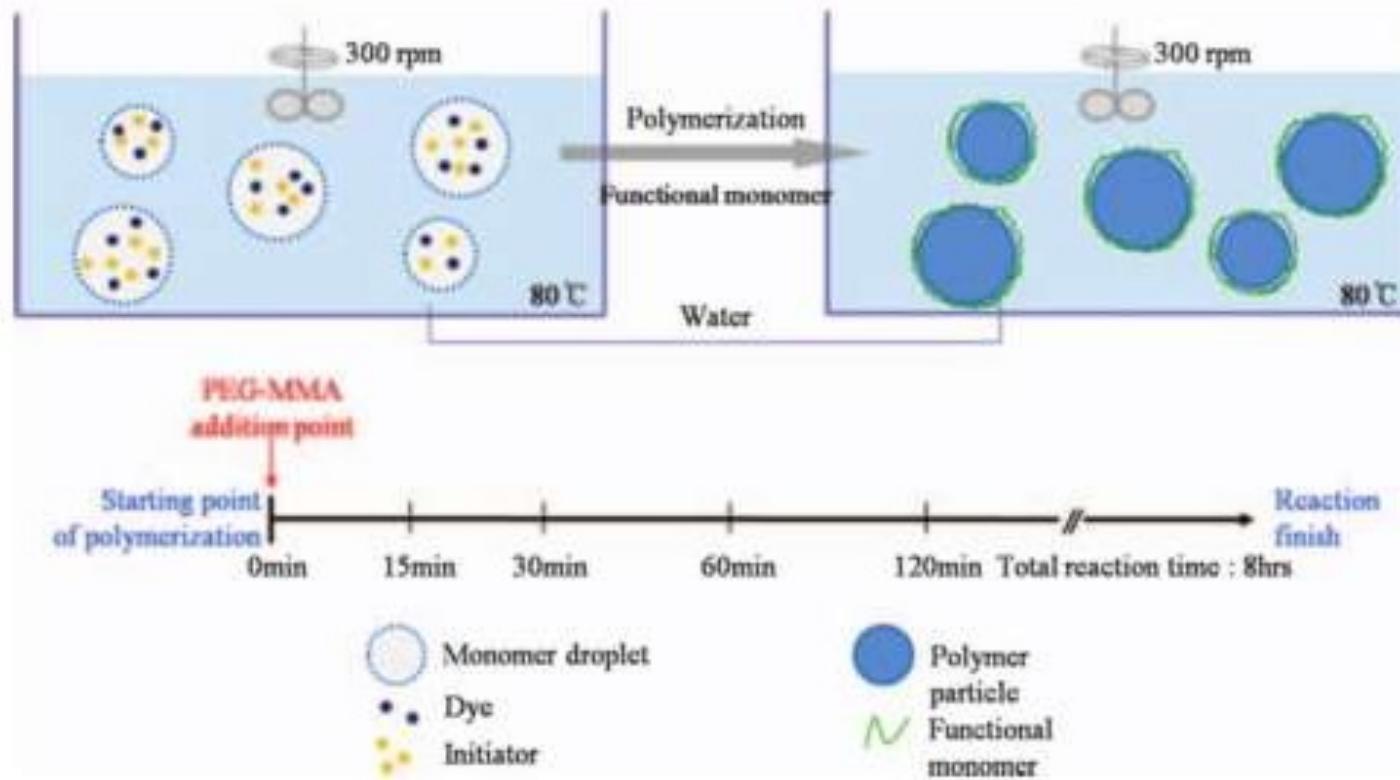


Figure 1. Schematic diagram of suspension polymerization of polystyrene and PEG-MA.

Polystyrene Suspension Polymerization

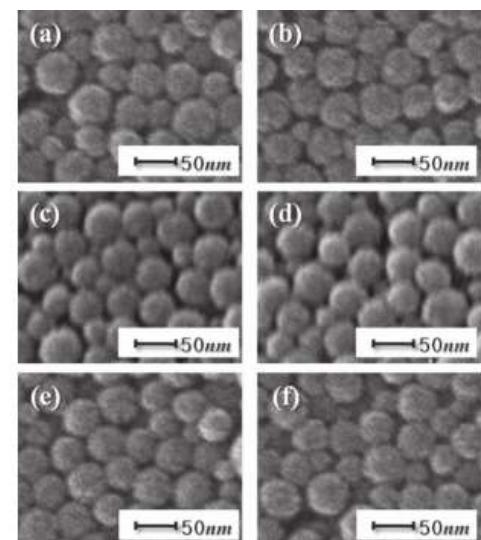
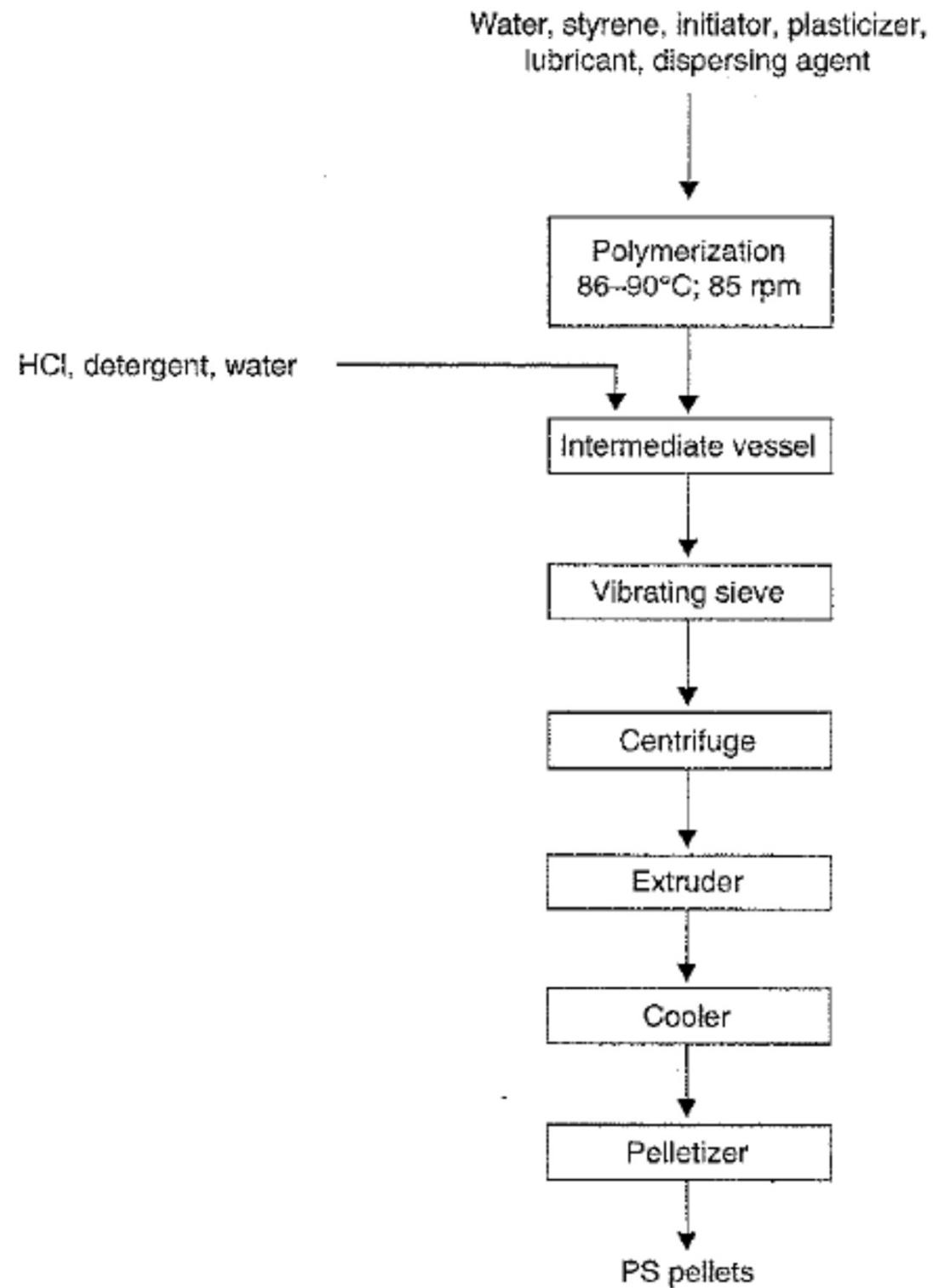


Figure 2. SEM images of (a) PS, (b) PM 300-1, (c) PM 300-5, (d) PM 300-9, (e) PM 475, (f) PM 950.

Flow Diagram for the Suspension Polymerization of Polystyrene



Polystyrene – Suspension Polymerization



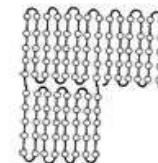
Raw polystyrene beads
from reactor/pelletizer.



Polystyrene is an Amorphous Polymer

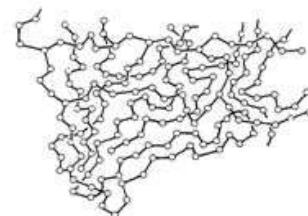
- ***Crystalline:***

- Periodic 3-D, repeating array of molecules



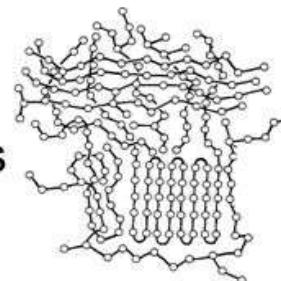
- ***Amorphous:***

- Literally “without structure”
 - No repeating array



- ***Semi-crystalline:***

- Structure containing regions of both crystalline and amorphous molecular arrangements



MOLECULAR MOTION IN POLYSTYRENE

Molecular Transitions In Atactic Polystyrene

(b)

$$T < T_g$$



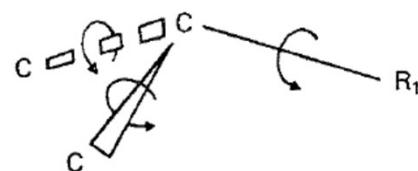
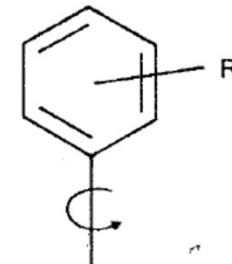
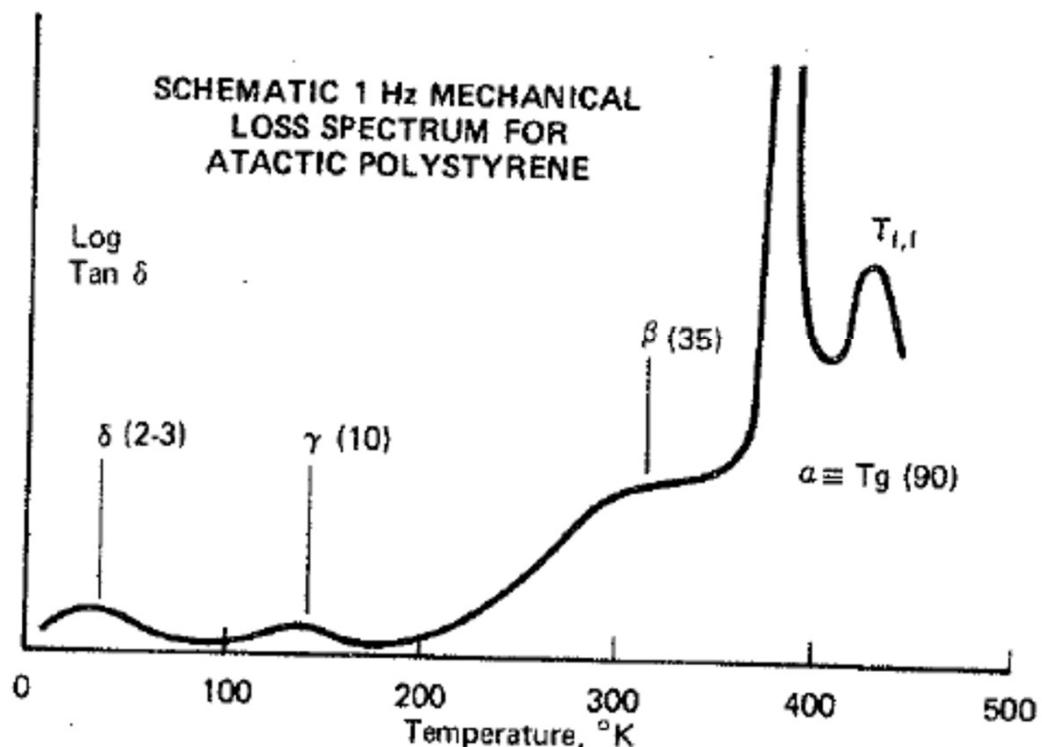
$$T > T_g$$



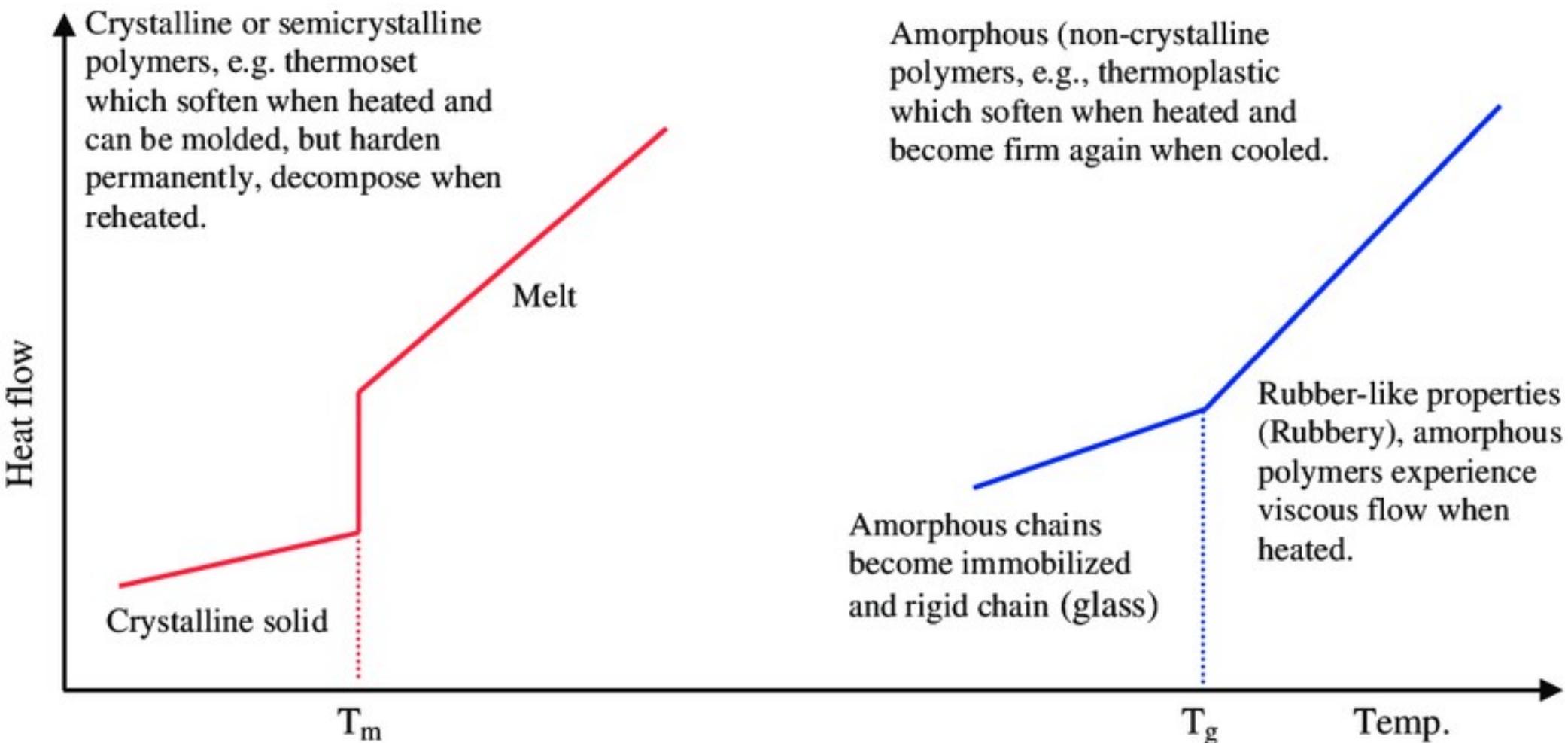
"frozen" backbone

crankshaft-like
chain motion

T_g the
Glass Transition Temperature



Heat Flow for Amorphous and Semi-Crystalline Polymers



T_g as a Function of Molecular Weight

The glass transition temperature of polystyrene is identified as ~100 C.

Table 1 The Molecular Weights and Molecular Weight Distributions of the PS Samples

Sample	Mw	Mn	Mw/Mn
PS 1	1940	1690	1.15
PS 2	4380	3570	1.23
PS 3	5480	5200	1.04
PS 4	12600	12000	1.05
PS 5	35100	30500	1.15
PS 6	65000	63700	1.02
PS 7	275000	258000	1.07
PS 8	950000	925000	1.03

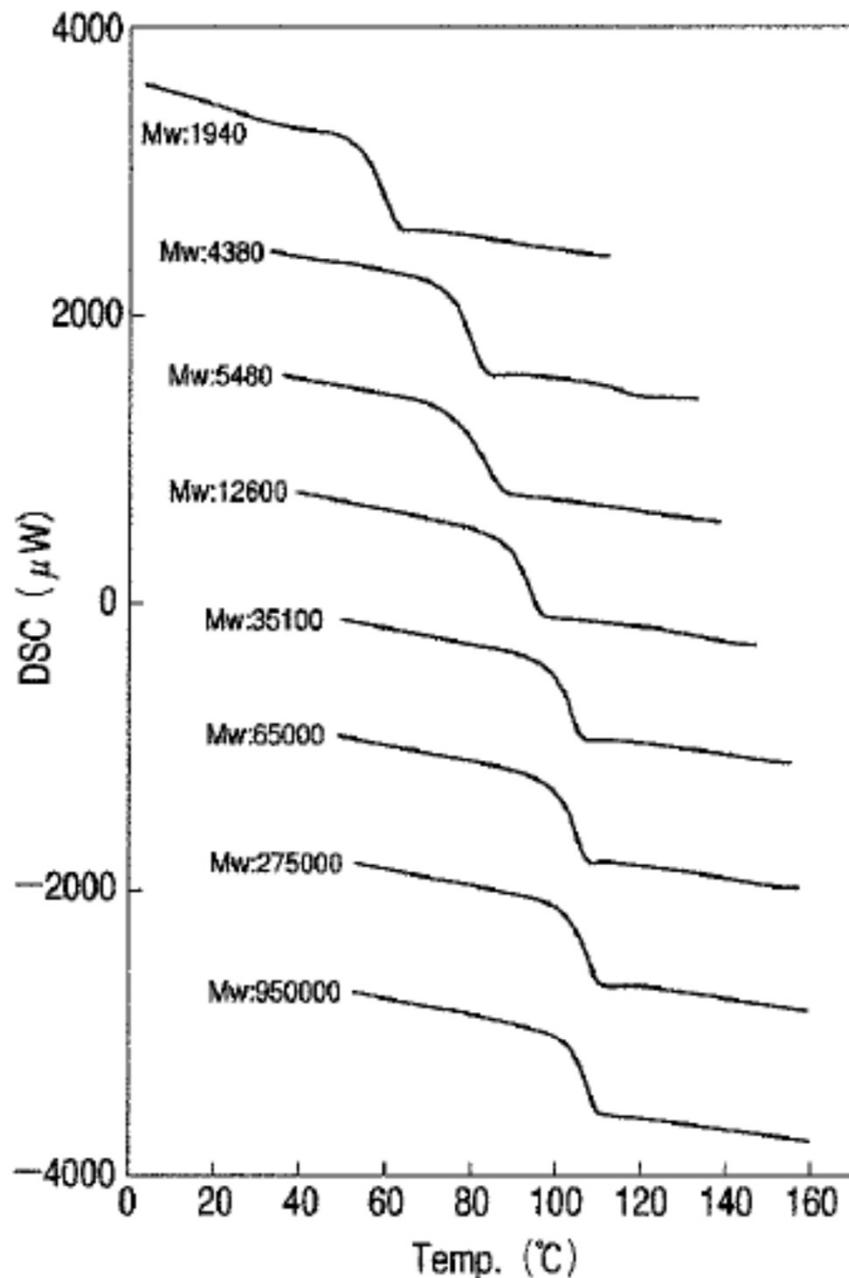


Figure 2 DSC Measurement Results for the PS Samples

Tg as a Function of Molecular Weight

Table 1 The Glass Transition Temperature (Tg) Measurement Results for the PS Samples

Sample	Mw	Tg (°C)		
		Tig ^{*1}	Tmg ^{*2}	Teg ^{*3}
PS 1	1940	56.8	60.4	64.2
PS 2	4380	76.2	79.9	83.7
PS 3	5480	77.0	82.4	87.8
PS 4	12600	89.6	93.4	96.7
PS 5	35100	100.2	103.1	105.9
PS 6	65000	100.6	104.0	107.3
PS 7	275000	103.5	106.4	109.4
PS 8	950000	103.9	106.7	109.7

*1 Onset temperature of Tg

*2 Mid-point temperature of Tg

*3 End temperature of Tg

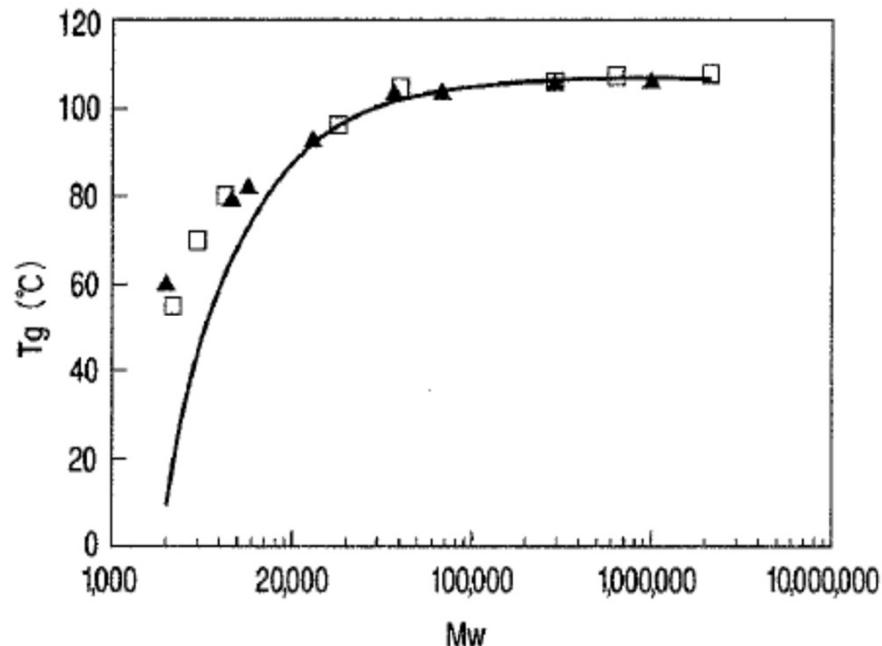
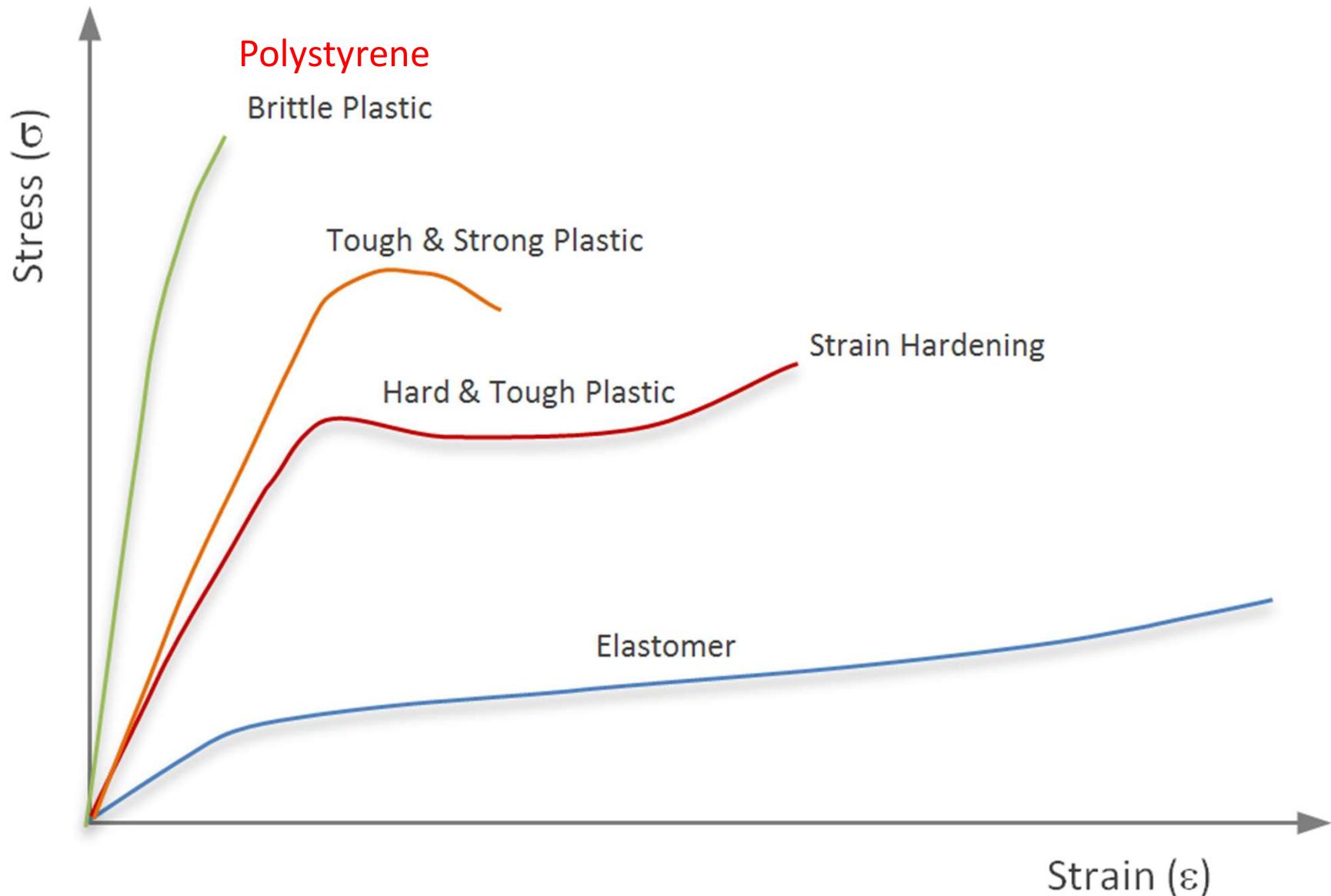


Figure 3 Dependence of Glass Transition Temperature on Molecular Weight
▲ Measurement results from this experiment (Figure 2 and Table 2)
□ Measurement results of P.Claudy et al.
— Results calculated from the theoretical formula of T.G.Fox et al.

Unmodified Polystyrene is a Very Brittle Material



Patented Oct. 5, 1948

US 2,450,436

UNITED STATES PATENT OFFICE

MANUFACTURE OF CELLULAR THERMOPLASTIC PRODUCTS

Otis Ray McIntire, Midland, Mich

assignor to

The Dow Chemical Company, Midland,
a corporation of Delaware

Application July 28, 1947, Serial No. 763,989

12 Claims. (Cl 18-48).

This invention concerns an improved method for the manufacture of cellular thermoplastic products. It pertains especially to the production of such products in the form of substantially uniform cellular masses of considerable size, e.g., of 2 inches, or greater, thickness or diameter, from the resinous benzene-soluble polymers and copolymers of nonovinyl aromatic compounds having the vinyl group attached directly to a carbon atom of the aromatic nucleus, particularly styrene.



Overcoming the Brittle Deficiency of PS

- **Ray McIntire: Styrofoam Inventor**
- Dow Chemical Company scientist **Ray McIntire** invented foamed polystyrene aka Styrofoam. McIntire said his invention of foamed polystyrene was purely accidental. His invention came about as he was trying to find a flexible electrical insulator around the time of World War II.
- Polystyrene, which already had been invented, was a good insulator **but too brittle**. McIntire tried to make a new rubber-like polymer by combining styrene with a volatile liquid called isobutylene under pressure. The result was a foam polystyrene with bubbles and was 30 times lighter than regular polystyrene. The Dow Chemical Company introduced Styrofoam products to the United States in 1954.

UNITED STATES PATENT OFFICE

MANUFACTURE OF CELLULAR THERMOPLASTIC PRODUCTS

Otis Ray McIntire, Midland, Mich

1. In a method for the production of a substantially uniform solid cellular thermoplastic article which is composed of individual closed cells having thin walls of a solid thermoplastic polymer, the smallest linear dimension of which article is at least 2 inches, the steps which consist in charging a vessel with a solid thermoplastic polymer, also introducing into the vessel a normally gaseous agent capable of being dissolved by the polymer so that the polymer and the normally gaseous agent are in contact with one another, subjecting the mixture to supers-atmospheric pressure while at a temperature within the range of from room temperature to below the critical temperature of said agent for a time sufficient to form a gel of the polymer, which gel is capable of flowing, the normally gaseous agent having been introduced and dissolved in the polymer gel in amount such as to be vaporized substantially completely upon release of the pressure with resultant swelling and cooling, due principally to the heat of vaporization of said agent, of the polymer to form a cellular mass which, when formed, is at a temperature within the range of between -30° C. and ten degrees above the heat distortion temperature of the polymer, and opening an outlet, having an aperture of minimum cross sectional area corresponding to that of a circle of at least three fourths inch diameter, near the bottom of the vessel so as to cause the gel to flow from the vessel and form the cellular product.
10. The method, as described in claim 7, where in the polymer is one selected from the class consisting of the thermoplastic polymers of mono vinyl-aromatic compounds and thermoplastic copolymers of monovinyl-aromatic compounds, and the normally gaseous agent is composed for the most part of at least one olefin having from three to four carbon atoms in the molecule.
11. The method described in claim 7 wherein the polymer is polystyrene.

Extruded Polystyrene Foam - XPS

Styrofoam is a trademarked brand owned and manufactured by The Dow Chemical Company comprising closed cell extruded polystyrene foam (XPS), commonly called *Blue Board*. This material is used as foam building insulation board used in walls, roofs, and foundations for thermal insulation and water barrier.



Patented June 15, 1954

US 2,681,321

UNITED STATES PATENT OFFICE

PRODUCTION OF POROUS MATERIALS FROM FILM-FORMING ORGANIC THERMOPLASTIC MASSES

Fritz Stastny, Weinheim (Bergstrasse), and
Rudolf Gaeth, Ludwigshafen (Rhine), Germany,
assignors to Badische Arilin- & Soda
RFhaibnrei,k GAekrtmeanngeysellschaft, Ludwigshafen
No Drawing. Application February 24, 1951,
Serial No. 212,66
Claims priority, application Germany
February 27, 1950
12 Claims. (C. 260-2.5)

12. A process for the production of porous polystyrene which comprises homogeneously dispersing in monostyrene a non-reactive volatile organic liquid in which polystyrene is insoluble, polymerizing this mixture at temperatures below the boiling point of the liquid under the conditions employed, and heating the resulting mass to a temperature above the boiling point of the liquid and above the Softening point but not more than about a few degrees above the softening point of the resulting polystyrene by contacting said mass with hot water, the relative proportions of mono-styrene and said liquid employed being such that the polymerization product is a solid body containing the liquid dispersed throughout.

Patented August 23, 1960

US 2,950,261

UNITED STATES PATENT OFFICE

PROCESS OF MAKING EXPANSIBLE PARTICULATE STYRENE POLYMER BY DIFFUSION OF A VOLATILE LIQUID HYDROCARBON INTO SAID POLYMER PARTICLES

Kari Buchholz, Ludwigshafen (Rhine), Fritz Siaastny, Weinheim, Bergstrasse,
and Rudolf Gaeth, Ludwigshafen (Rhine), Germany,
assignors to Badische Anilin & Soda-Fabrik Aktiengesellschaft, Ludwigshafen (Rhine), Germany
No Drawing. Filed Sept. 8, 1954, Ser. No. 454,848

Claims priority, application Germany Sept. 25, 1953

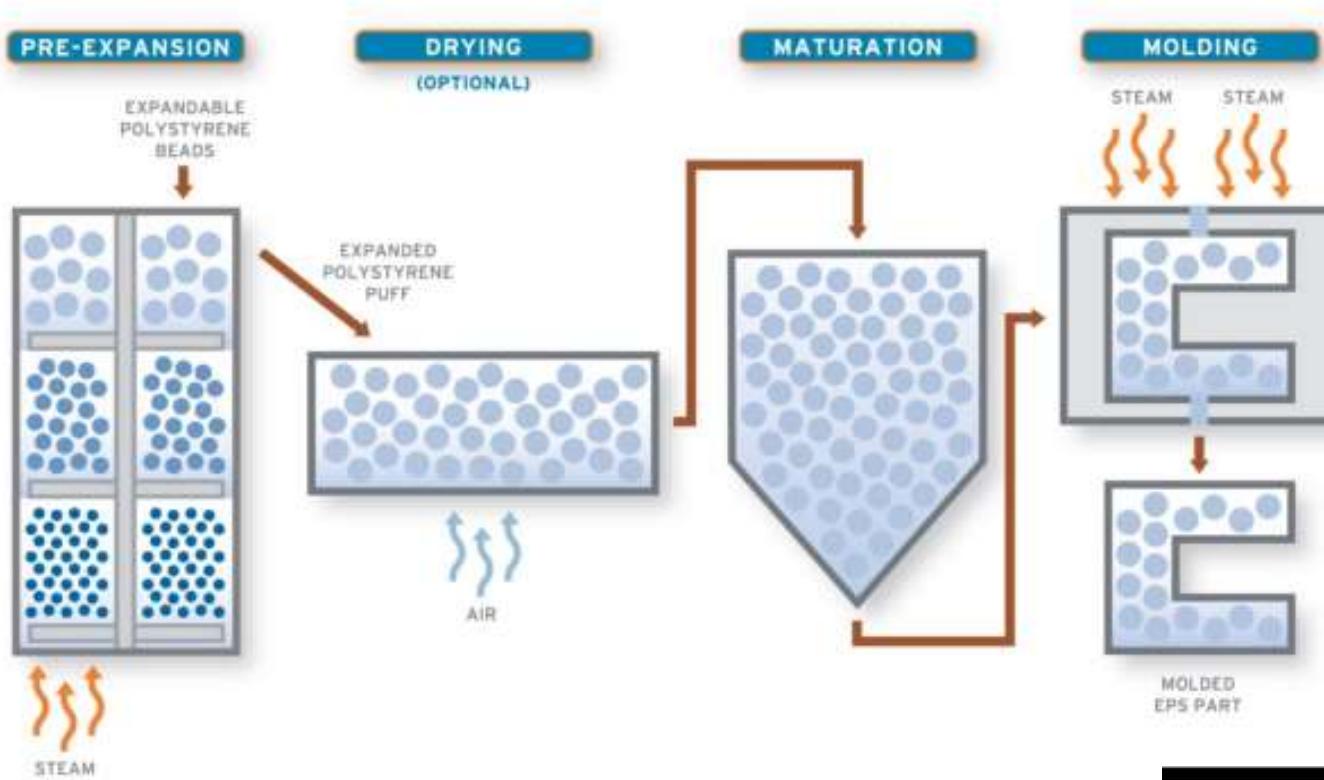
7 Claims. (C. 260-2.5)

1. In a process for the production of an **expansible particulate styrene polymer by diffusing a volatile liquid hydrocarbon into fine particles of a styrene polymer**, wherein said hydrocarbon is selected from the class consisting of aliphatic and cycloaliphatic hydrocarbons in which said polymer is insoluble and boiling below the softening point of said polymer, the improvement which comprises contacting said polymer particles in a closed vessel with a diffusion mixture in which said polymer is insoluble and consisting essentially of a major proportion of water and a minor proportion of said hydrocarbon, and maintaining said particles and said mixture in contact at a temperature above 40° C. and below the softening point of said polymer to diffuse said hydrocarbon into said particles.

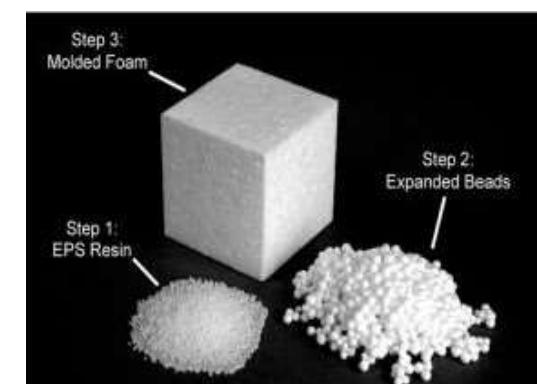
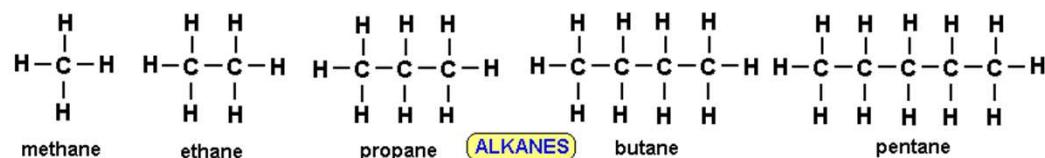
Expanded Polystyrene - EPS

Manufacturing

Expanded Polystyrene (EPS) - Manufacturing Process



Blowing Agents for Expanded Polystyrene (EPS)



Difference Between Extrudable Polystyrene Foam (XPS) and Expandable Polystyrene Foam (EPS)



XPS



EPS

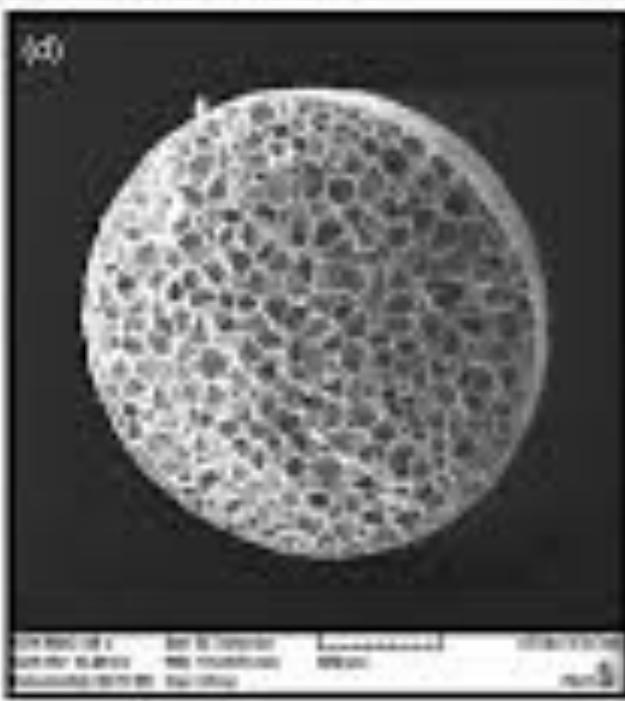
Expanded Polystyrene Foam - EPS

In the United States and Canada, the colloquial use of the word *styrofoam* refers to another material that is usually white in color and **expanded (not extruded)** polystyrene foam (EPS). It is commonly used in food containers, coffee cups, and as cushioning material in packaging.

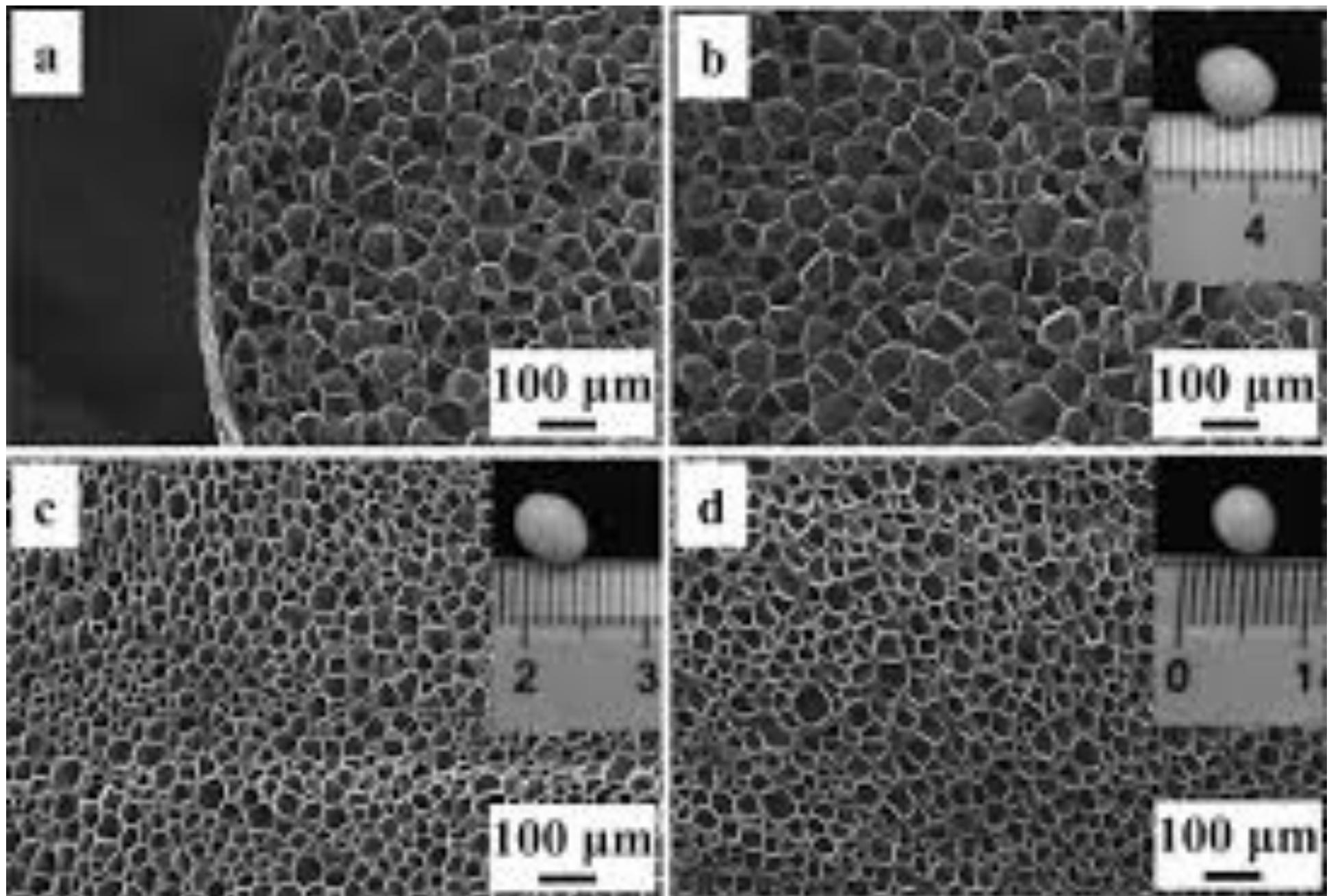
Therefore, the trademarked term **Styrofoam** is different from the generic term *styrofoam*.



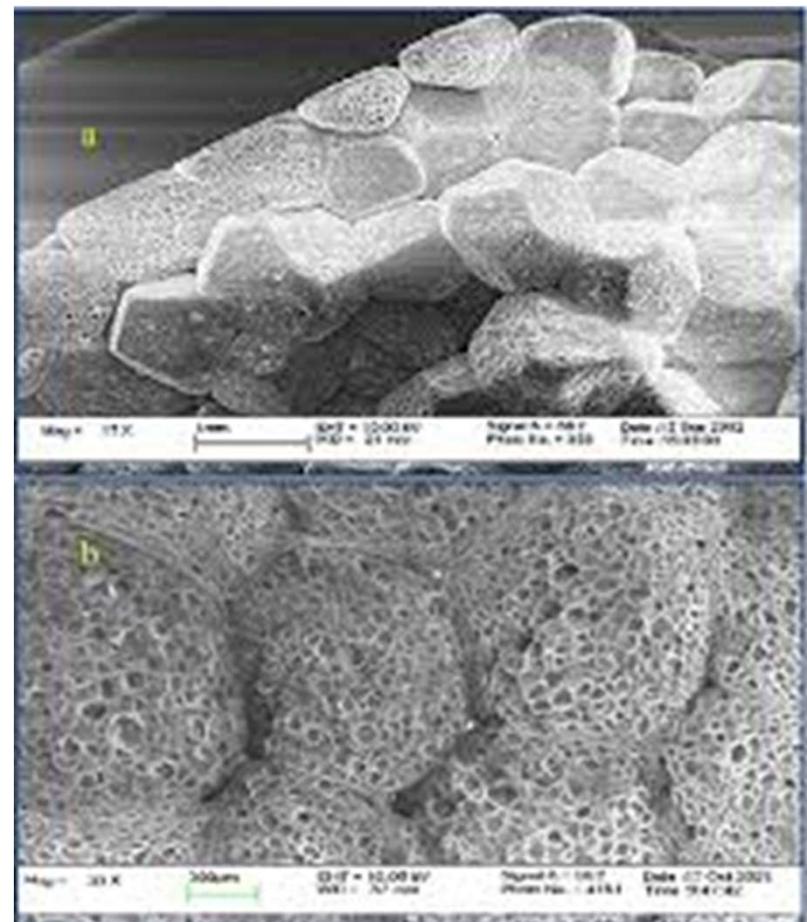
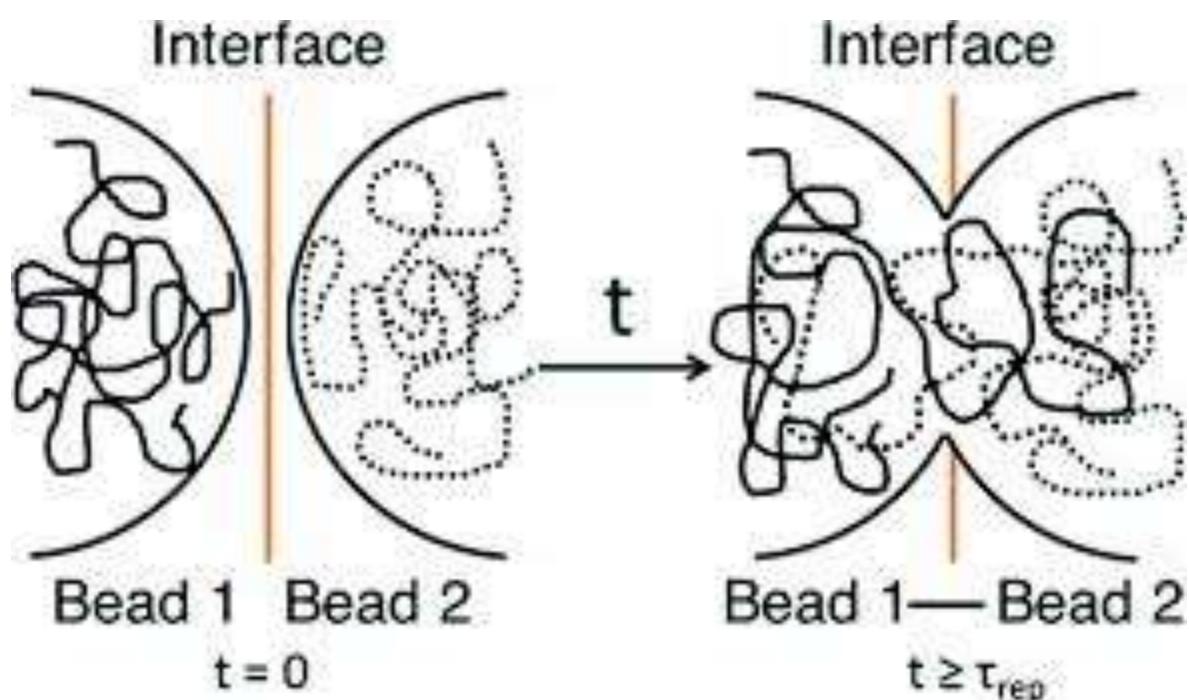
EPS Morphology before Molding



Cell Morphology of EPS



Molding of EPS



Morphology of EPS after Molding

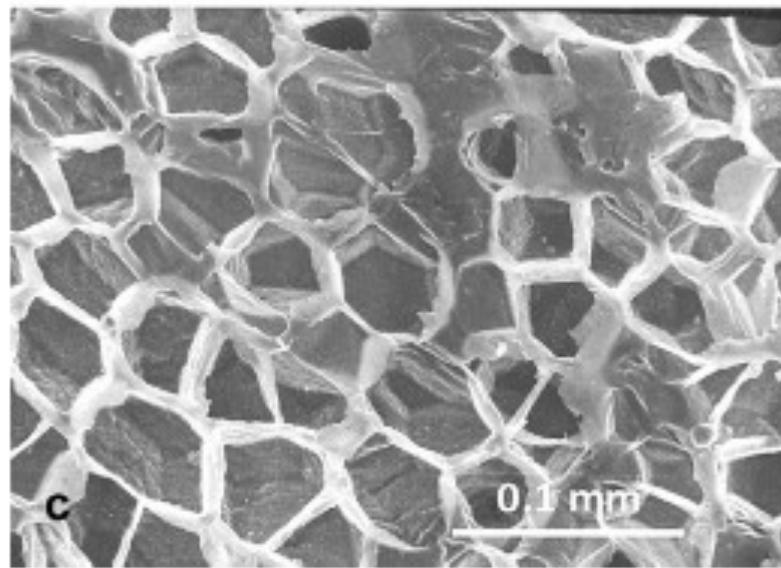
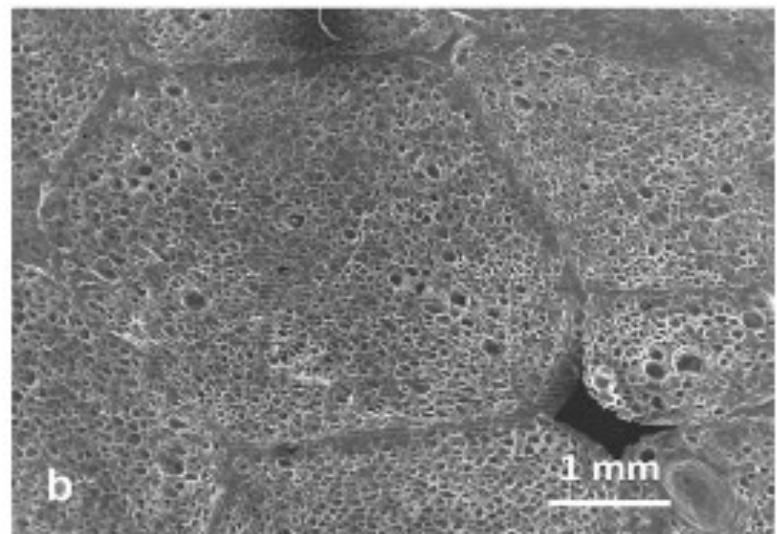
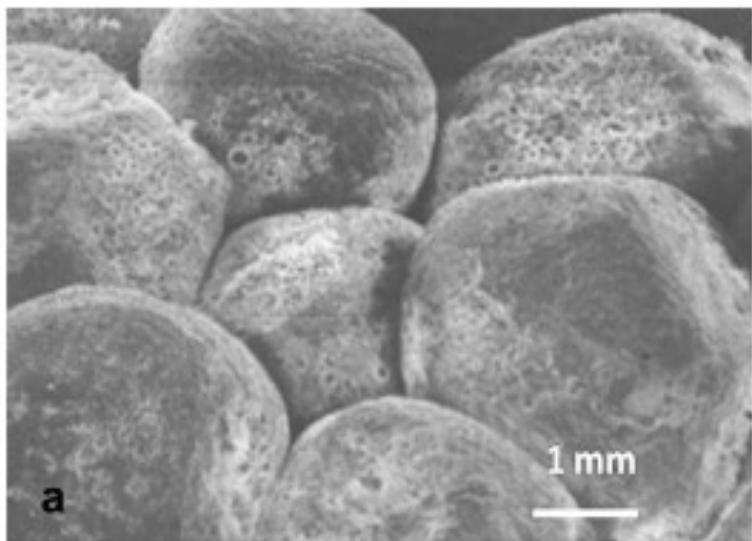
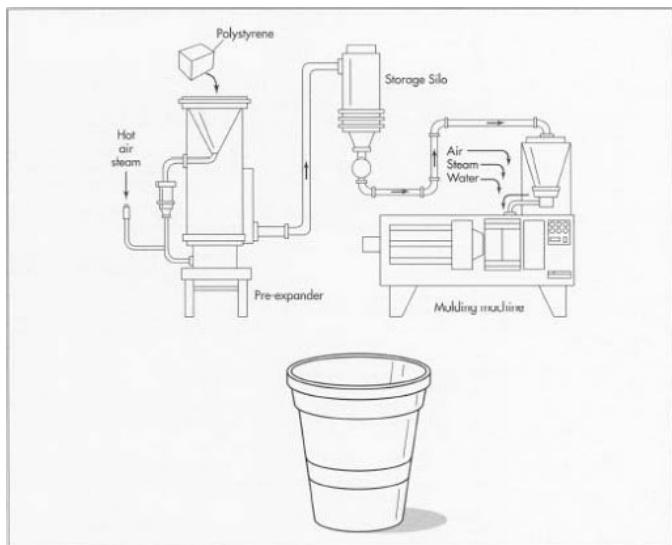


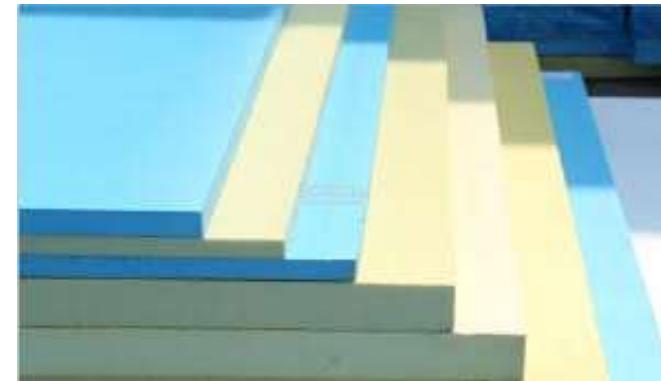
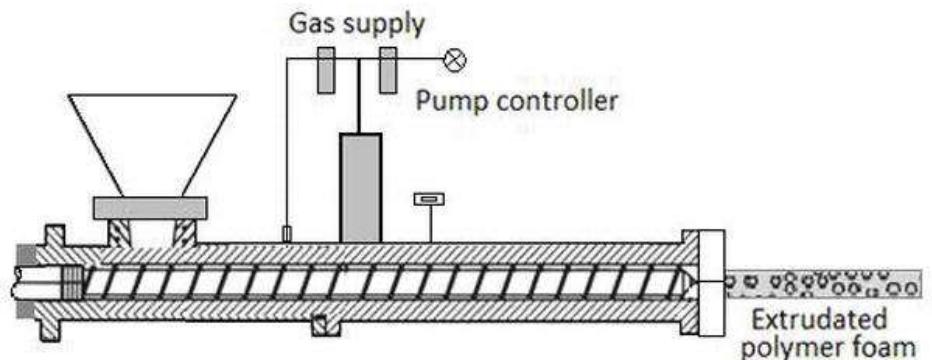
Fig. 1. Internal structure of expanded polystyrene. a) beads, b) beads and closed cells, c) closed cells.

EPS vs XPS

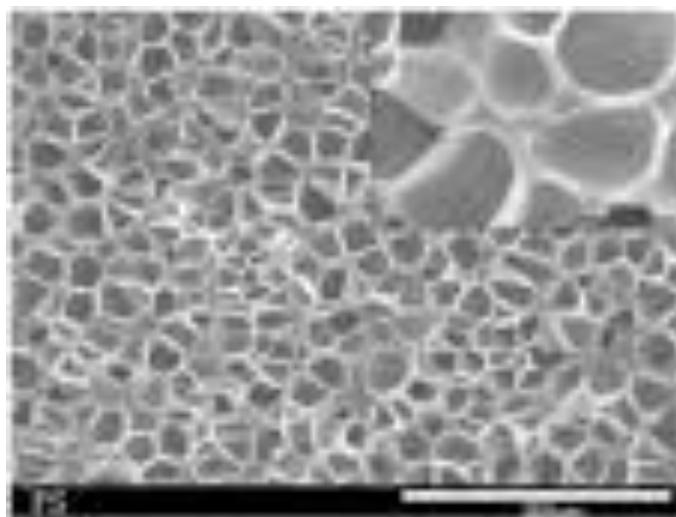
EPS – Expanded Polystyrene



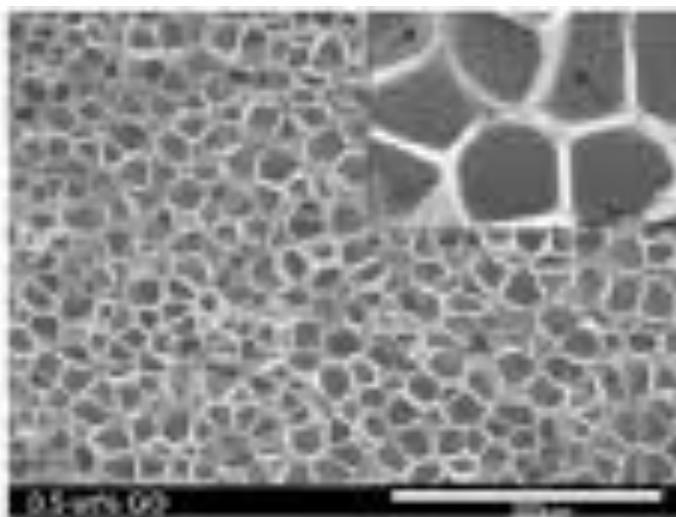
XPS – Extruded Polystyrene



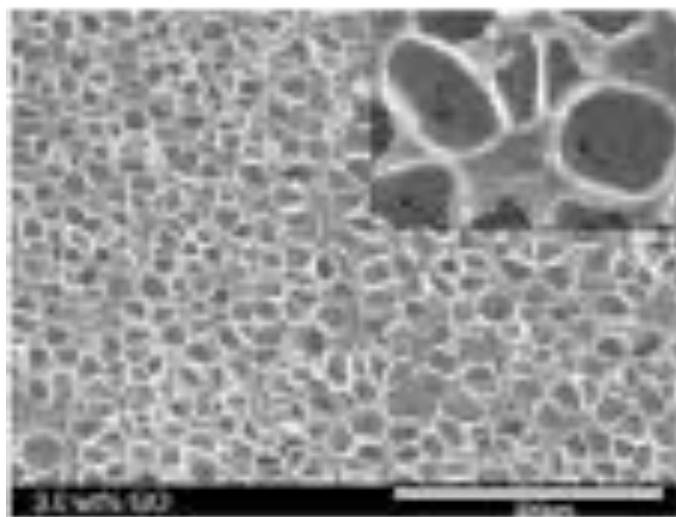
Morphology of XPS



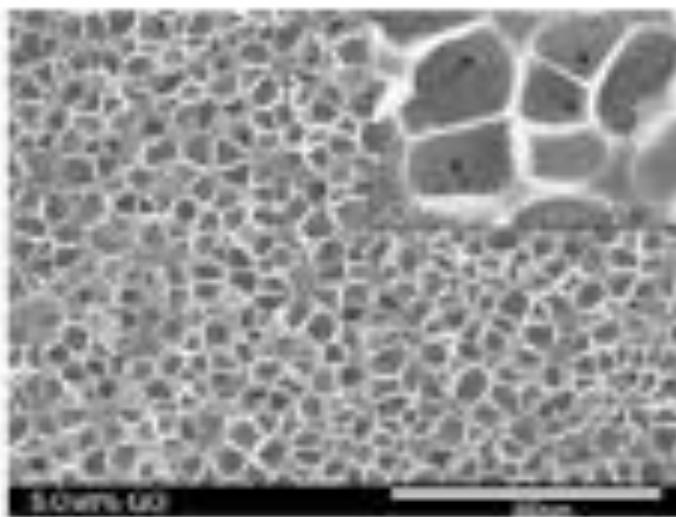
Average cell size: 19.2 μm
Cell density: $1.1 \times 10^6 \text{ cells/cm}^3$



Average cell size: 18.5 μm
Cell density: $1.4 \times 10^6 \text{ cells/cm}^3$



Average cell size: 16.0 μm
Cell density: $1.6 \times 10^6 \text{ cells/cm}^3$



Average cell size: 15.0 μm
Cell density: $2.0 \times 10^6 \text{ cells/cm}^3$

EPS is Used in Movie Set Design



EPS vs XPS

Expanded vs Extruded Polystyrene

More Information Online

WWW.DIFFERENCEBETWEEN.COM

DEFINITION

Expanded Polystyrene

Expanded polystyrene or EPS is a thermoplastic foam material that we produce from solid beads of polystyrene.

Extruded Polystyrene

Extruded polystyrene or XPS is a foam material that we produce from solid polystyrene crystals.

RAW MATERIAL

We produce expanded polystyrene from solid beads of polystyrene.

We produce extruded polystyrene using solid polystyrene crystals.

PRODUCTION PROCESS

Produced via the expansion of gas that is trapped inside the polystyrene beads by heating.

Produced via extruding a hot, thick fluid of polystyrene crystals.

EFFECT ON ENVIRONMENT

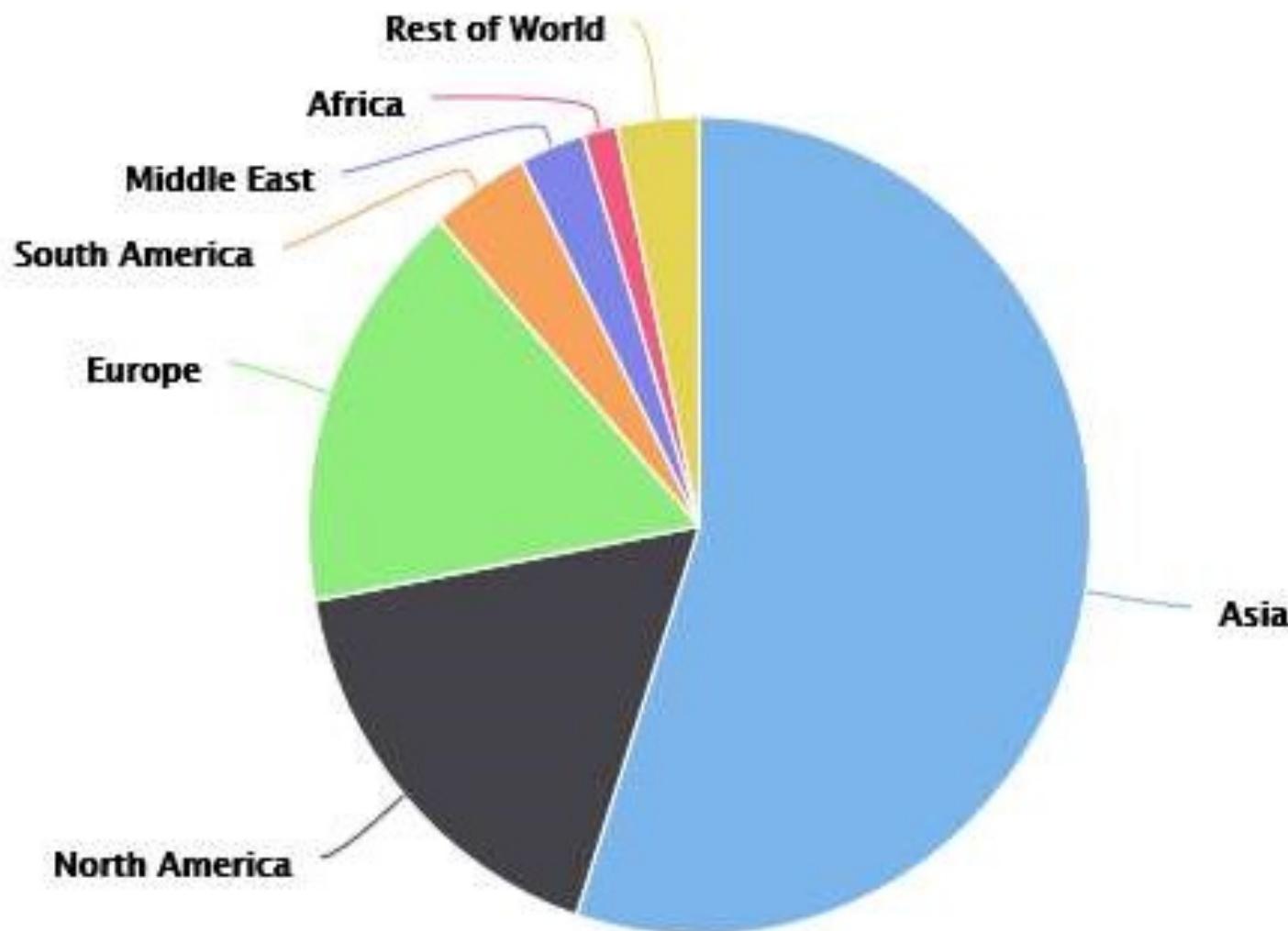
The production of expanded polystyrene has a minimum harmful effect on the environment.

The production of extruded polystyrene has considerable harm to the environment.

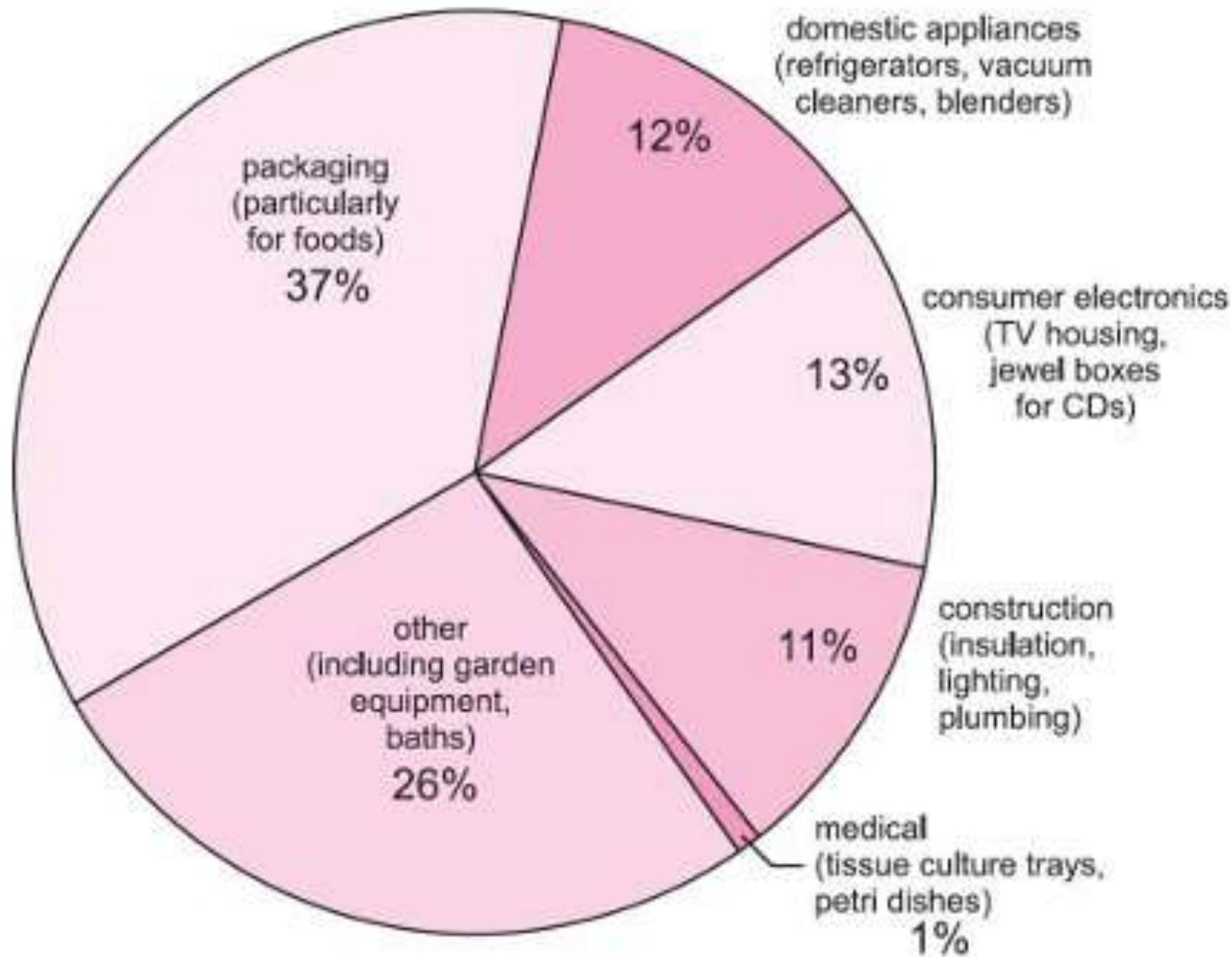
Where is it made? - Geographically

Global Polystyrene Production Capacity – 2016 (In %)

Production Capacity – 14.7 million tons

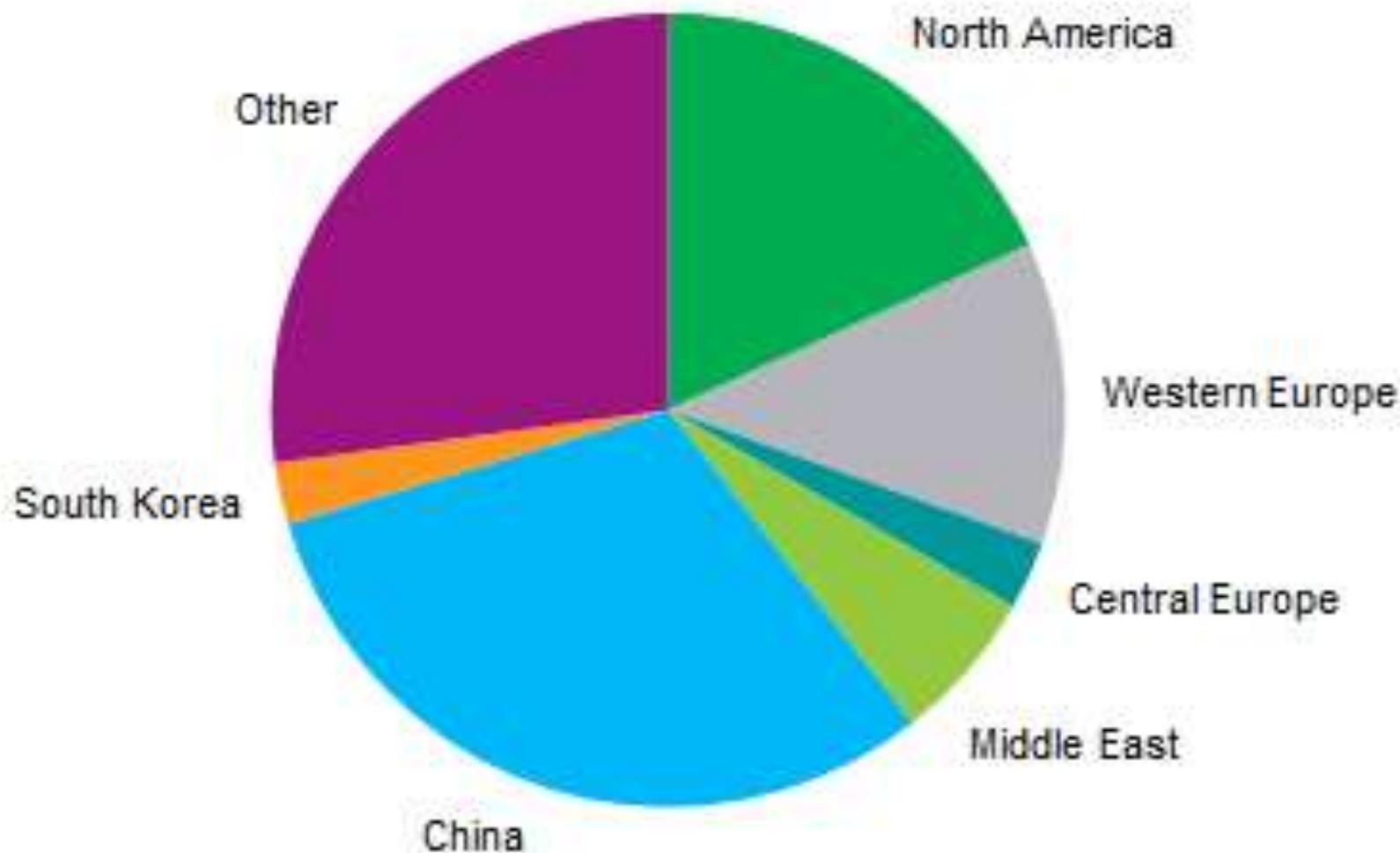


Where does it go? – Applications



Where does it go – Geographically?

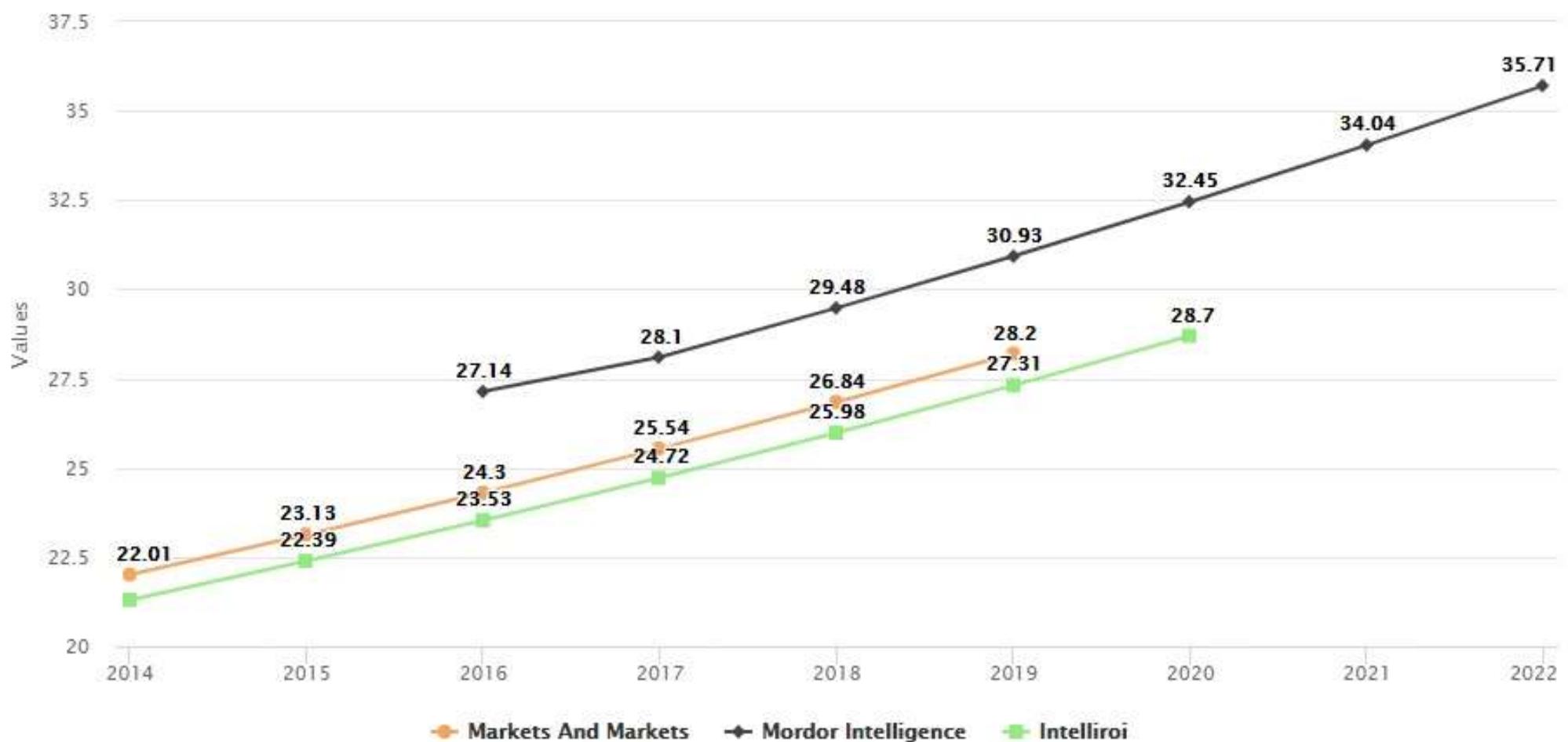
World consumption of polystyrene—2019



Market Size

World Polystyrene Market

(In US\$ bn)



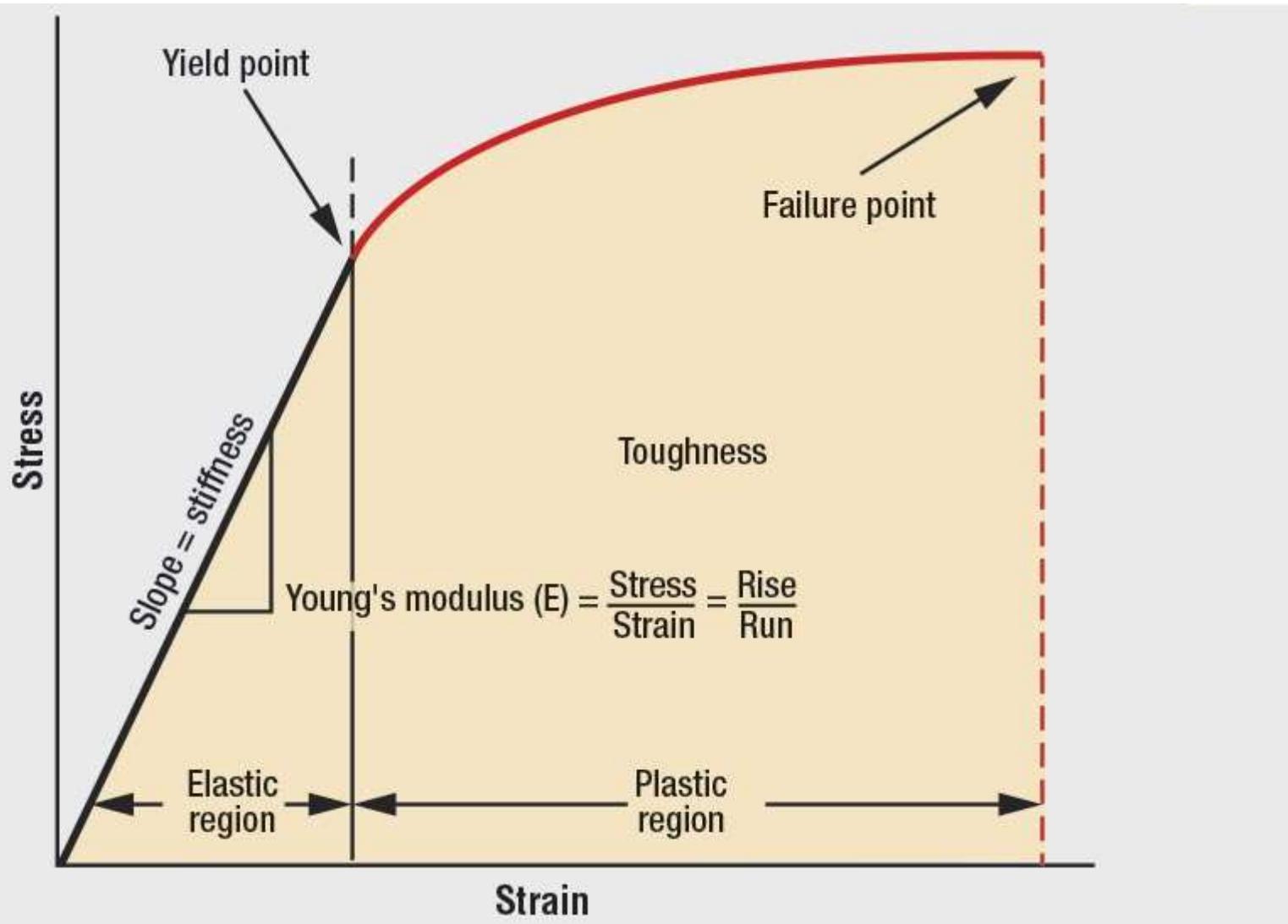
Comparative Pricing

Market Prices Effective Mid-December 2018

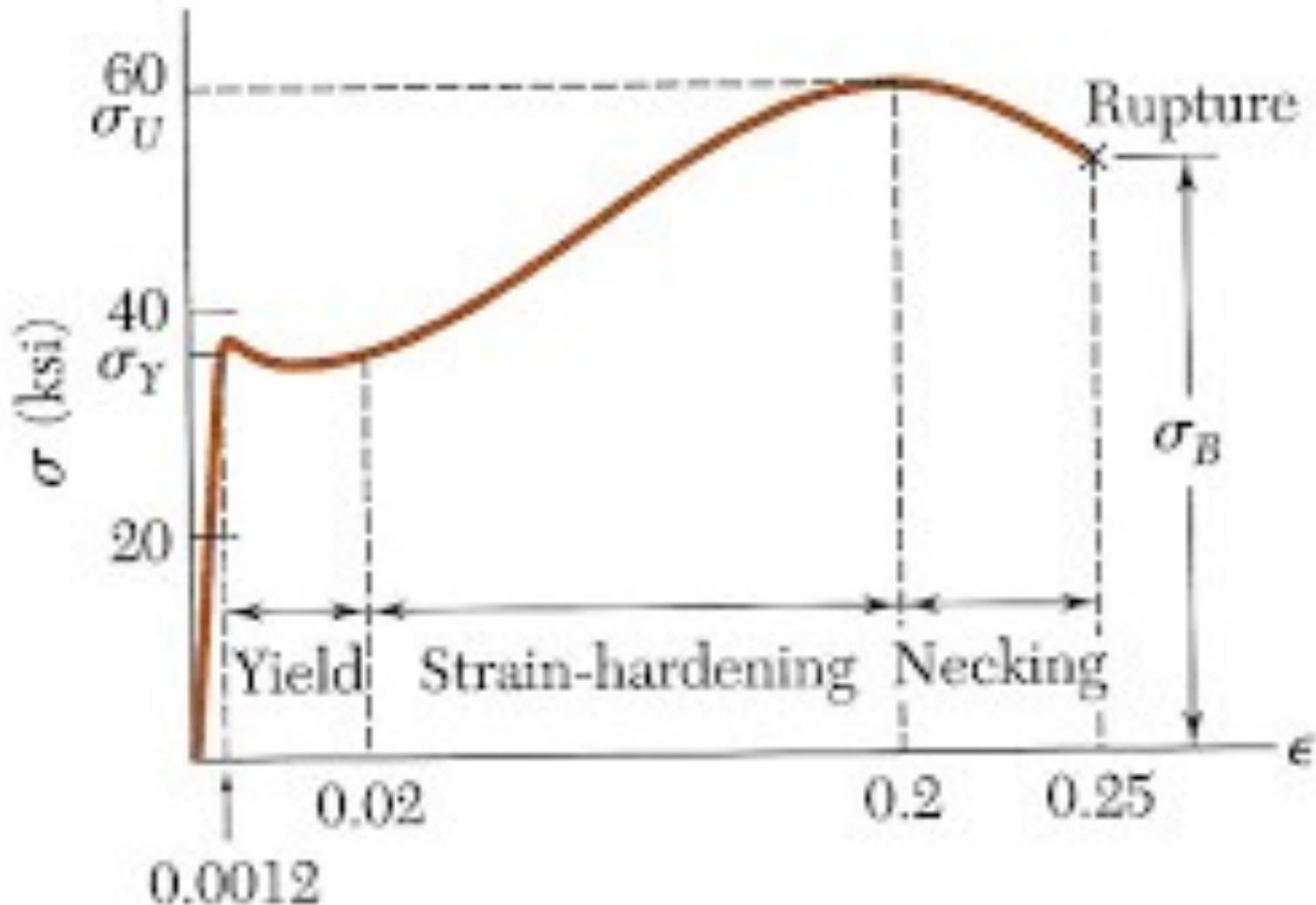
Resin Grade	¢/lb
POLYETHYLENE (railcar)	
LDPE, LINER	98-100
LLDPE BUTENE, FILM	81-83
NYMEX 'FINANCIAL' FUTURES	43
JANUARY	43
HDPE, G-P INJECTION.....	103-105
HDPE, BLOW MOLDING.....	93-95
NYMEX 'FINANCIAL' FUTURES	48
JANUARY	48
HDPE, HMW FILM	110-112
POLYPROPYLENE (railcar)	
G-P HOMOPOLYMER, INJECTION	82-84
NYMEX 'FINANCIAL' FUTURES	72
JANUARY	72
IMPACT COPOLYMER.....	84-86
POLYSTYRENE (railcar)	
G-P CRYSTAL.....	108-110
HIPS.....	114-116
PVC RESIN (railcar)	
G-P HOMOPOLYMER.....	83-85
PIPE GRADE.....	82-84
PET (truckload)	
U.S. BOTTLE GRADE	73-75



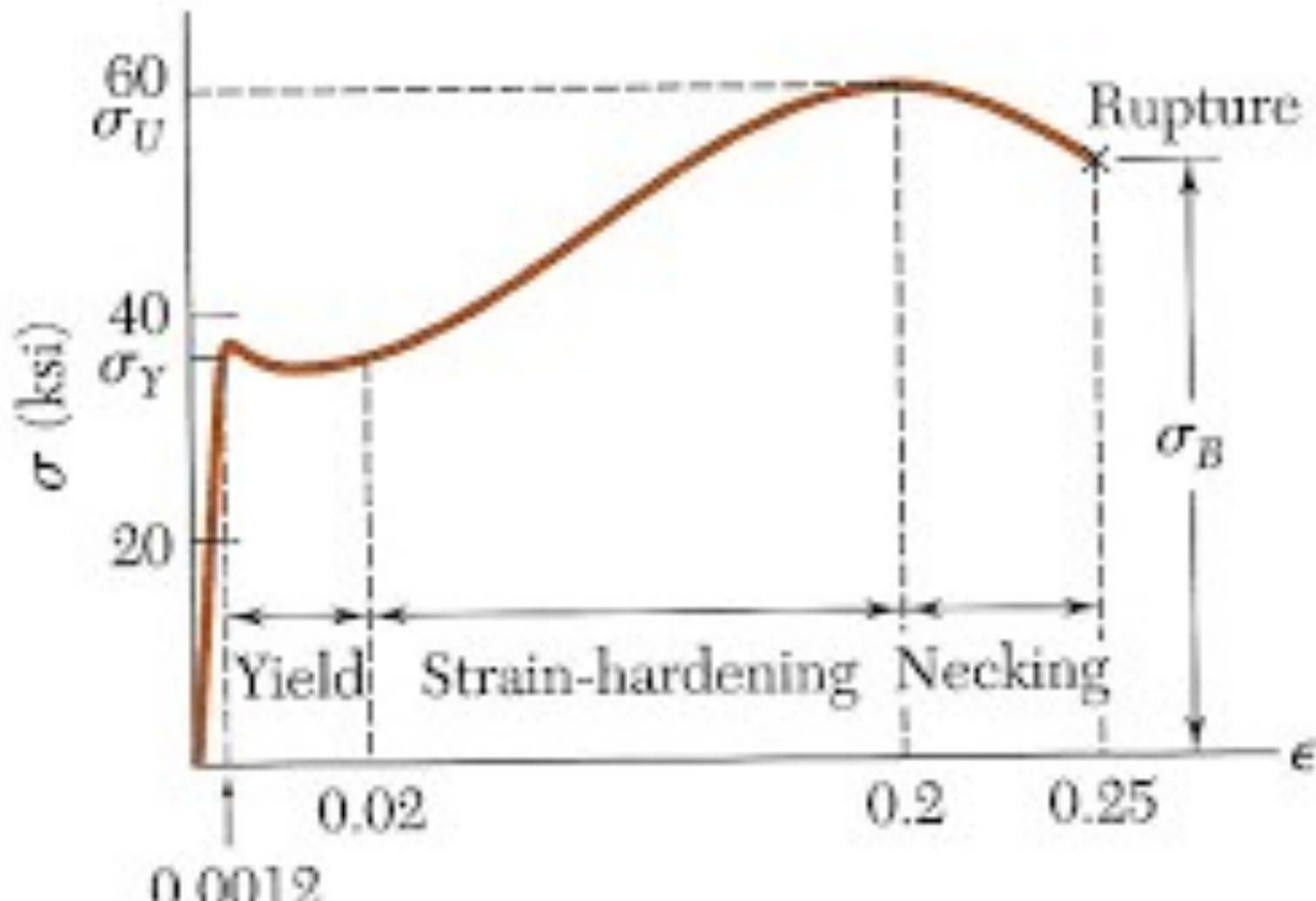
Next Time – Variations on the Theme Polystyrene



Next Time – Variations on the Theme Polystyrene

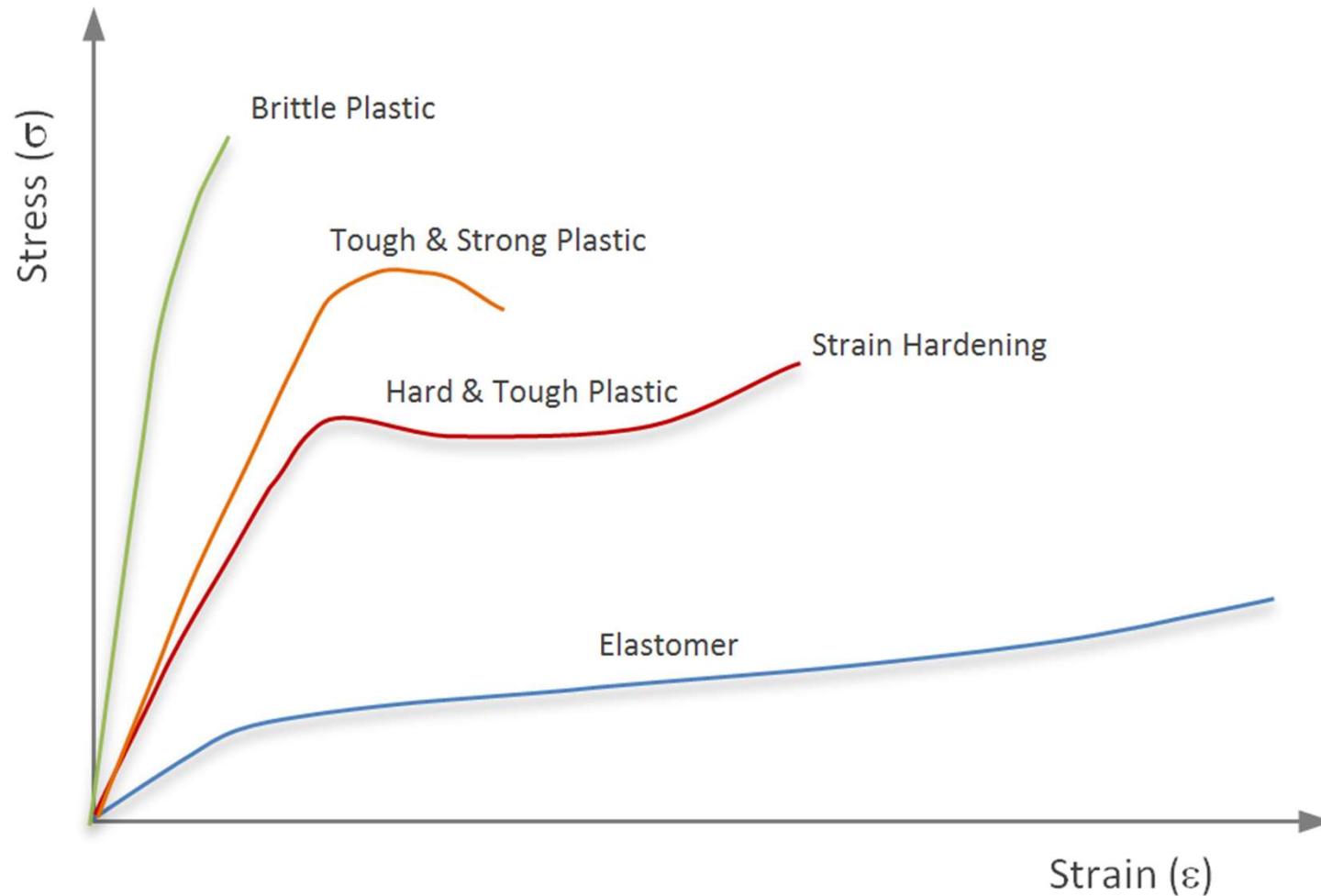


Next Time – Variations on the Theme

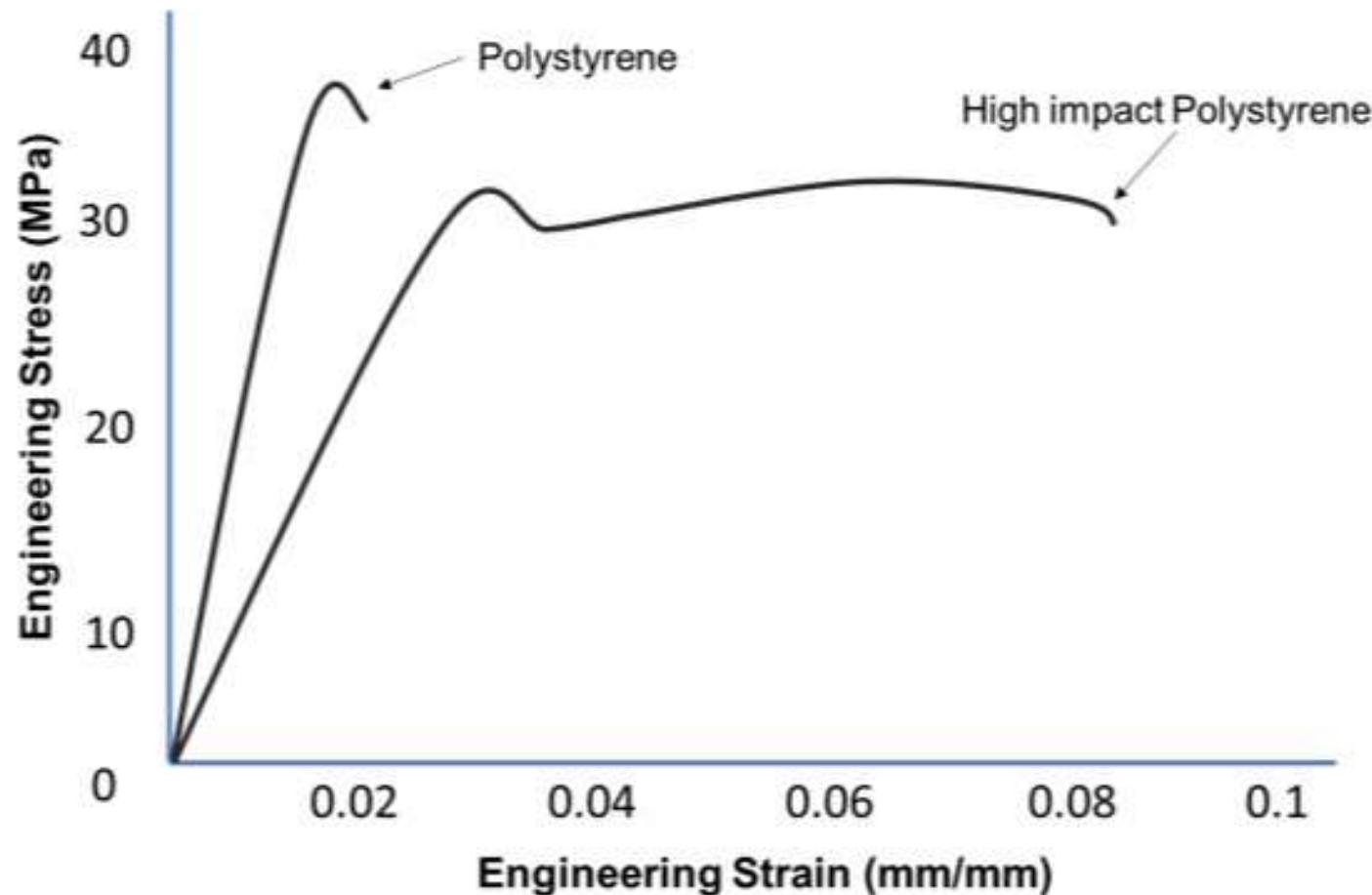


(a) Low-carbon steel

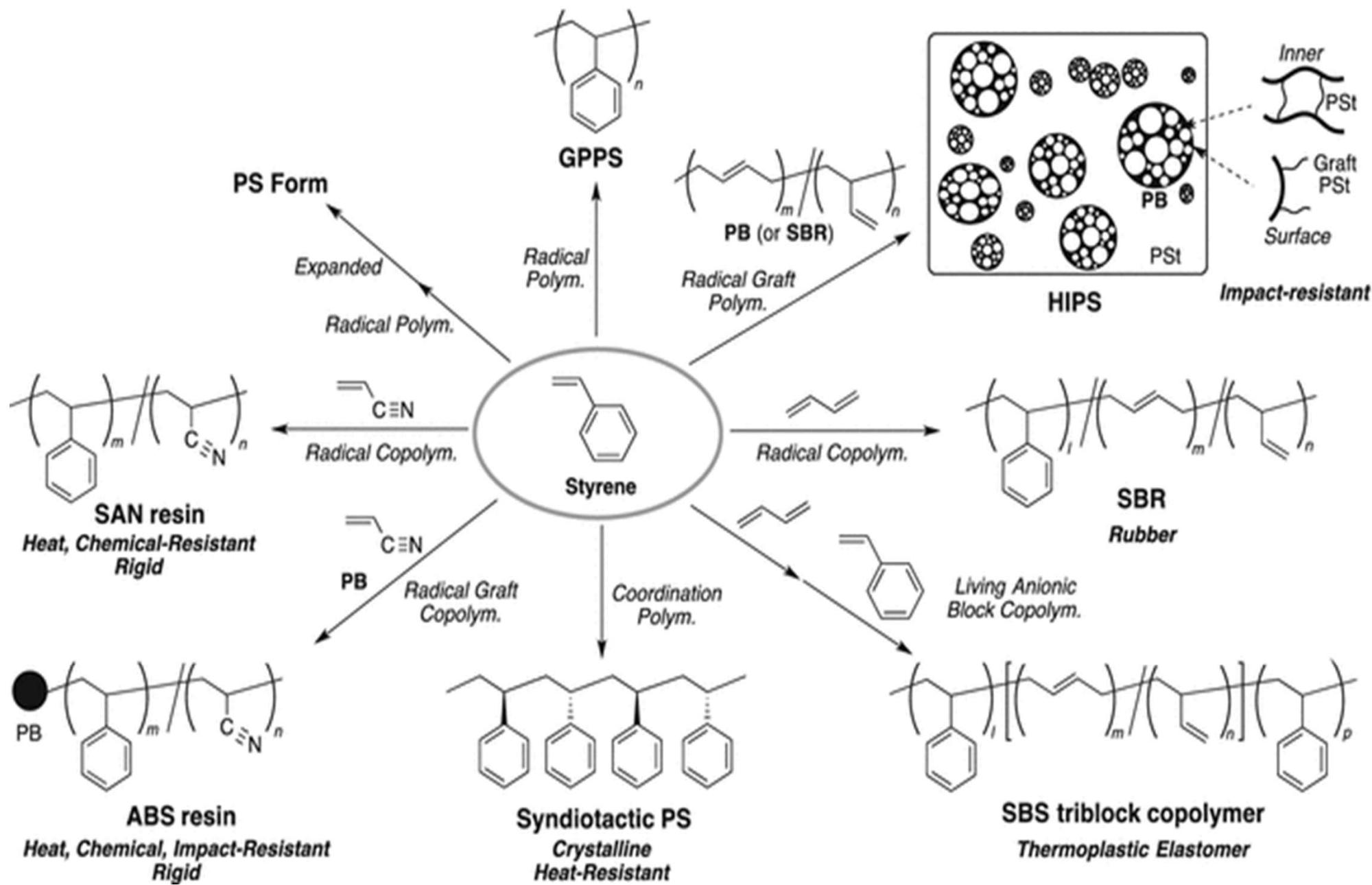
Next Time – Variations on the Theme Polystyrene



Next Time – Variations on the Theme Polystyrene



Numerous Styrenic Forms



Lesson 2: Polystyrene and Styrofoam

Questions?



There was a very cautious man
Who never laughed or played
He never risked, he never tried,
He never sang or prayed.
And when he one day passed away,
His insurance was denied,
For since he never really lived,
They claimed he never really died.

Unknown

Dr. Andy Olah, amo5@case.edu, C: 216-272-0505

“I’m at that age where my mind still thinks I’m 29, my humor suggests I’m 12, while my body mostly keeps asking if I’m sure I’m not dead yet.”

There will be a Quiz on Monday

January **24**, 2025



* From the Hitchhikers Guide to the Galaxy – Douglas Adams

EMAC 276 - Homework Assignment #1

Due: Friday January 24, 2025

Dr. Olah

We have spent some time on the Hierarchical Structure concept within several disciplines; i.e., biology, polymer science, mechanical engineering, management, etc.

Other than the examples we have provided in class, your assignment is to identify one additional example of the hierarchical structure concept.

In your description you must:

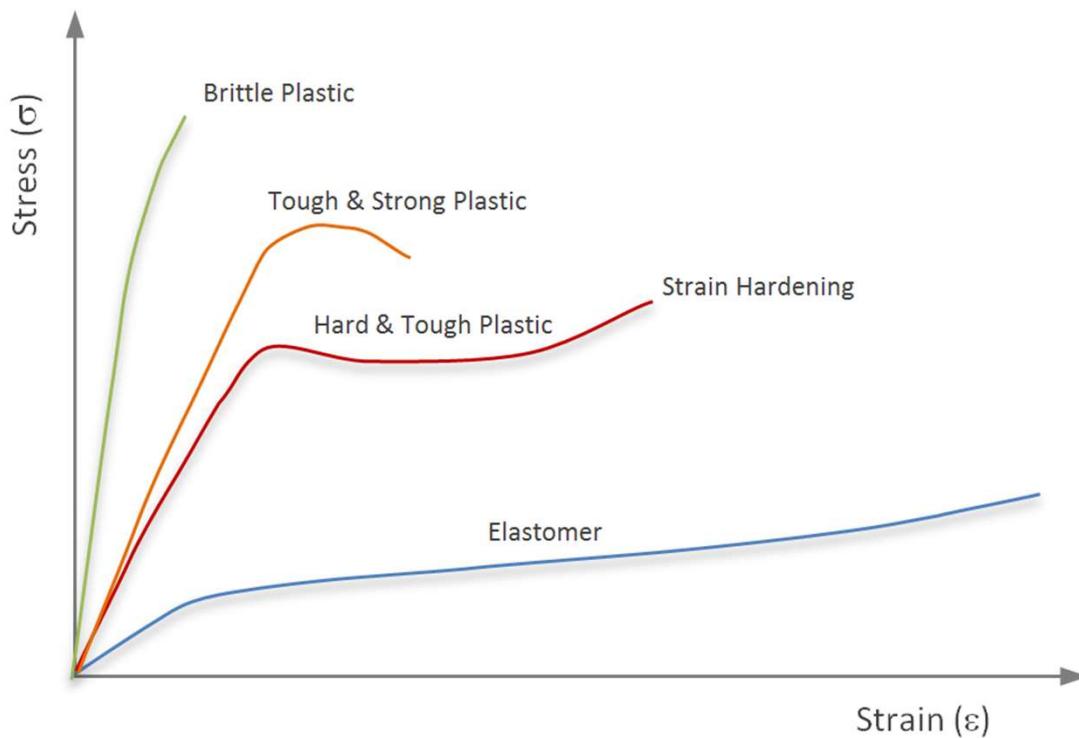
1. Identify the example and the discipline it involves.
2. Explain the number of hierarchical levels and the scale of each level.
3. Identify the relationship in your example of the three concepts of hierarchical structures:
 - a. Scale
 - b. Interaction
 - c. Architecture
4. Please keep your answer to one page.

EMAC 276

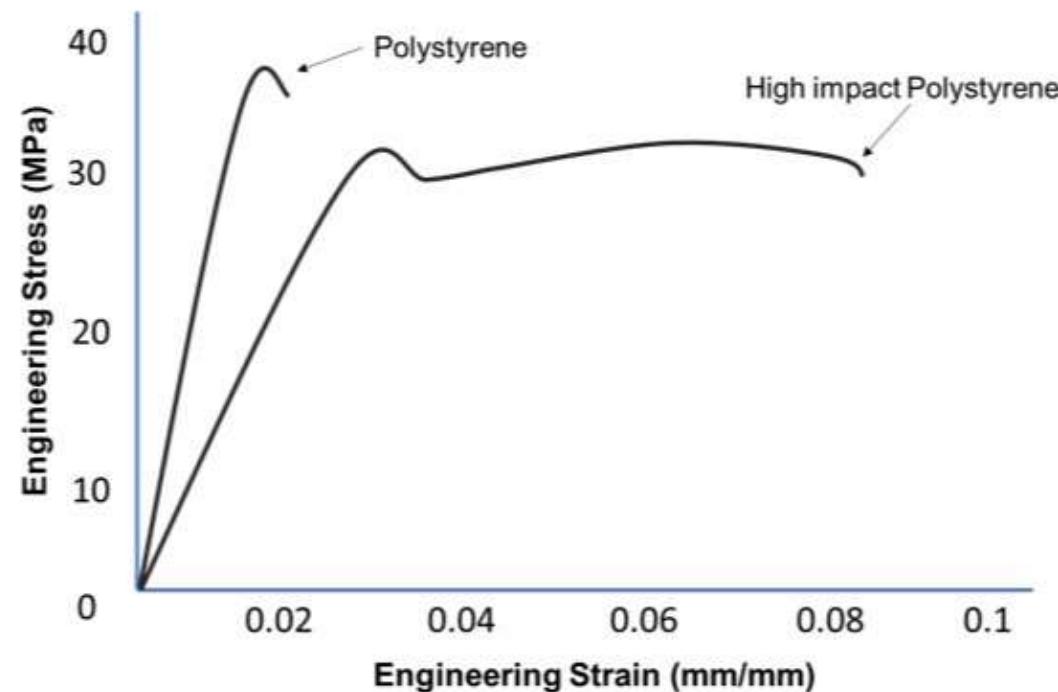
Lesson 4: SAN, ABS, HIPS

Andy Olah, Ph.D.
January 22, 2025

Variations on the Theme - Polystyrene



Unmodified Polystyrene is a Brittle Material



Tensile Testing and Relationship to The Tensile Properties of Plastics



Instron® 3300 Floor Model

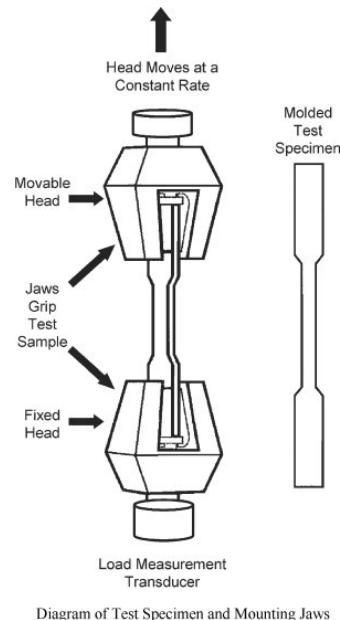
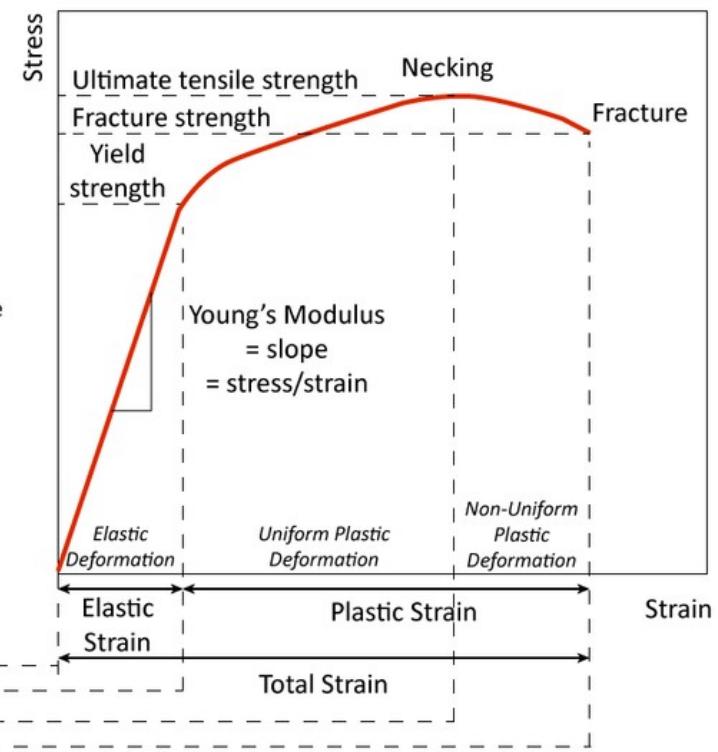
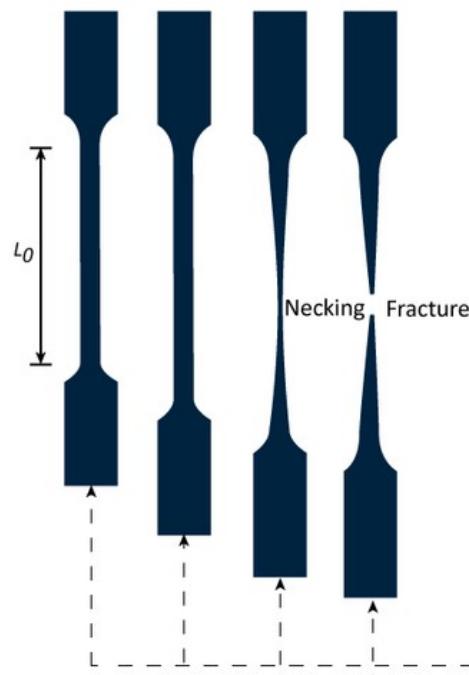
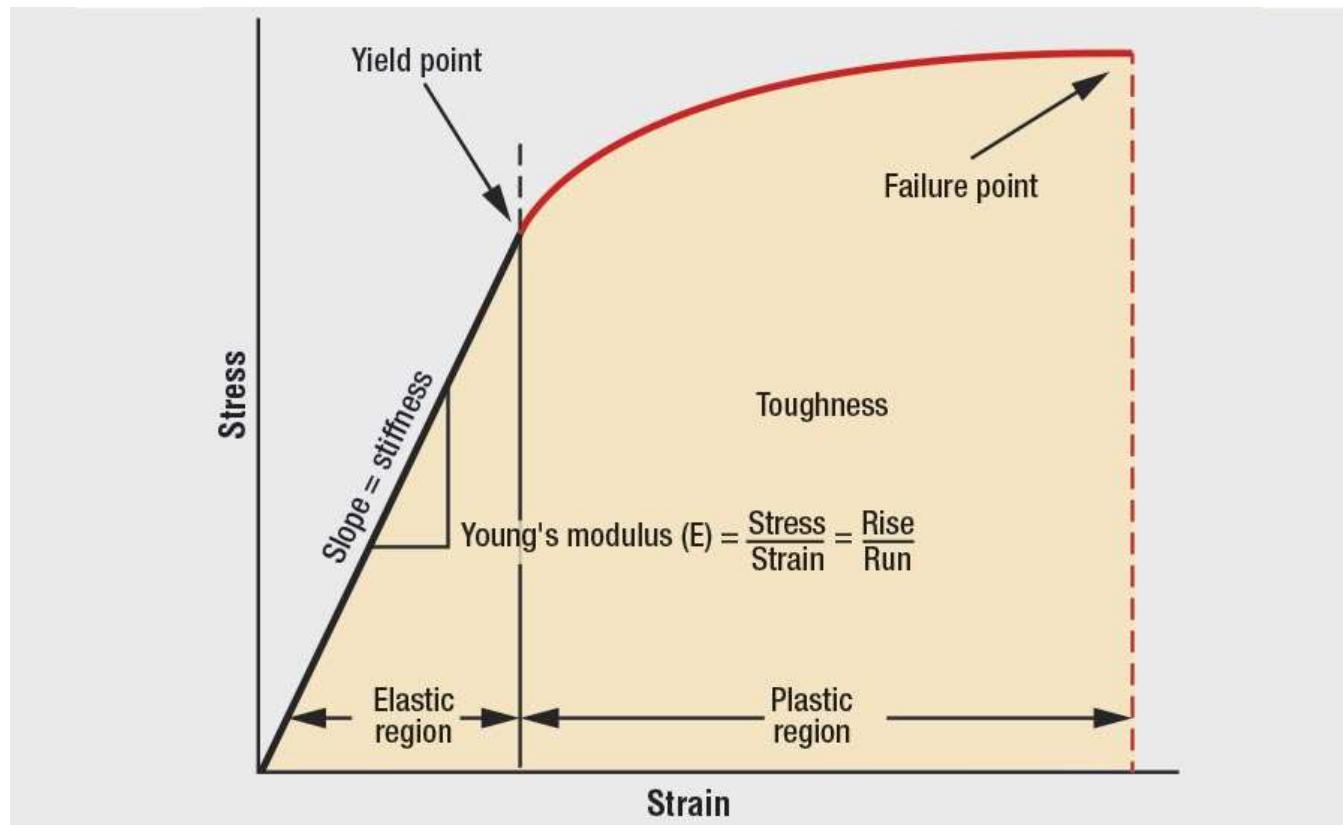


Diagram of Test Specimen and Mounting Jaws

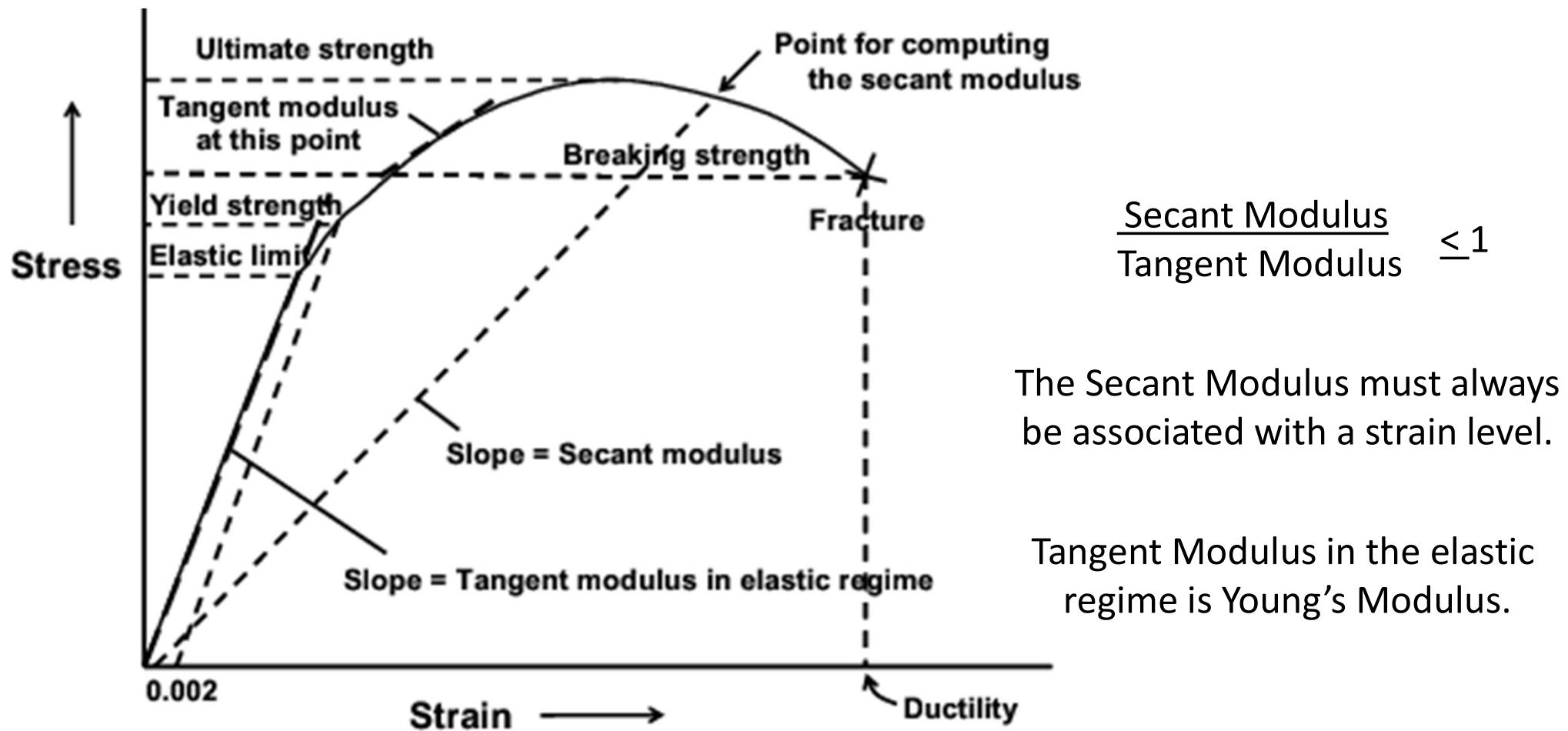


ASTM D638: Standard Test Method for Tensile Properties of Plastics

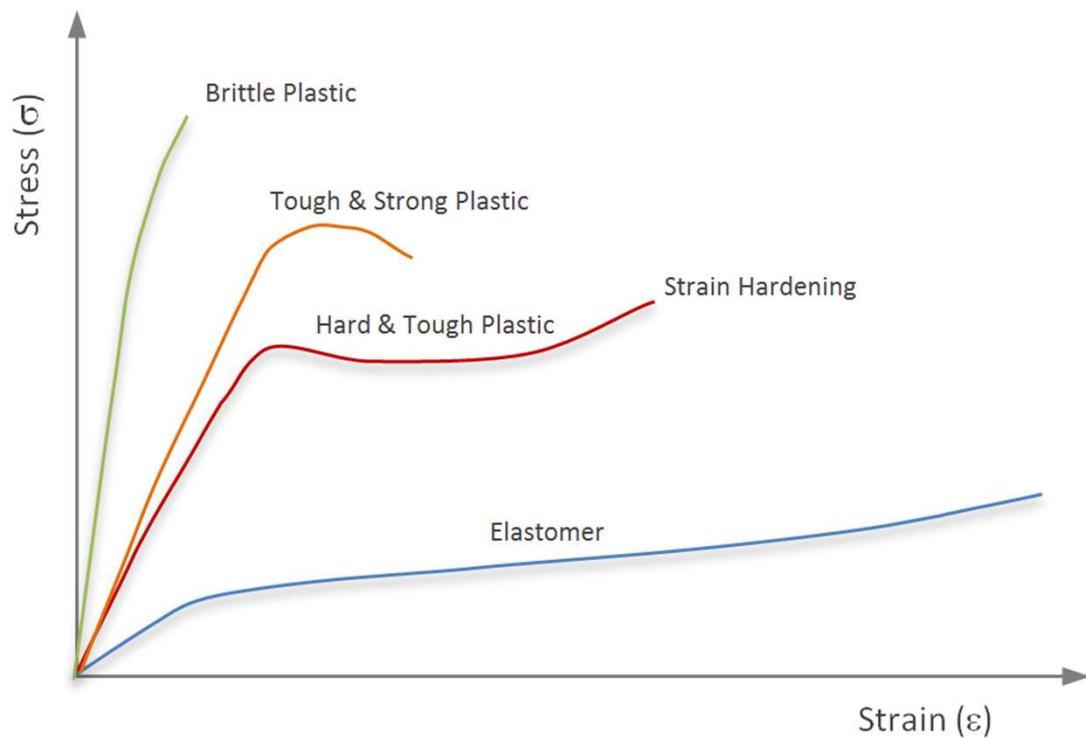
Tensile Properties of Plastics is a Fingerprint of the Mechanical Performance



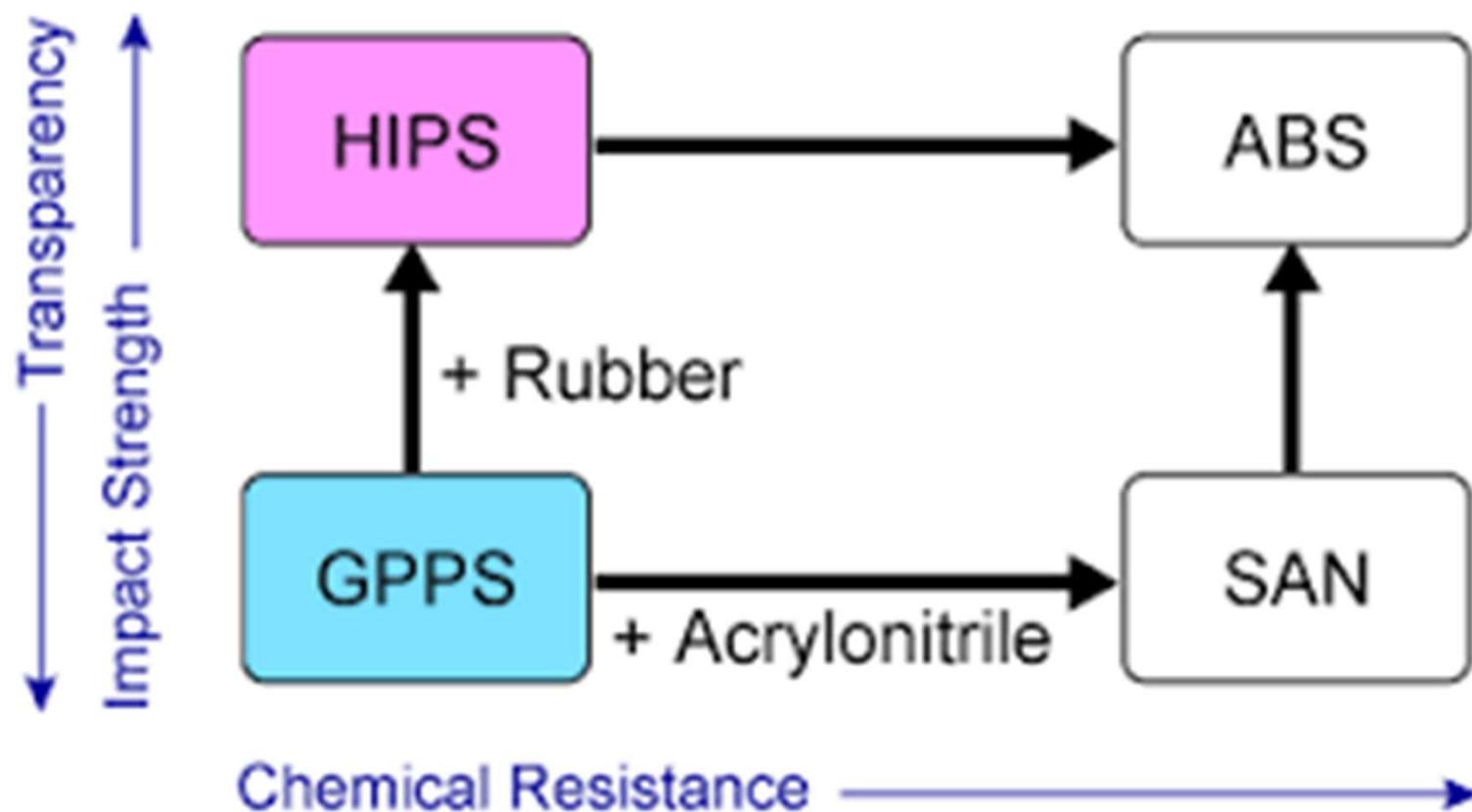
Tensile Properties of Plastics is a Fingerprint of the Mechanical Performance



Tensile Properties of Polymers can Vary Greatly



Polystyrene Derivatives for Improved Performance

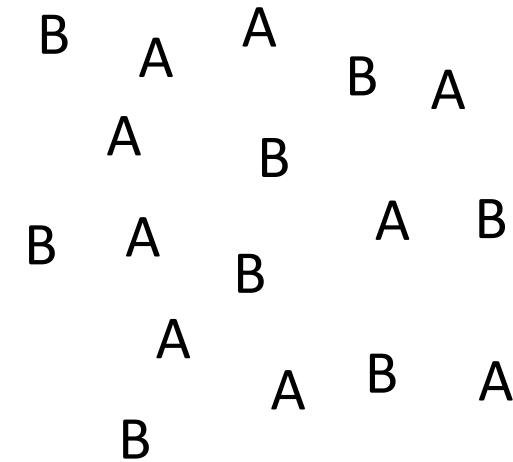
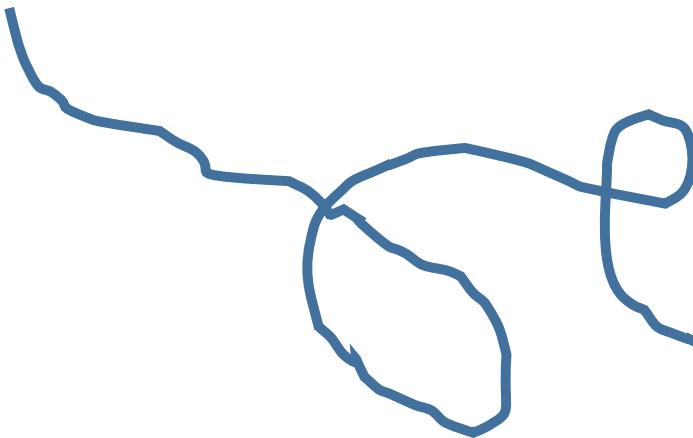


GPPS = general purpose polystyrene

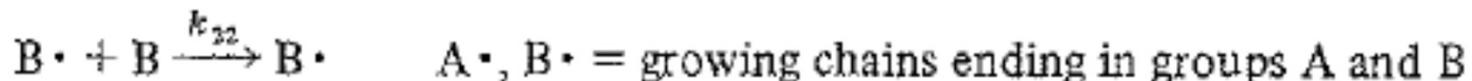
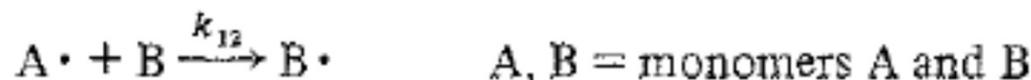
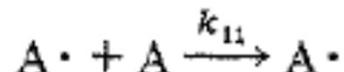
Reactivity Ratios for Free Radical Polymerization

Assumptions:

1. Concentration of free radicals doesn't change over time.
2. Only the last monomer unit on a polymer chain determines reactivity.
3. Chain propagation is the only reaction of importance; i.e., disregard initiation or termination.



Reactivity Ratios for Free Radical Polymerization



Rate of consumption (disappearance) of monomers A and B:

$$-\frac{d[A]}{dt} = k_{11} [A \cdot] [A] + k_{21} [B \cdot] [A]$$

$$-\frac{d[B]}{dt} = k_{12} [A \cdot] [B] + k_{22} [B \cdot] [B]$$

Reactivity Ratios for Free Radical Polymerization

The reactivity ratios r_1 and r_2 are defined as:

$$r_1 = \frac{k_{11}}{k_{12}} \quad \text{The ratio of reactivity of monomer 1 (A) toward itself to the reactivity of monomer 1 toward monomer 2 (B).}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$

If the product of r_1 and r_2 is:

- a) $r_1 * r_2 \sim 1$ – Random Copolymer – A A B B B A A A B A B A A A A
- b) $r_1 * r_2 < 1$ – Alternating Copolymer – A B A B A B A B A B A B A B
- c) $r_1 * r_2 \gg 1$ – Block Copolymer – A A A A A A A B B B B B B B B B

Reactivity Ratios for Free Radical Polymerization

TABLE 2.11
REACTIVITY RATIOS FOR COPOLYMERIZATION AT 60°C

M_1	M_2	r_1	r_2
Styrene	Acrylonitrile	0.4 ± 0.05	0.04 ± 0.04
Styrene	Methyl methacrylate	0.52 ± 0.02	0.46 ± 0.02
Styrene	Butadiene	0.78 ± 0.01	1.39 ± 0.03
Styrene	Vinyl acetate	55 ± 10	0.01 ± 0.01
Styrene	Maleic anhydride	0.02	0
Methyl methacrylate	Acrylonitrile	1.2 ± 0.14	0.15 ± 0.07
Methyl methacrylate	Vinyl acetate	20 ± 3	0.015 ± 0.015
Methyl methacrylate	Methyl acrylate	1.69	0.34
Vinyl acetate	Acrylonitrile	0.061 ± 0.013	4.05 ± 0.3
Vinyl acetate	Vinyl chloride	0.23 ± 0.02	1.68 ± 0.08
Vinyldene chloride	Isobutene	3.3	0.05

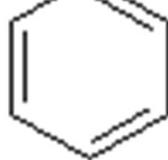
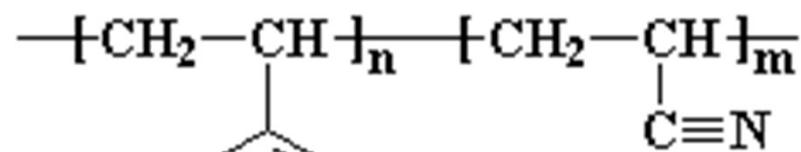
Reactivity Ratios for Free Radical Polymerization

Products of Monomer Reactivity Ratios in Copolymerization

Butadiene							
1.0	Styrene						
0.71	0.55	Vinyl Acetate					
0.30	0.34	0.39	Vinyl Chloride				
0.19	0.24	0.30	1.0	Methyl Methacrylate			
0.10	0.16	0.12	0.96	0.61	Vinylidene Chloride		
0.04	0.14	0.90	0.75	0.96	0.80	Methyl Acrylate	
0.02	0.02	0.25	0.13	0.24	0.34	0.84	Acrylonitrile

$r_1 * r_2 \ll 1$ – Alternating Copolymer

Styrene Acrylonitrile Copolymer - SAN



SAN



Commonly having 70% styrene and 30% Acrylonitrile.

Tensile Strength of SAN to Polystyrene

thermoplastic	tensile strength (MPa)	elongation at break (%)
polystyrene	46	2.2
styrene–acrylonitrile	72	3
acrylonitrile–butadiene–styrene (ABS)	48	8
flame-retardant ABS	40	5.1
polypropylene	32	15
polyethylene	30	9

Styrene Acrylonitrile Copolymer

Some of the advantages of SAN include:

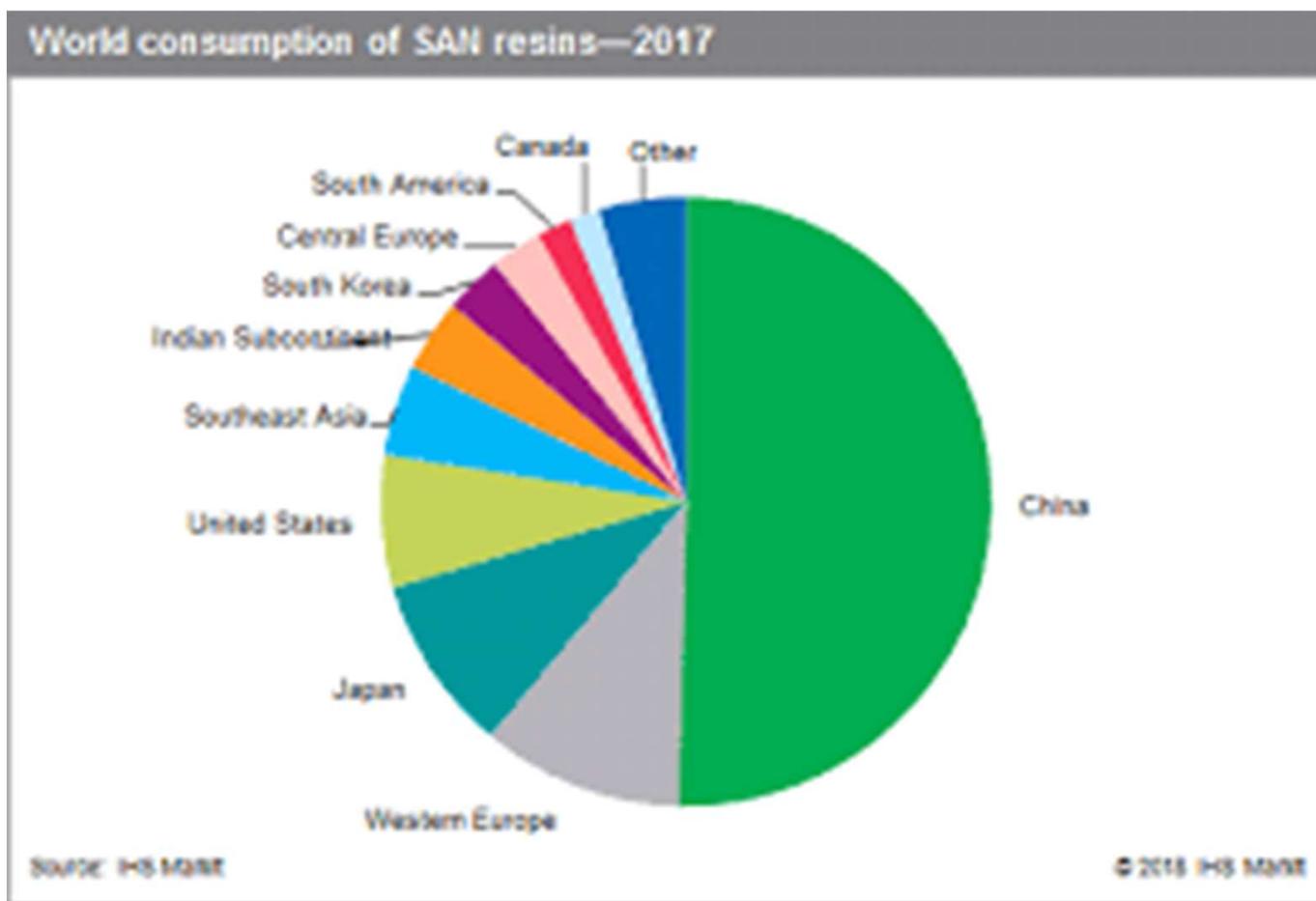
- Excellent Rigidity/Stiffness.
- Excellent Load-Bearing Capacity.
- Excellent Chemical **Resistance**.
- High Flexural **Strength**.
- Good Appearance.
- Good Clarity.
- Good Thermal **Resistance**.



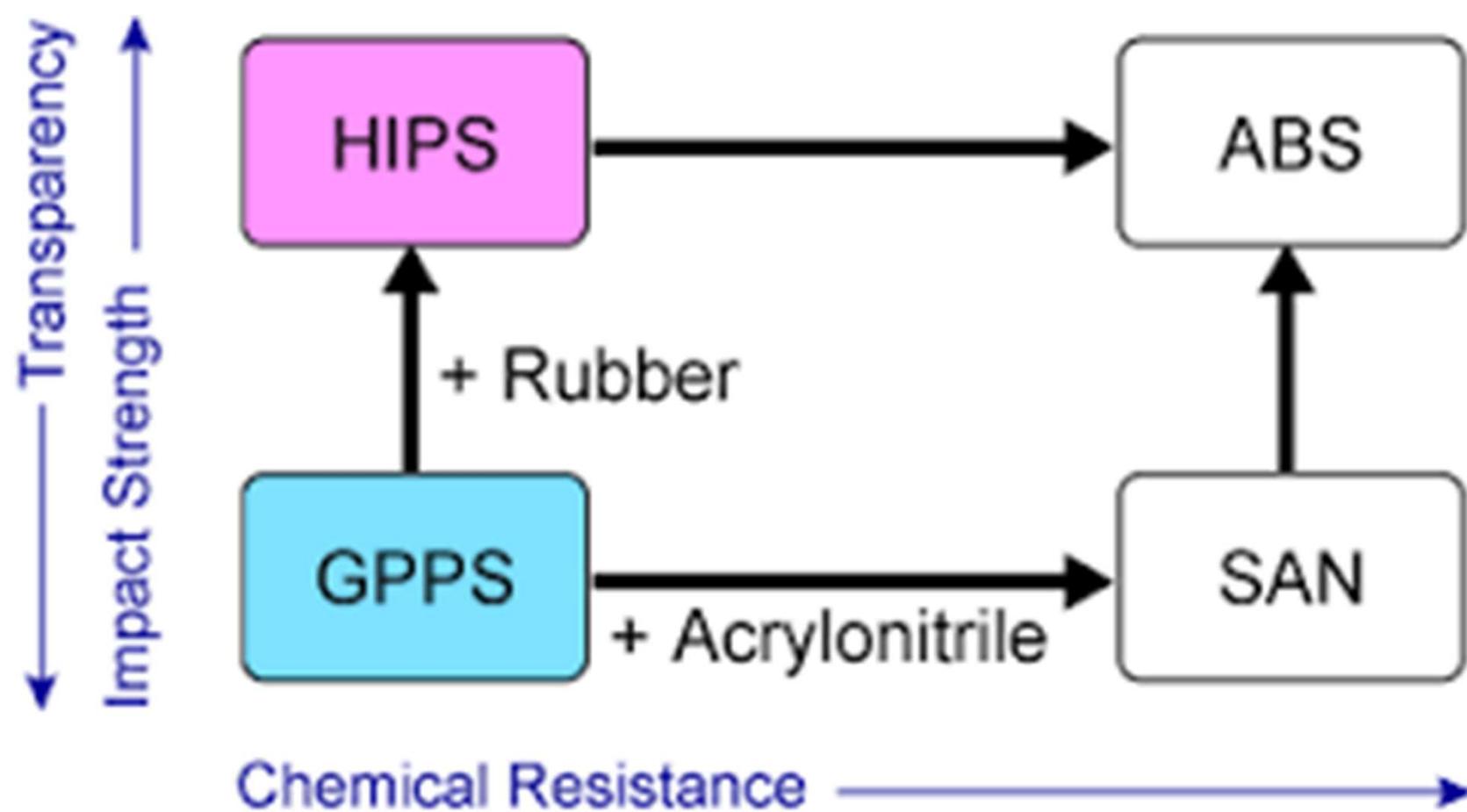
Uses

Electrical/Electronic Applications , Household Goods , Appliances, Cosmetic Packaging, Compounding, Automotive Applications, General Purpose, Stationary Supplies, Cups, Containers.

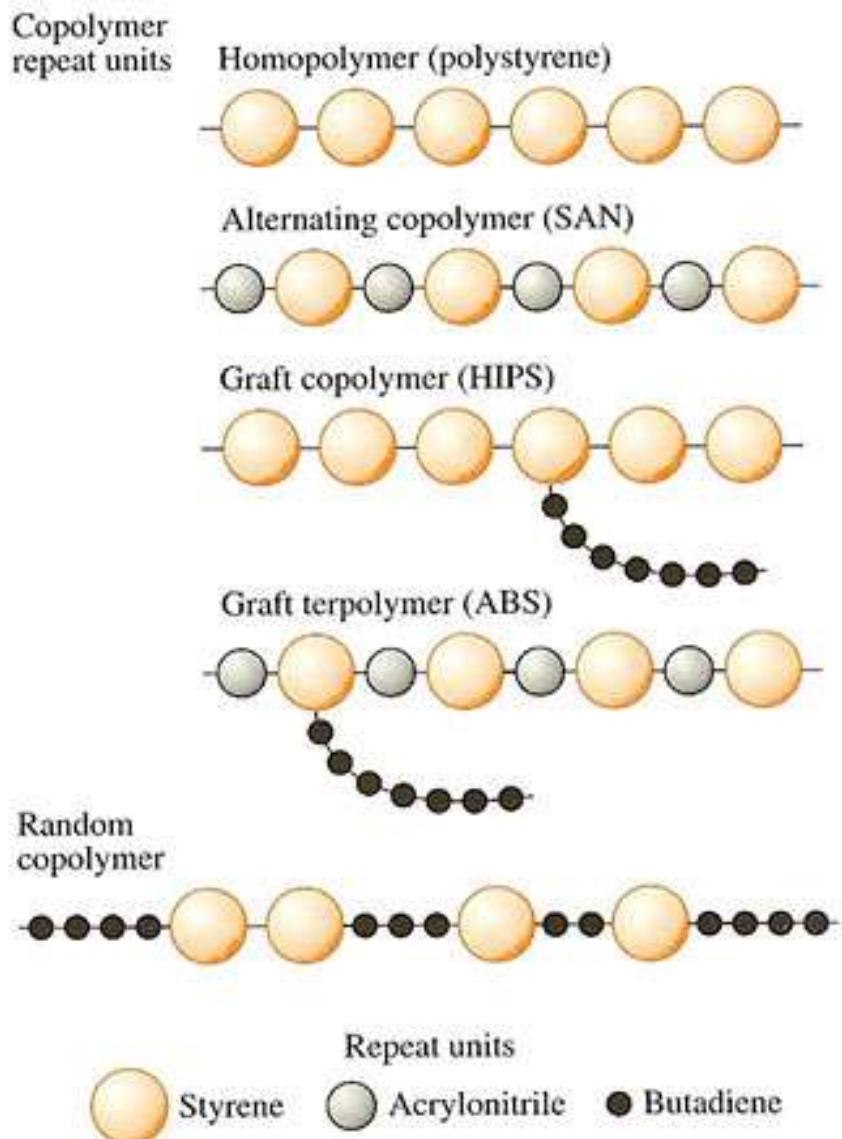
Styrene Acrylonitrile Copolymer



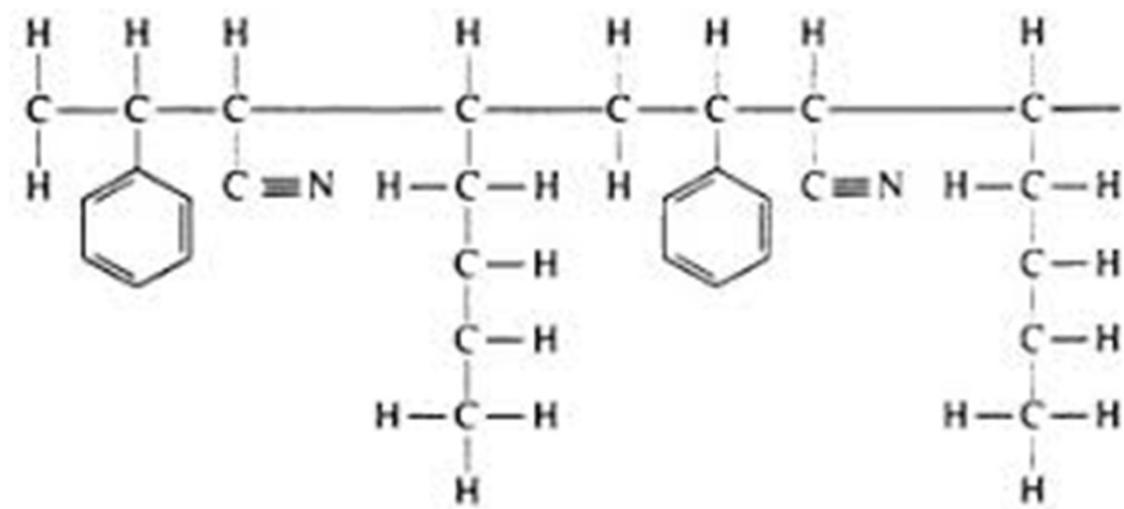
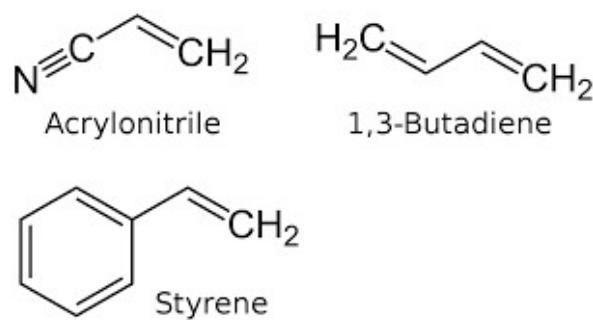
Polystyrene Derivatives for Improved Performance



ABS – Acrylonitrile, Butadiene, Styrene Copolymer



ABS – Acrylonitrile, Butadiene, Styrene Copolymer

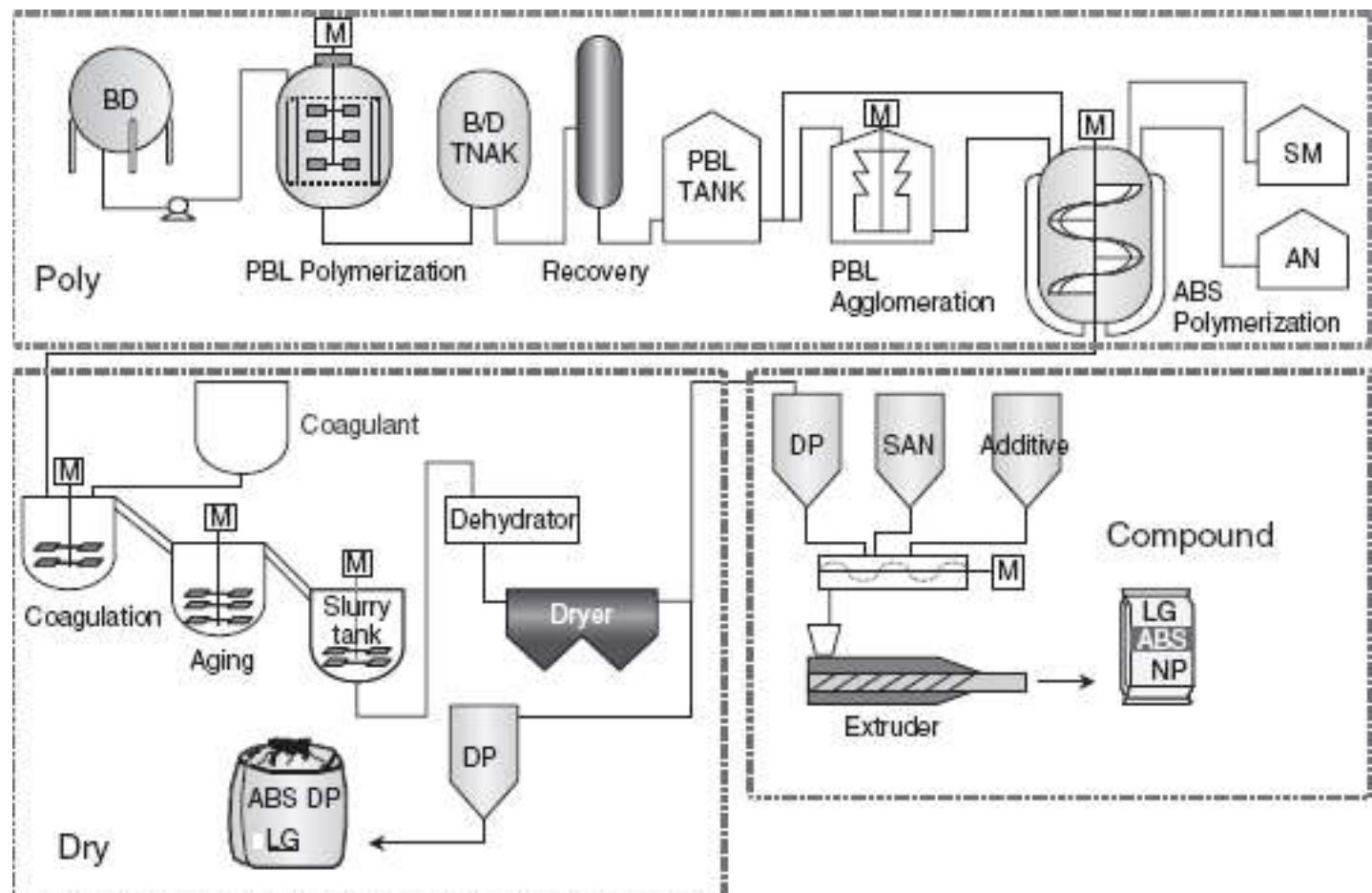


Borg-Warner Patent – 1948

B-W Commercialized - 1954

Production of ABS Polymer

40 – 60% Polystyrene
15 – 35% Acrylonitrile
5 – 30% Butadiene



ABS – Acrylonitrile, Butadiene, Styrene Copolymer



A Word of Caution on Recycling



+



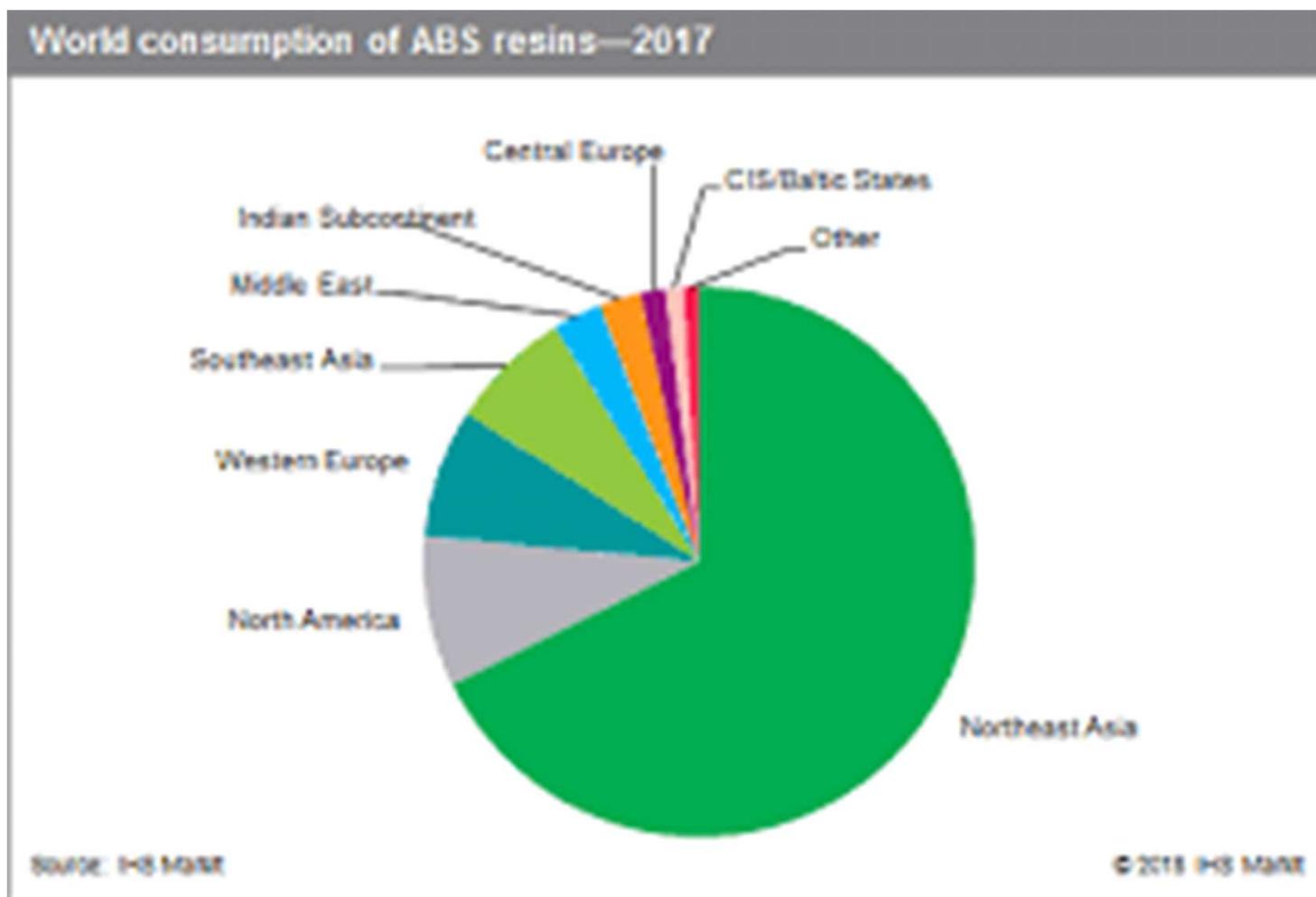
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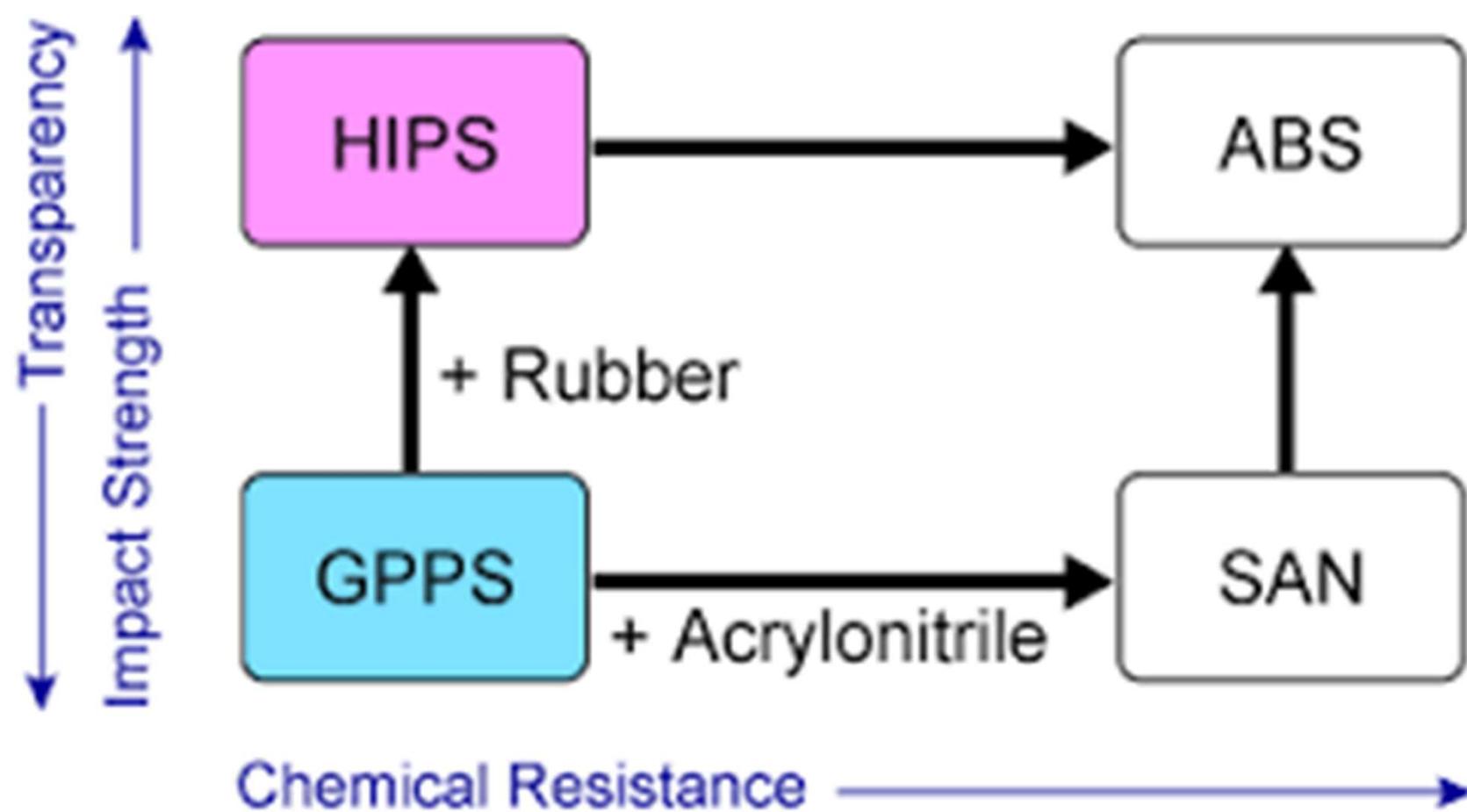
"All Black" defective black ABS plastic waste pipe manufactured in the mid 1980's failed by cracking. The result was litigation and some damage settlements.

ABS drain pipe material failures were reported for pipe made between 1985 and 1988. [1][2][5][6][7] below

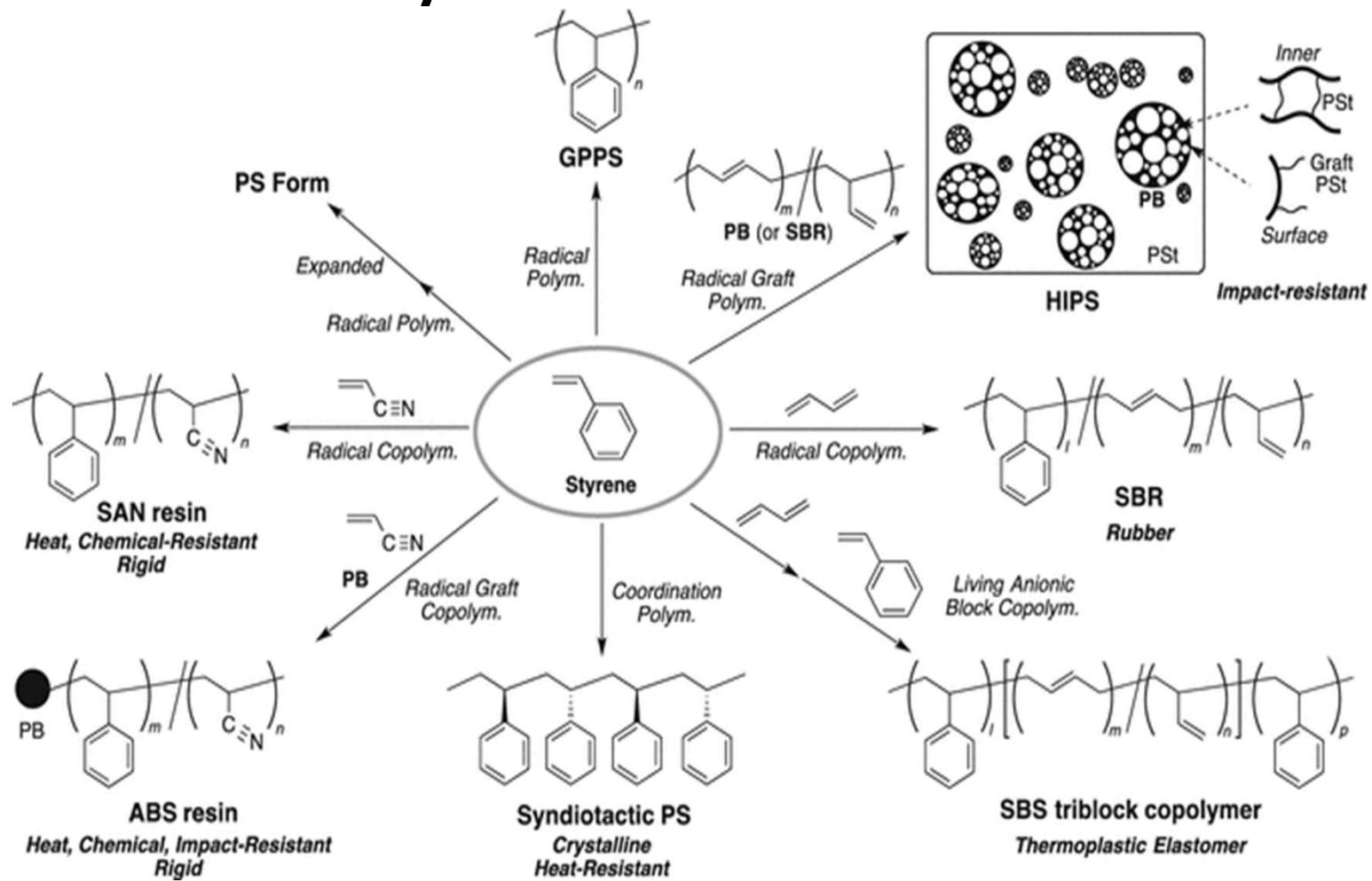
ABS – Acrylonitrile, Butadiene, Styrene Copolymer



Polystyrene Derivatives for Improved Performance



Styrenic Forms



Lesson 3: SAN, ABS, HIPS

Questions?



Dr. Andy Olah, amo5@case.edu, C: 216-272-0505

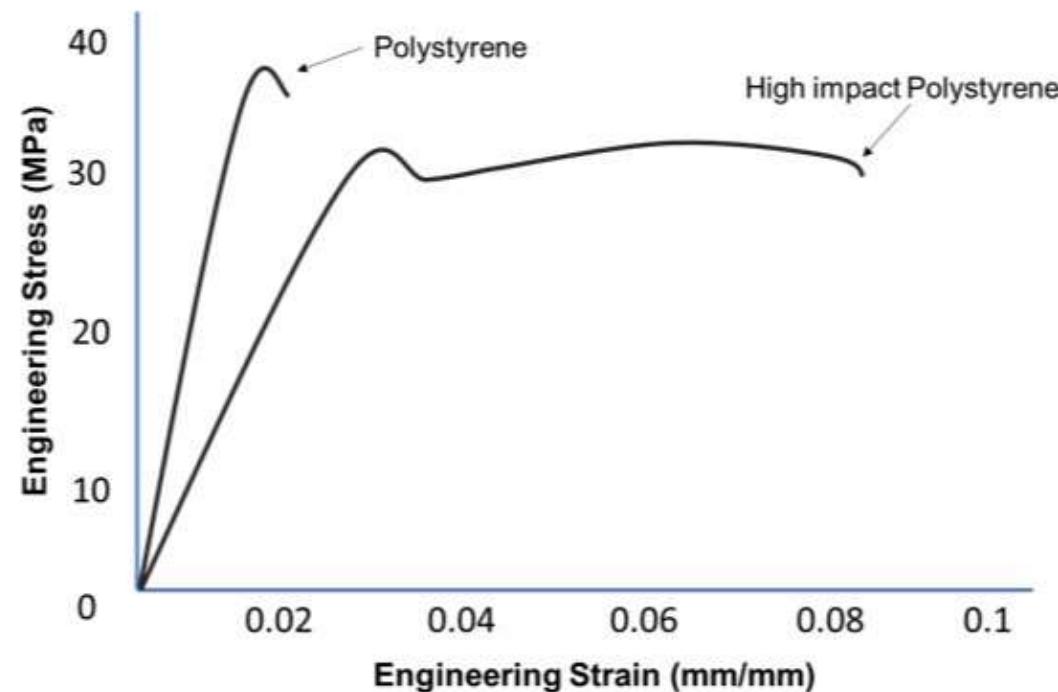
“When I was a kid, I wanted to be older **This is not what I expected!**

EMAC 276

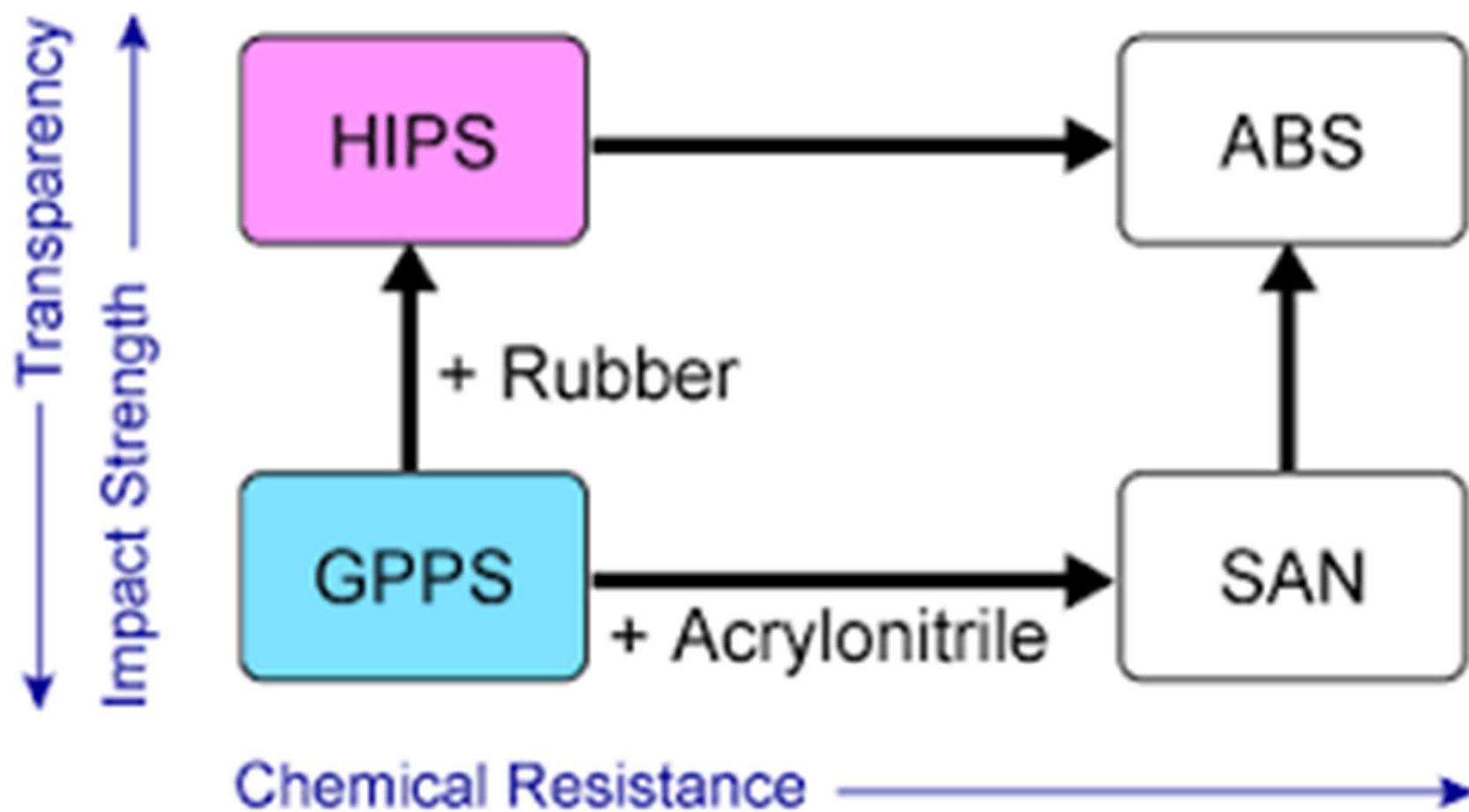
Lesson 5: ABS & HIPS: Basis for Impact Modification

Andy Olah, Ph.D.
January 27, 2025

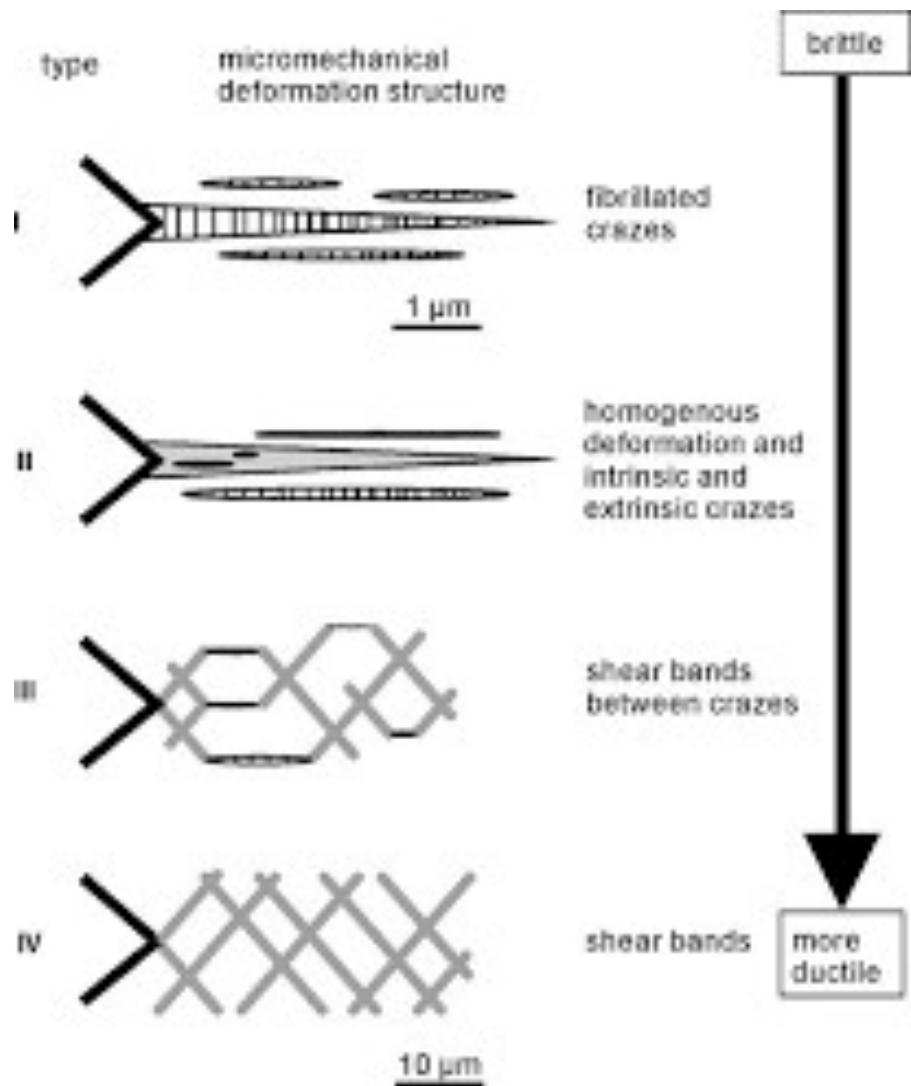
Unmodified Polystyrene is a Brittle Material



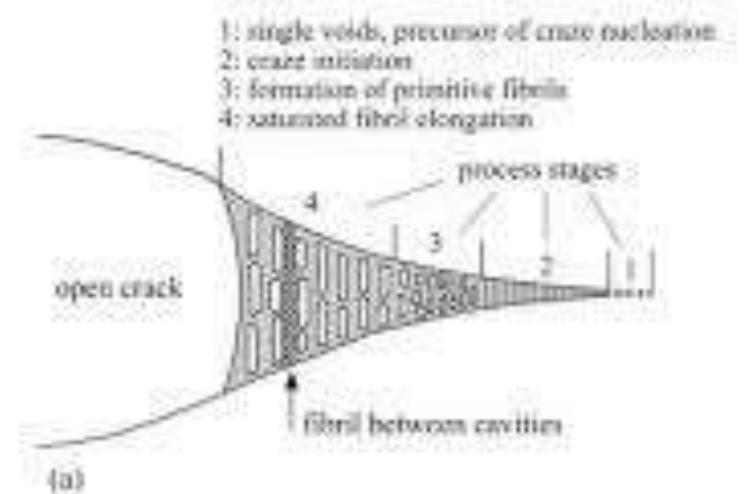
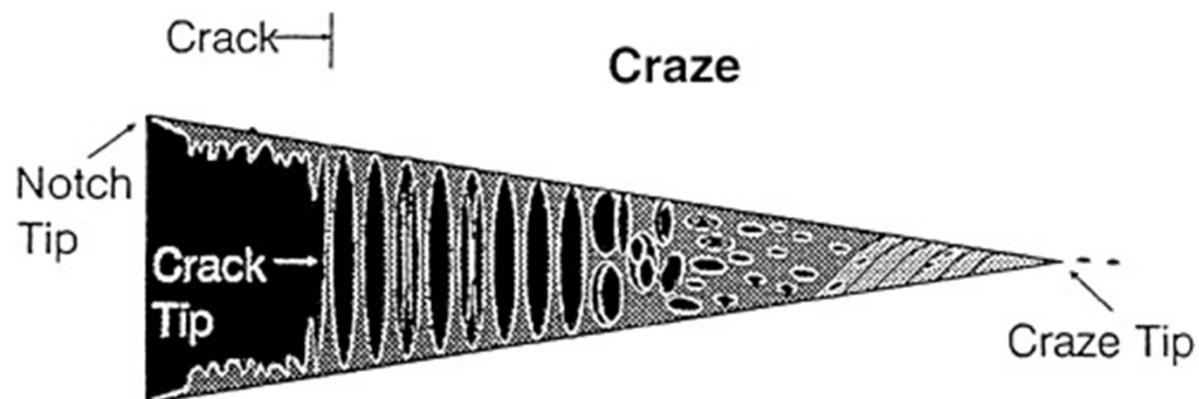
ABS and HIPS for Improved Impact Performance



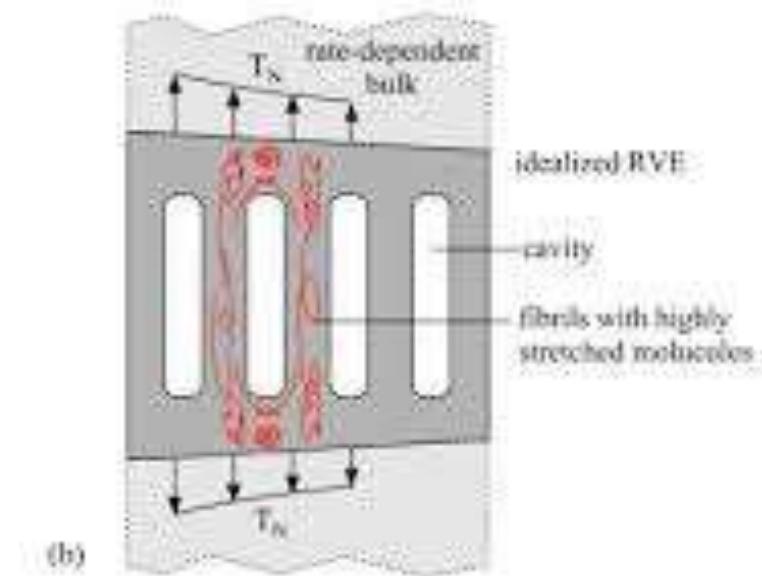
Failure Mechanism Difference Crazing and Shear Banding



Crack-Craze Morphology in PS

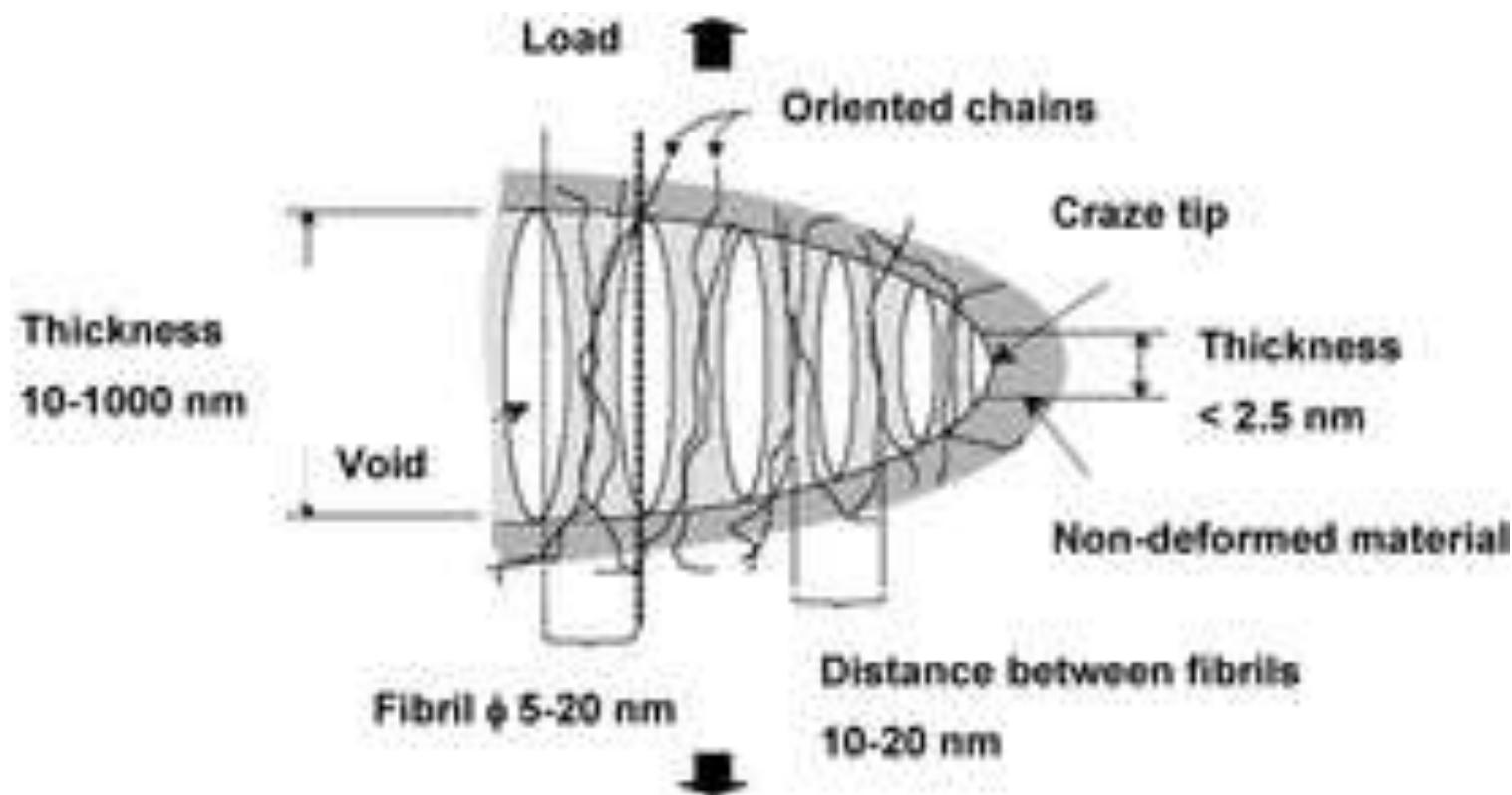


(a)

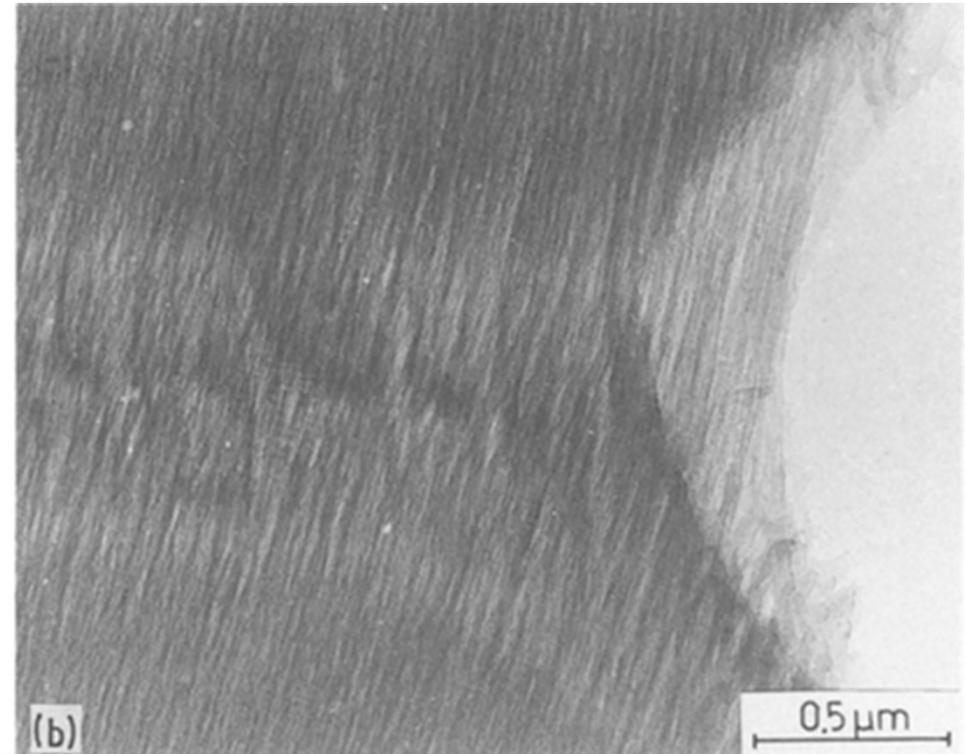
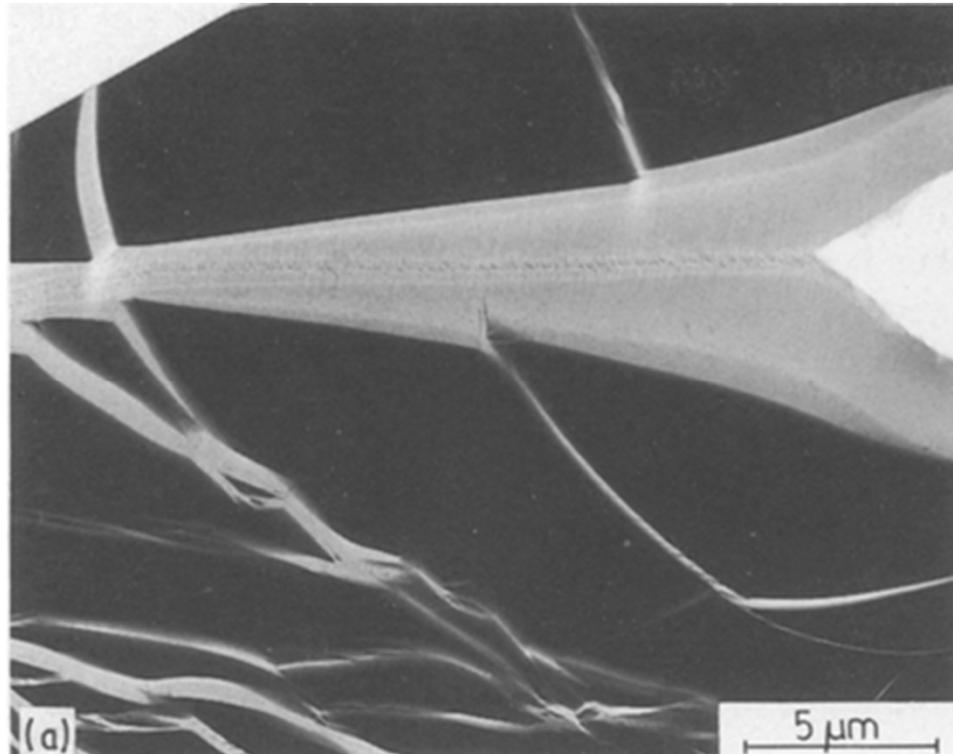


(b)

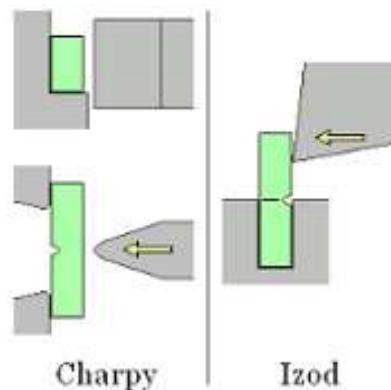
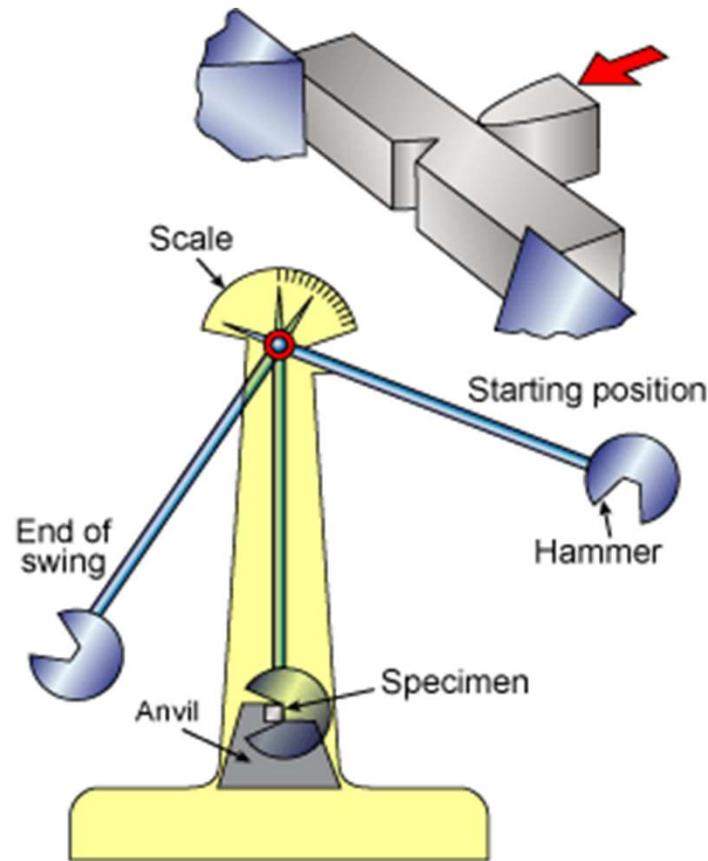
Morphology and Scale of a Craze



Craze Fibril Formation in PS at Crack Tip



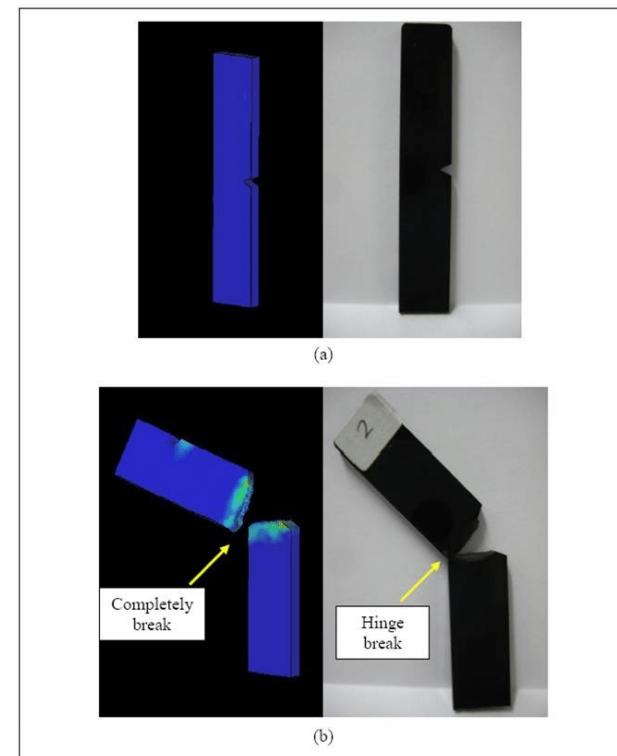
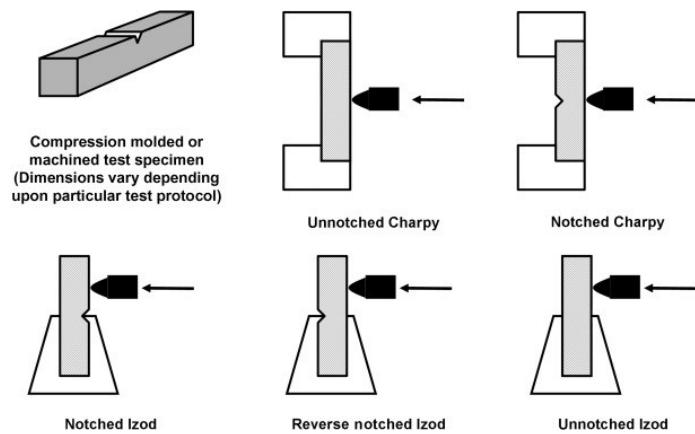
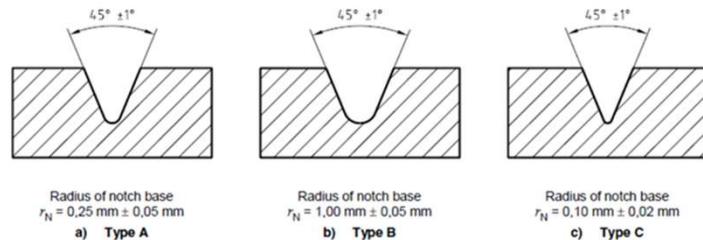
Charpy and Izod Impact Test Method



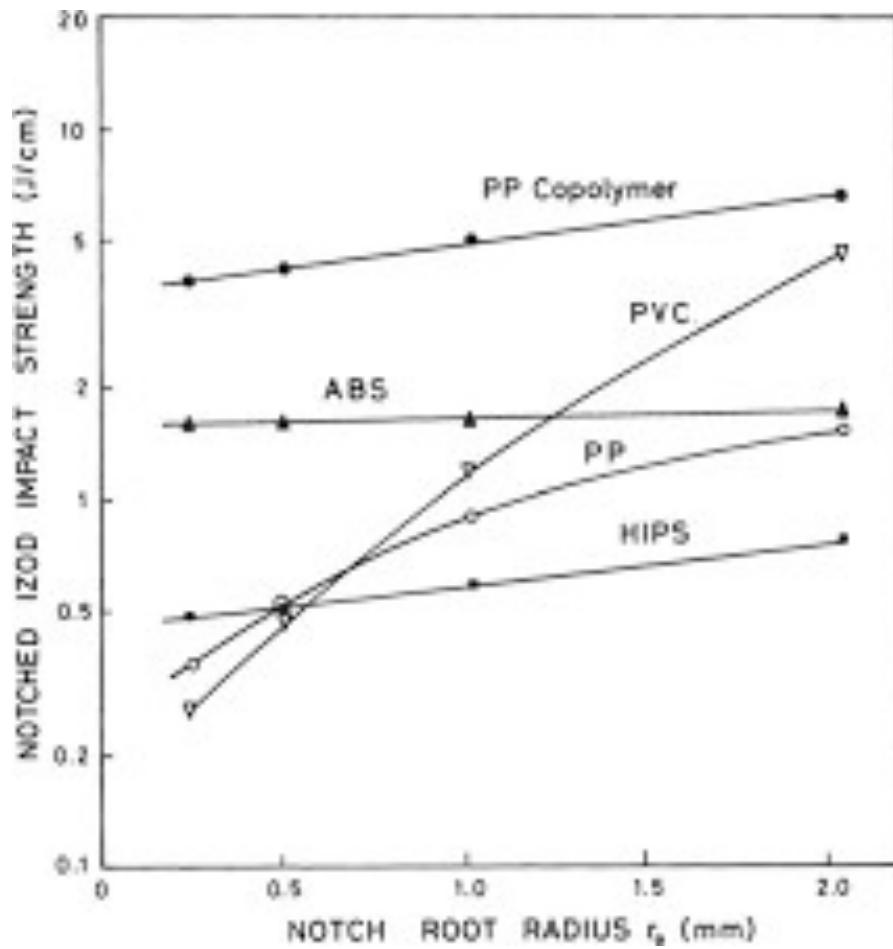
ASTM D6110: Standard Test Method for Determining the Charpy Impact Resistance of Notched Plastics

ASTM D256: Standard Test Method for Determining the Izod Pendulum Impact Resistance of Plastics

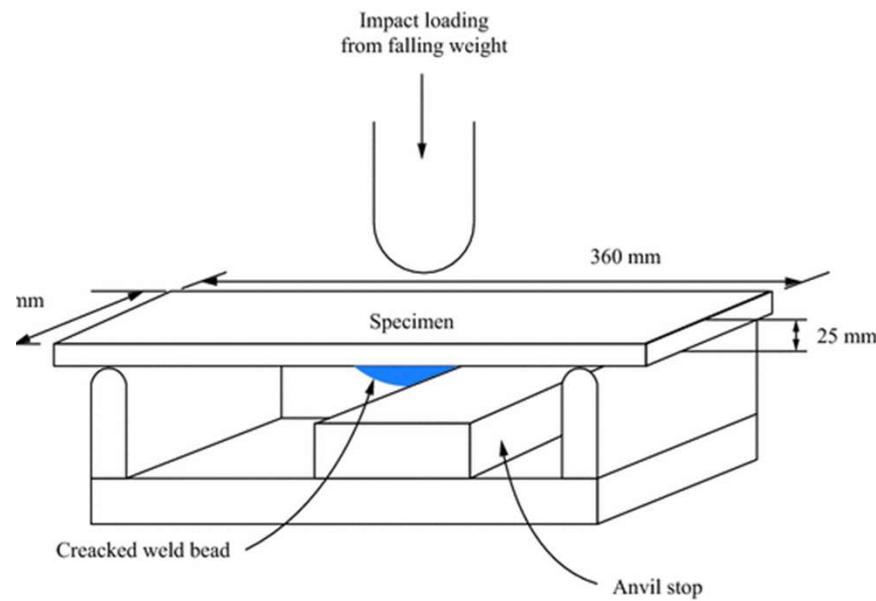
Details of Notch Geometry, Position and Break



Izod Impact Test Results for ABS & HIPS

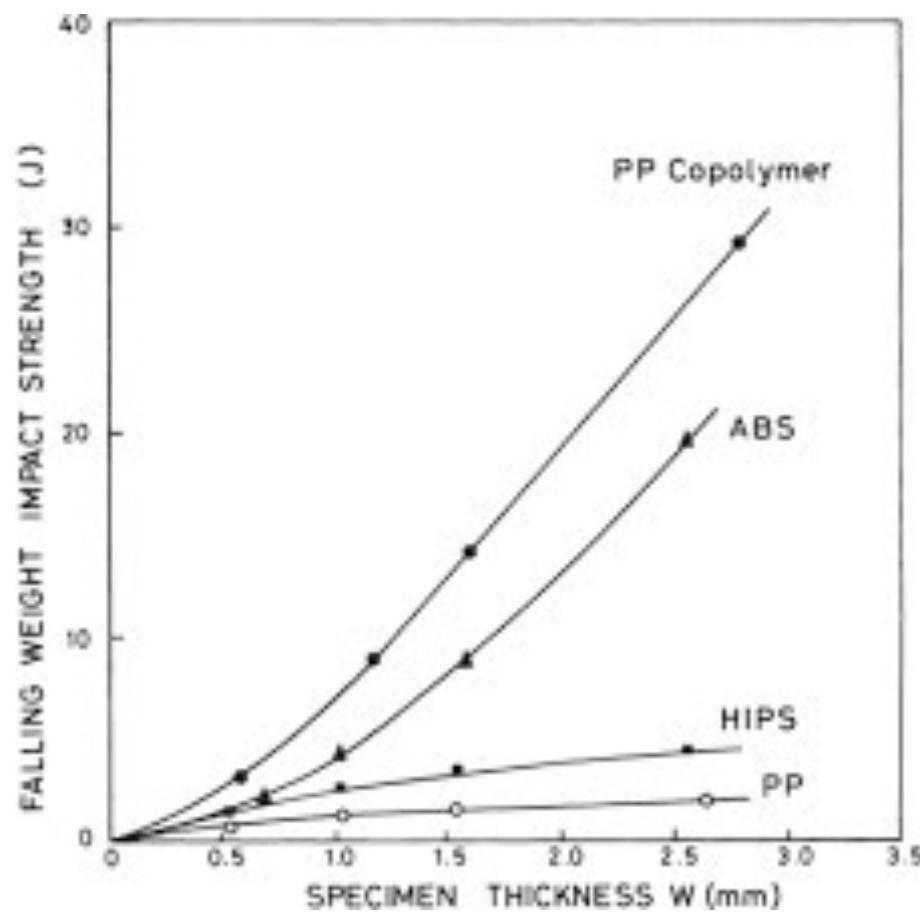


Falling Weight Impact Test Method

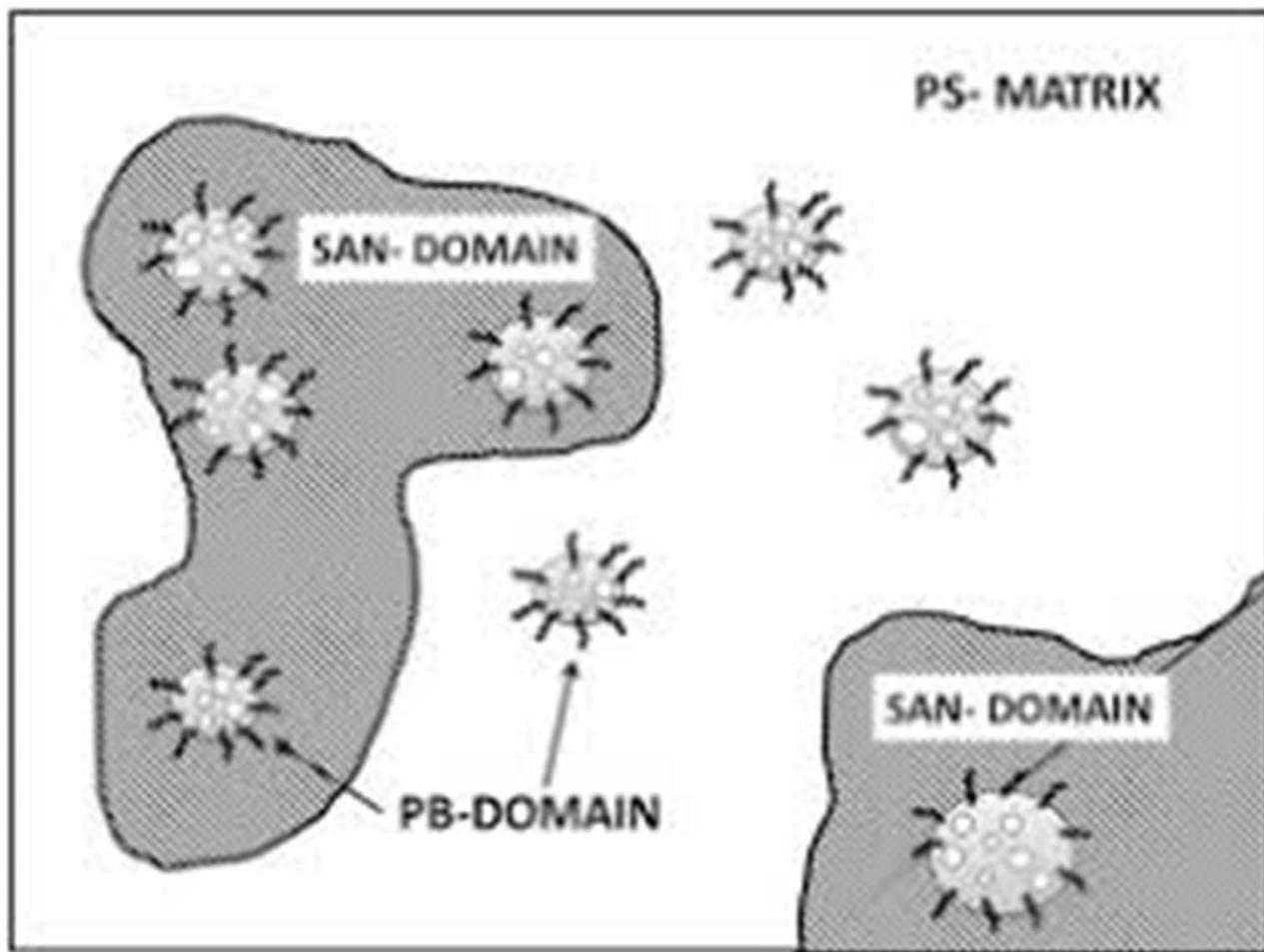


ASTM D5420: Standard Test Method for
Impact Resistance of Flat, Rigid Plastic Specimen by Means
of a Striker Impacted by a Falling Weight (Gardner Method)

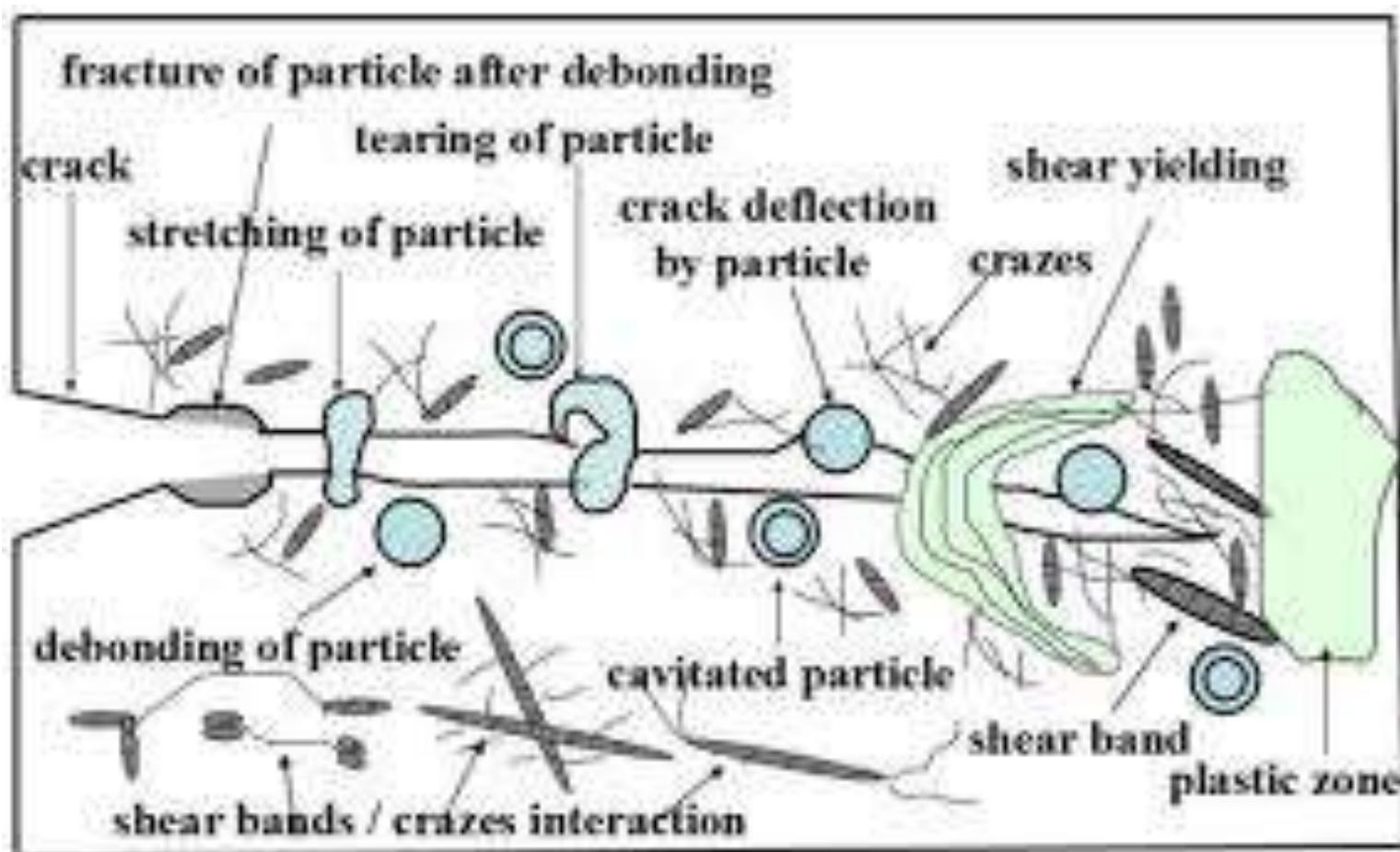
Falling Weight Impact Test Results for ABS & HIPS



Domain Morphologies Common to both ABS and HIPS



Energy Dissipation Mechanisms in Rubber Modified Styrenics



Impact Modification in ABS and HIPS

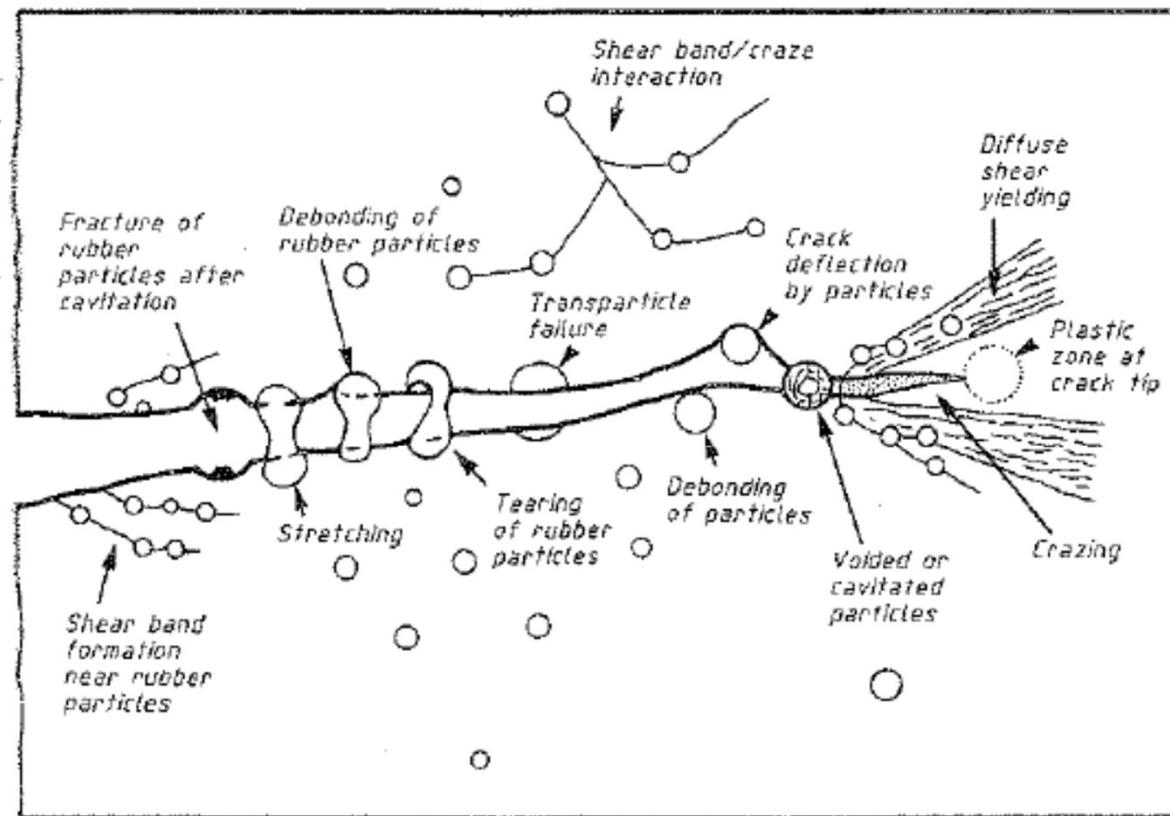
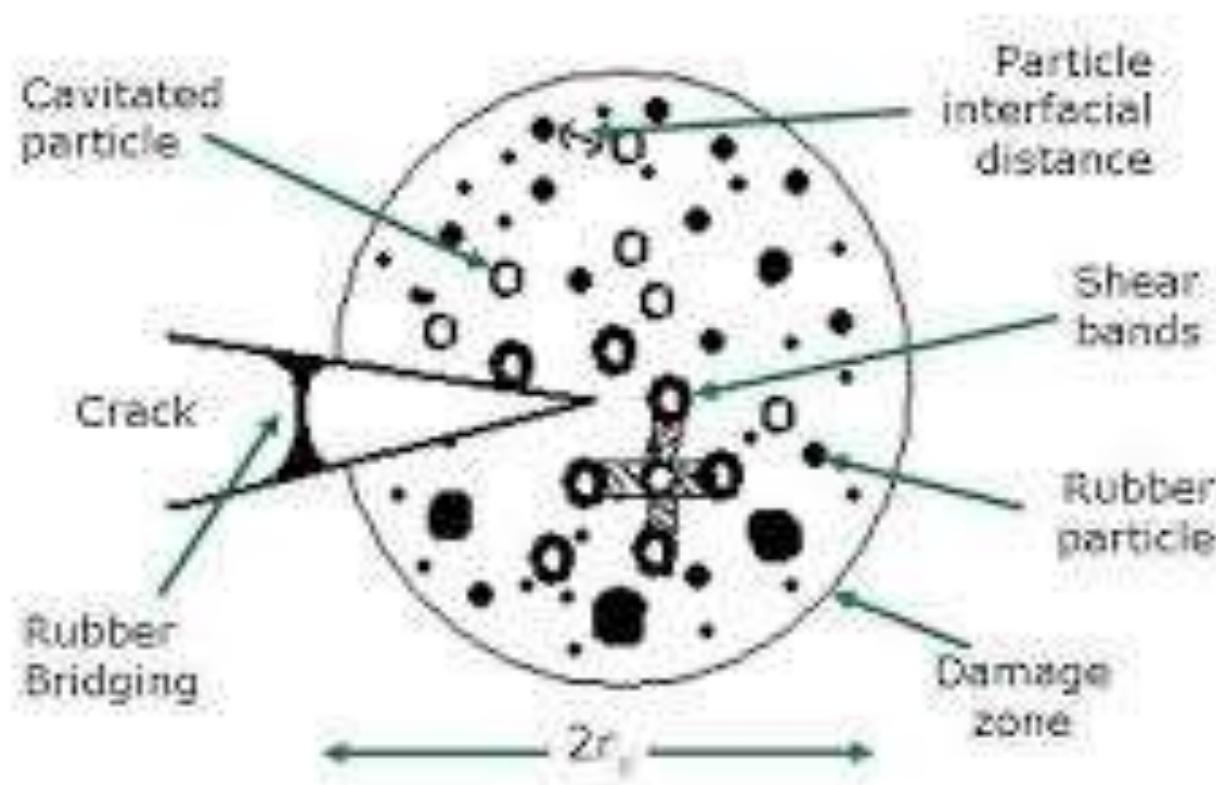


Fig. 3.1 Crack toughening mechanisms in rubber filled modified polymers.

Energy Dissipation by Occluded Rubber in ABS and HIPS



Energy Dissipation by Occluded Rubber in ABS and HIPS

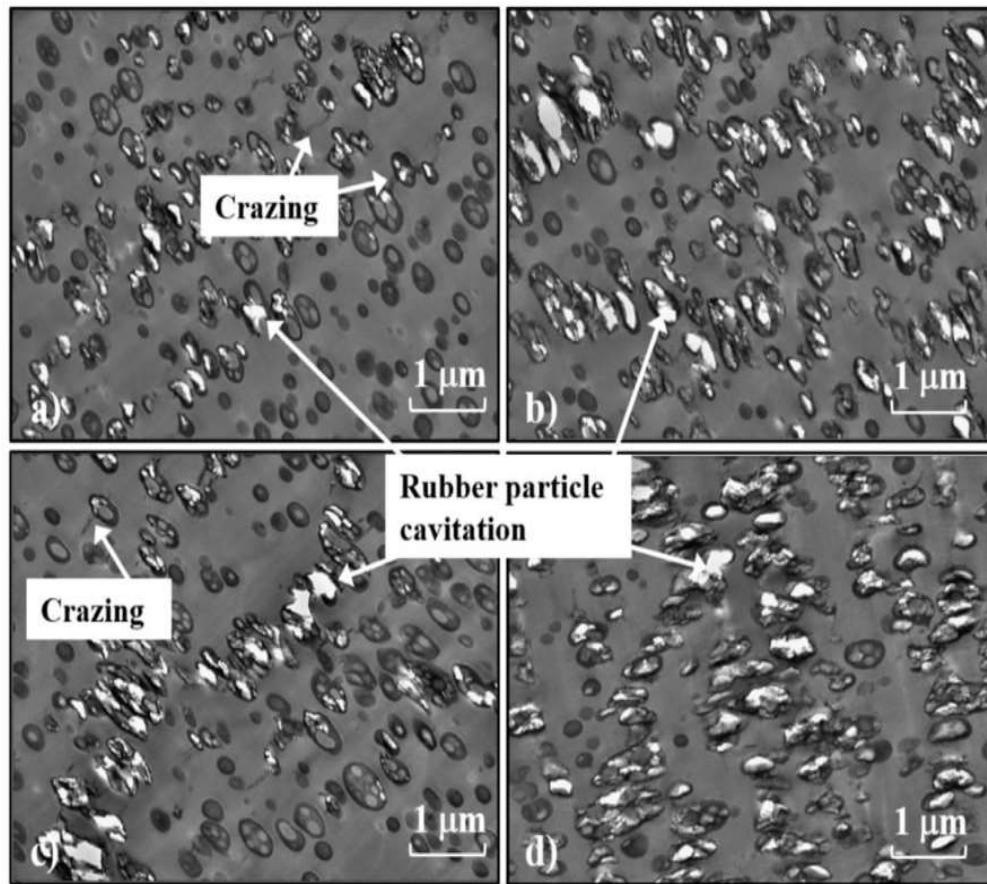


Fig. 10. TEM images taken to the inner region of specimens tested up to 0.2 of u_{pl}/W at different conditions: (a) 23 °C and 0.3 mm/min, (b) 23 °C and 300 mm/min, (c) 60 °C and 0.3 mm/min, (d) 60 °C and 300 mm/min. Rubber particle cavitation and matrix crazing are indicated.

Reaction Sequence for ABS

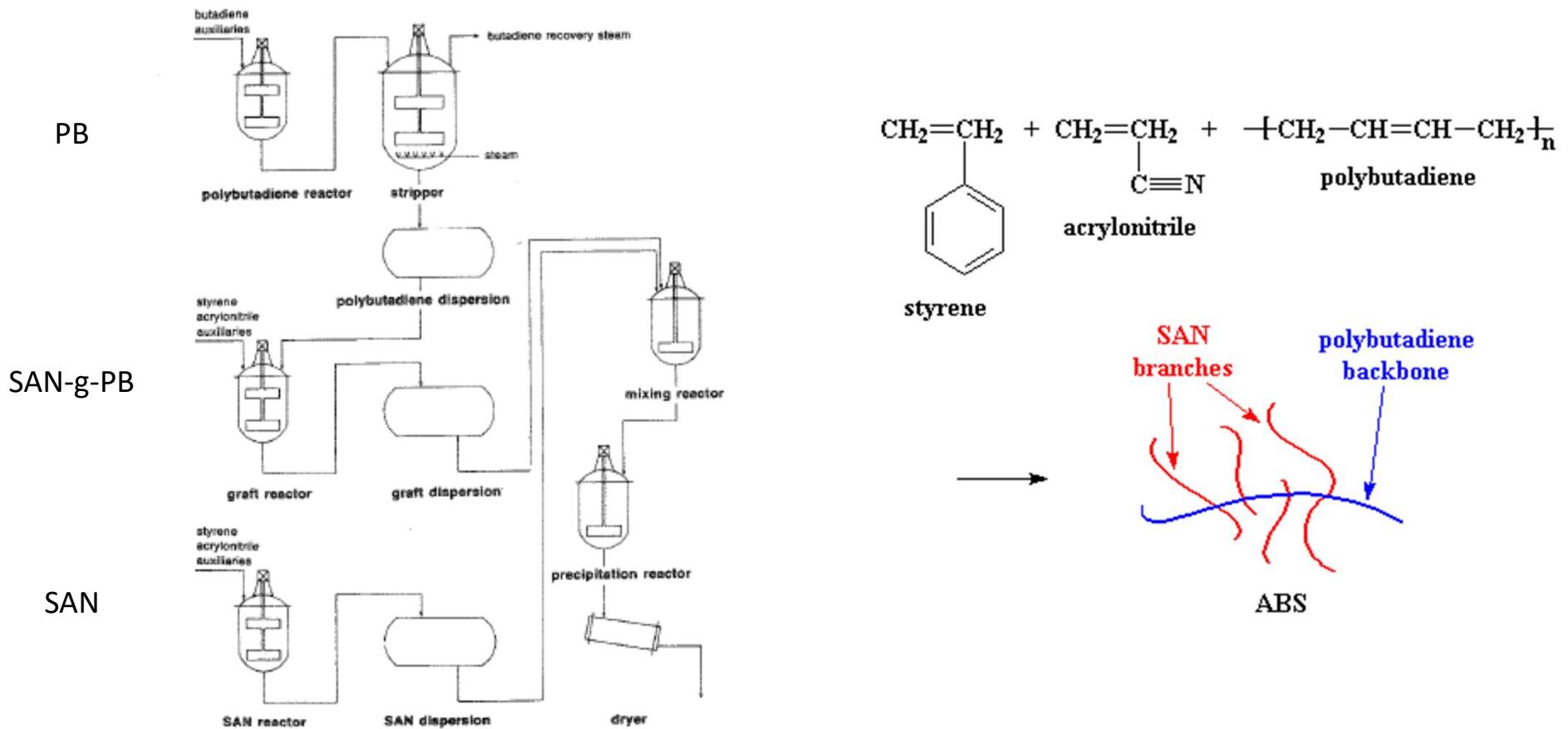
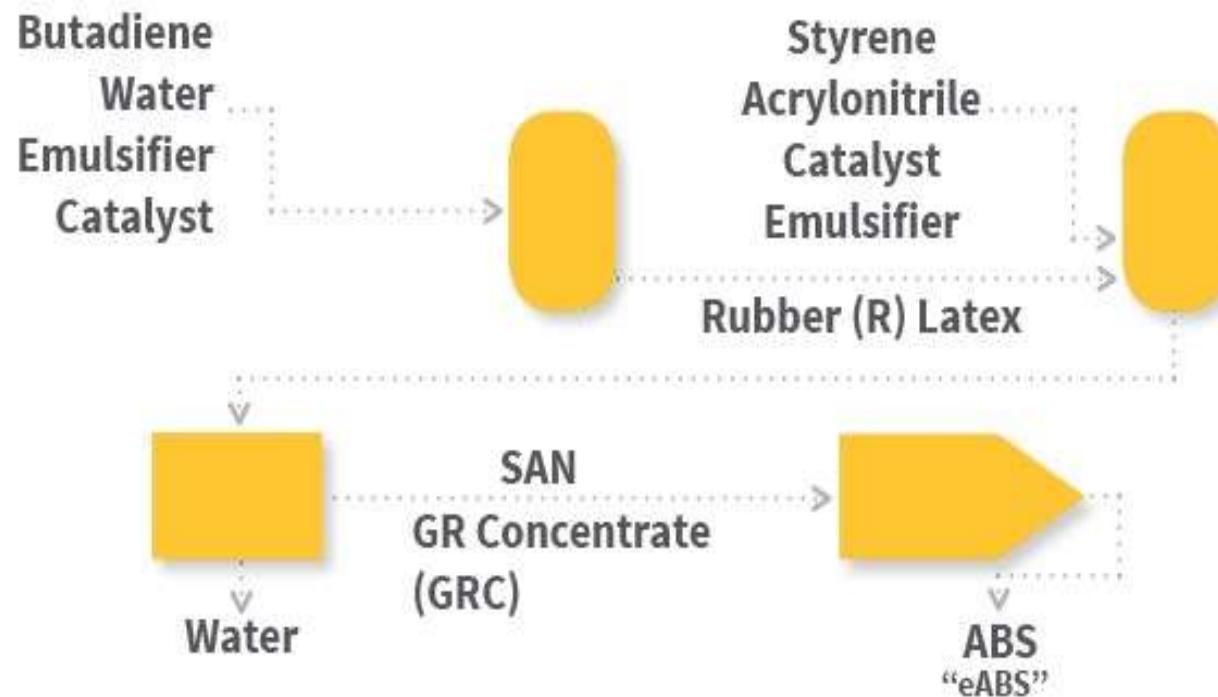


Figure 30. Production of ABS in emulsion.

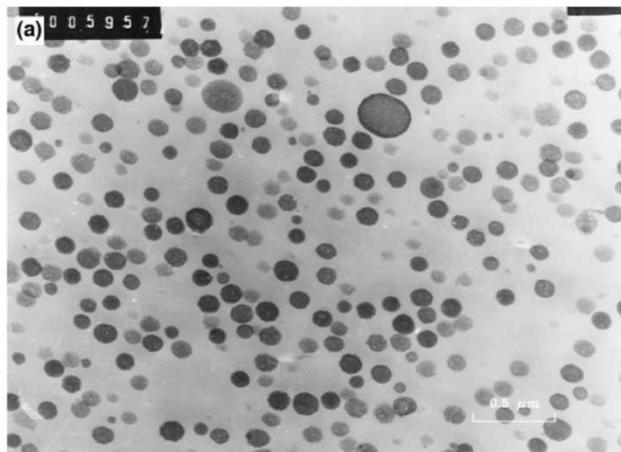
Emulsion Polymerization of ABS

EMULSION POLYMERIZATION

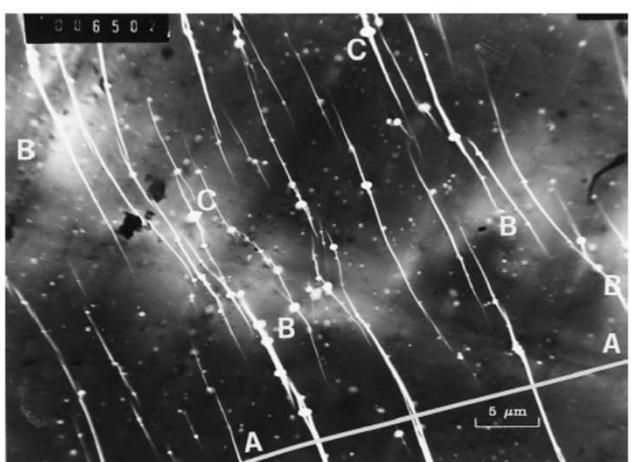
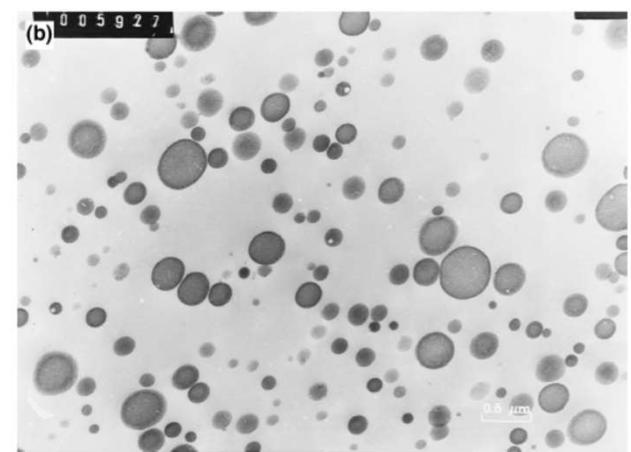


Emulsion polymerization uses a batch reaction process requiring emulsifiers and salts that remain in the ABS at detectable levels.

Morphology and Craze Structure in Emulsion ABS



E1:
PB ~ 49%
ST ~ 38%
AN ~ 12%



E2:
PB ~ 68%
ST ~ 24%
AN ~ 8%

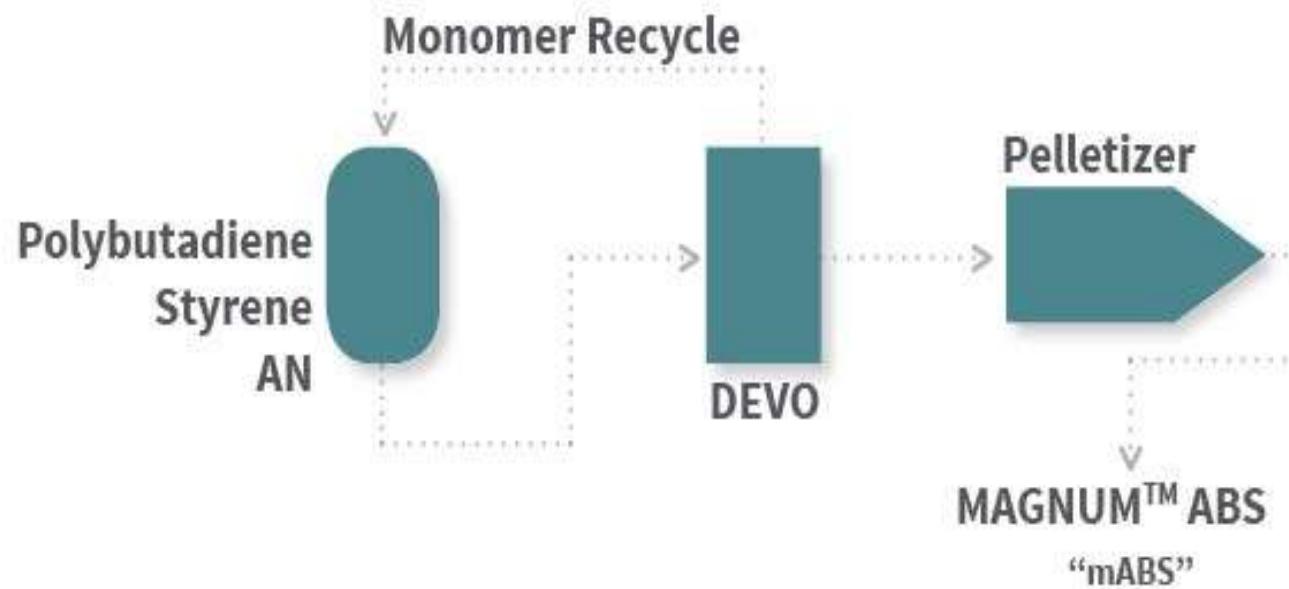


Figure 8 TEM micrograph of sample E1/2.5 after plastic deformation

Figure 9 TEM micrograph of sample E2/2.5 after plastic deformation

Mass Polymerization of ABS

MASS POLYMERIZATION



Mass polymerization is a continuous process that uses few additives, resulting in clean, pure ABS material with high consistency.

Morphology and Craze Structure in Mass ABS

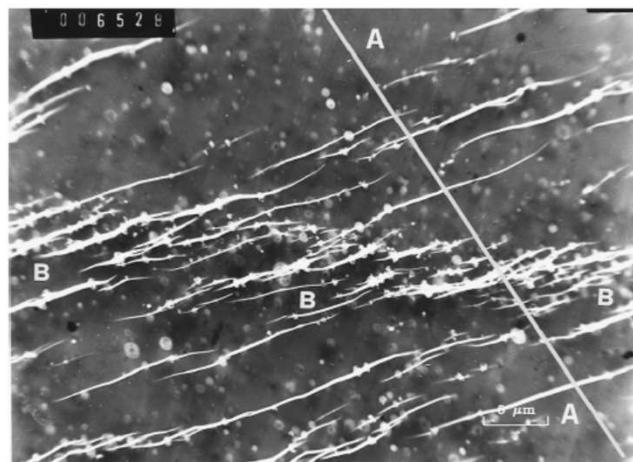
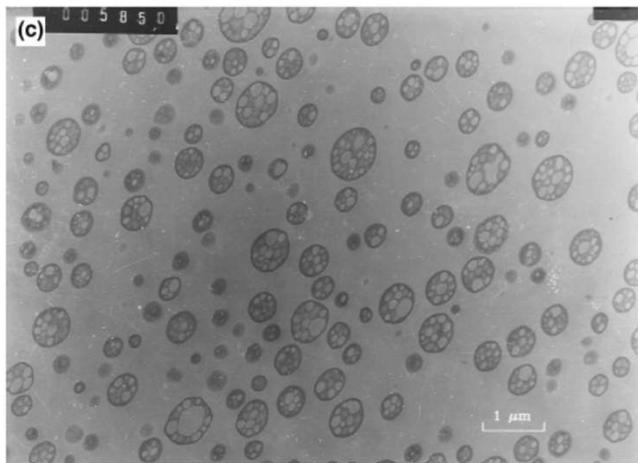
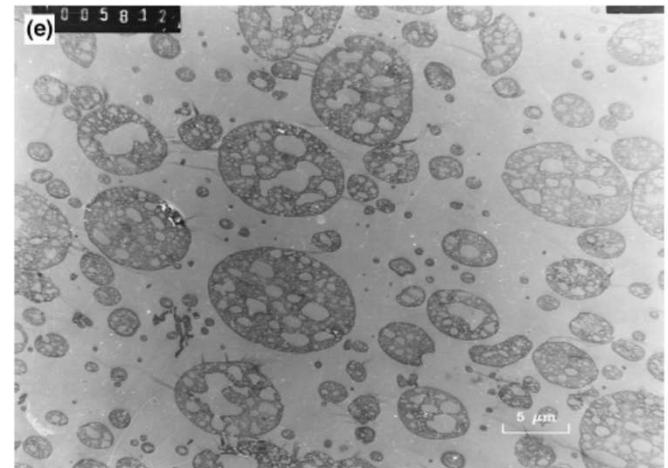


Figure 10 TEM micrograph of sample M1/2.5 after plastic deformation

M1:
PB ~ 11%
ST ~ 65%
AN ~ 23%

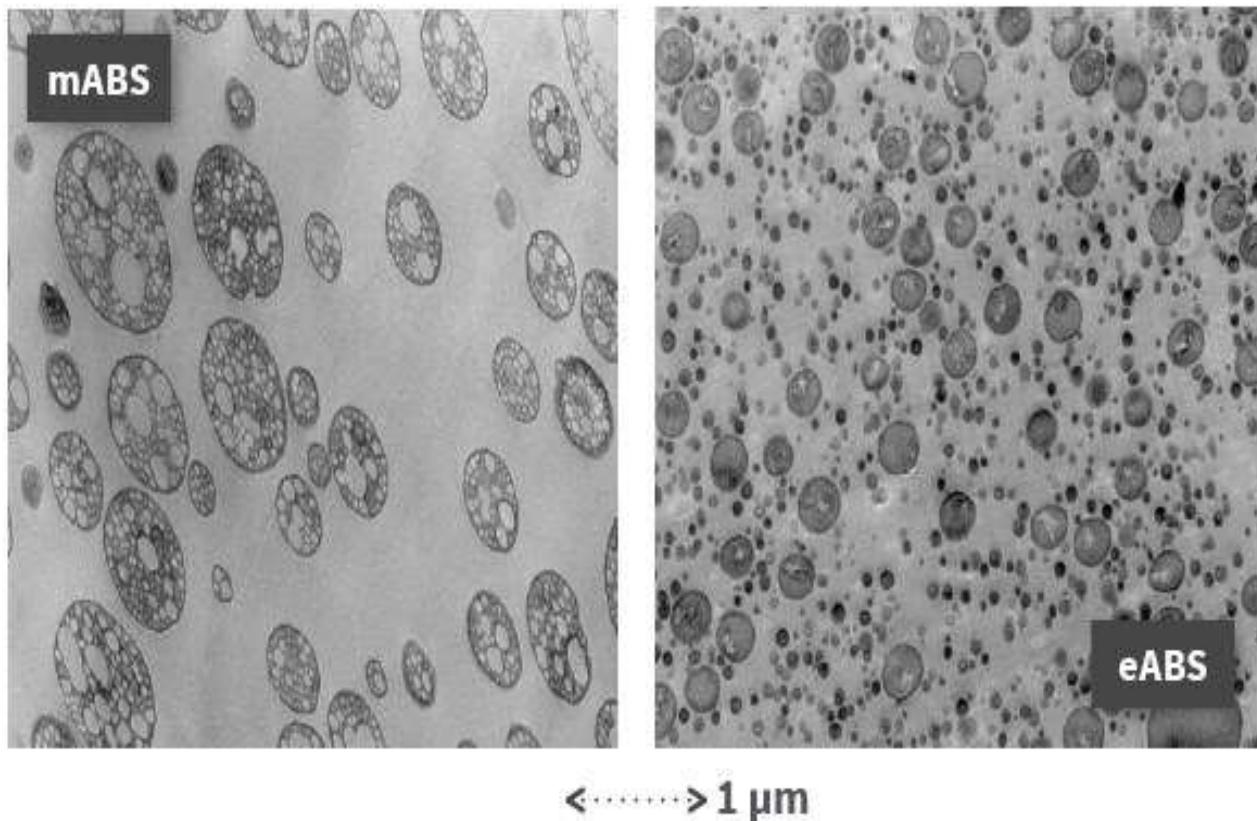


M3:
PB ~ 11%
ST ~ 66%
AN ~ 23%



Figure 12 TEM micrograph of sample M3/2.5 after plastic deformation

Comparison of Mass and Emulsion Polymerized ABS



Morphology is the result of in situ formation of rubber particles during the SAN matrix polymerization.

Pictured below are examples where:

- Light gray background = SAN matrix polymer
- Dark gray spherical particles = rubber particles
- Darker color is the result of a sample pre-treatment process, called staining, and this staining process works specifically on carbon-carbon double covalent bonds that are present in the rubber.

Comparison of Mass and Emulsion Polymerized ABS

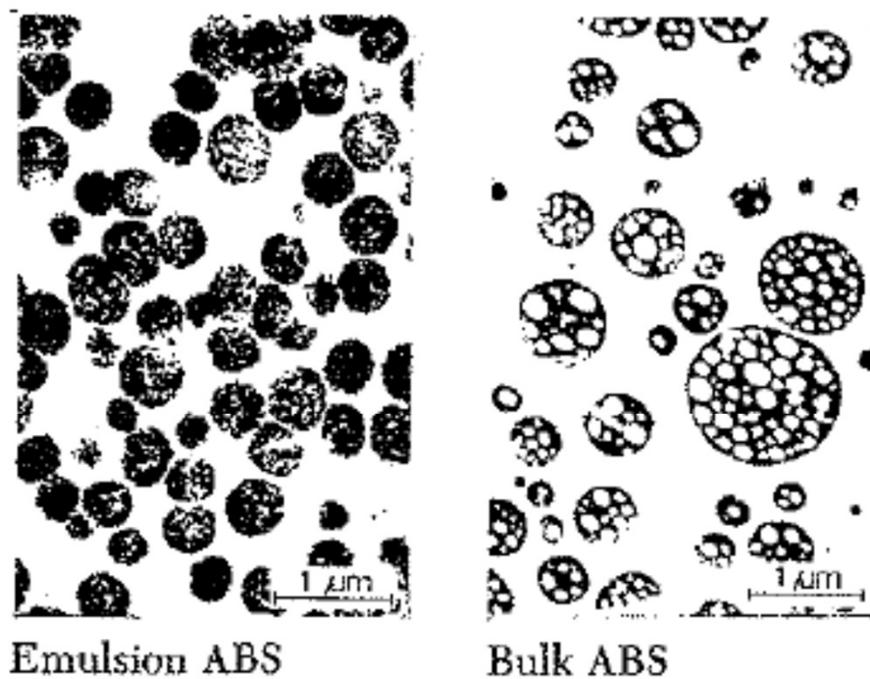


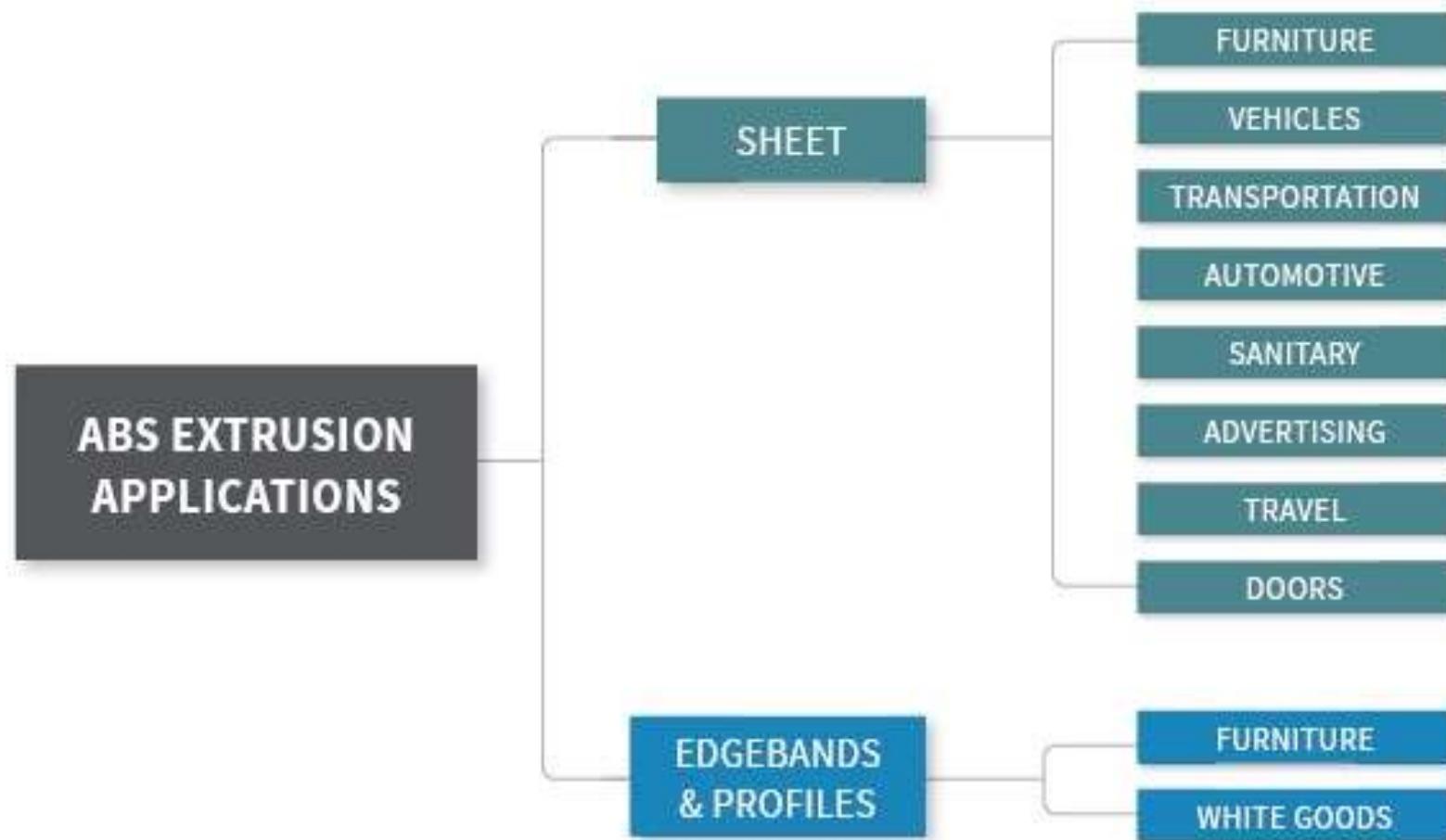
Figure 3. Morphology of ABS polymerized in emulsion or in bulk. (Reproduced with permission from ref. 4. Copyright 1979 Verlag Chemie.)

Comparison of Mass and Emulsion Polymerized ABS

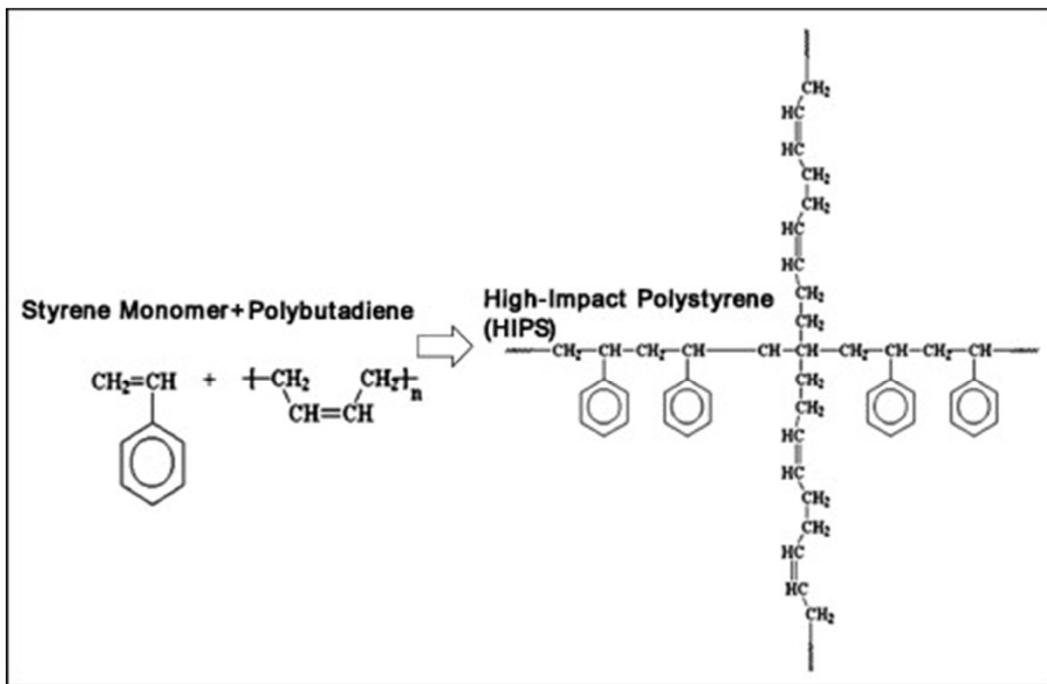
mABS: rubber particles are larger and contain SAN occlusions, therefore the ABS rubber particle morphology is characterized by a high rubber efficiency, which makes it less sensitive to rubber degradation.

eABS: rubber particles are smaller and dense because they are in essence produced in a separate process (rubber latex and GRC production) from the SAN matrix polymerization. This allows a higher control on the rubber particle size and hence the possibility to produce smaller rubber particles, which can be beneficial in case one seeks the highest gloss levels.

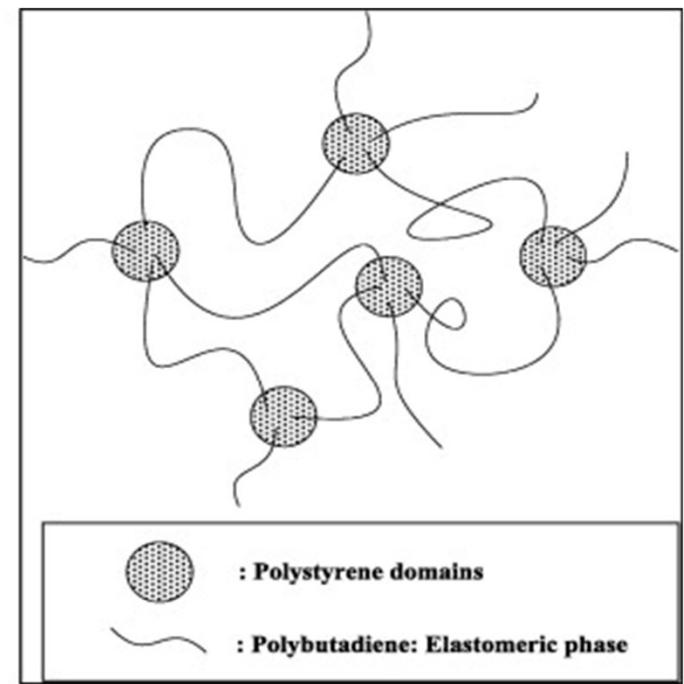
Applications for ABS



HIPS Structure and Morphology

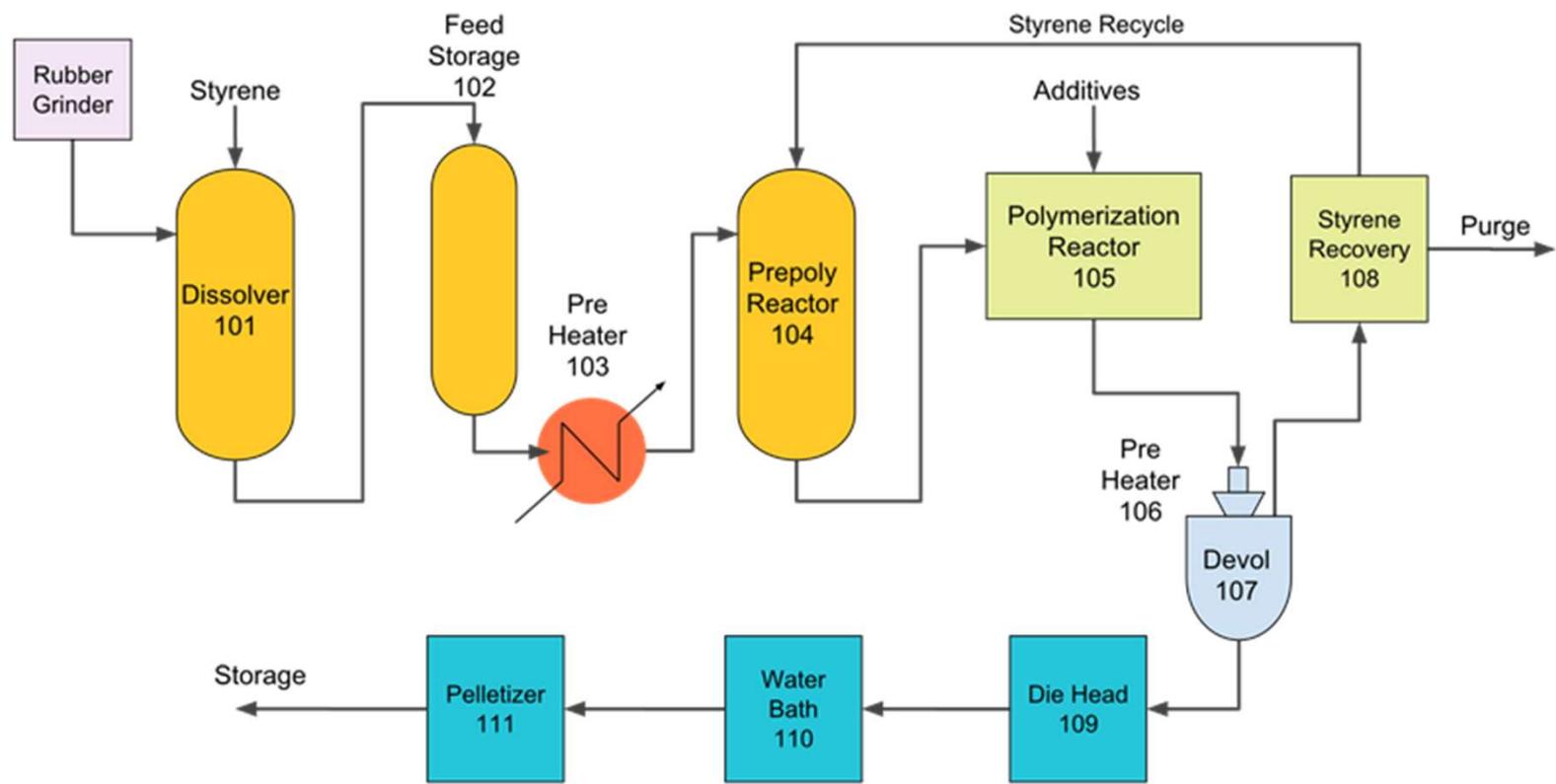


(a)



(b)

One Reaction Sequence for HIPS



Various Reaction Sequences for the Polymerization of HIPS

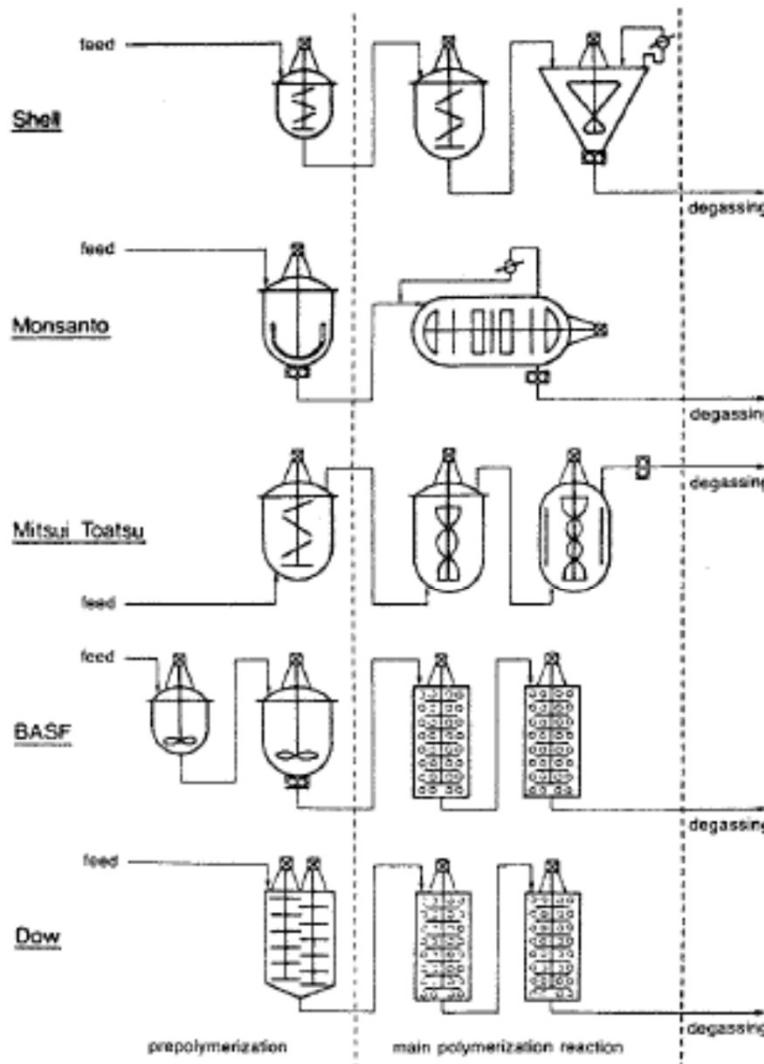


Figure 27. Reactor cascades for HIPS production. (Reproduced with permission from ref. 32. Copyright 1982 Hanser.)

Varying Morphologies can be Imparted into HIPS

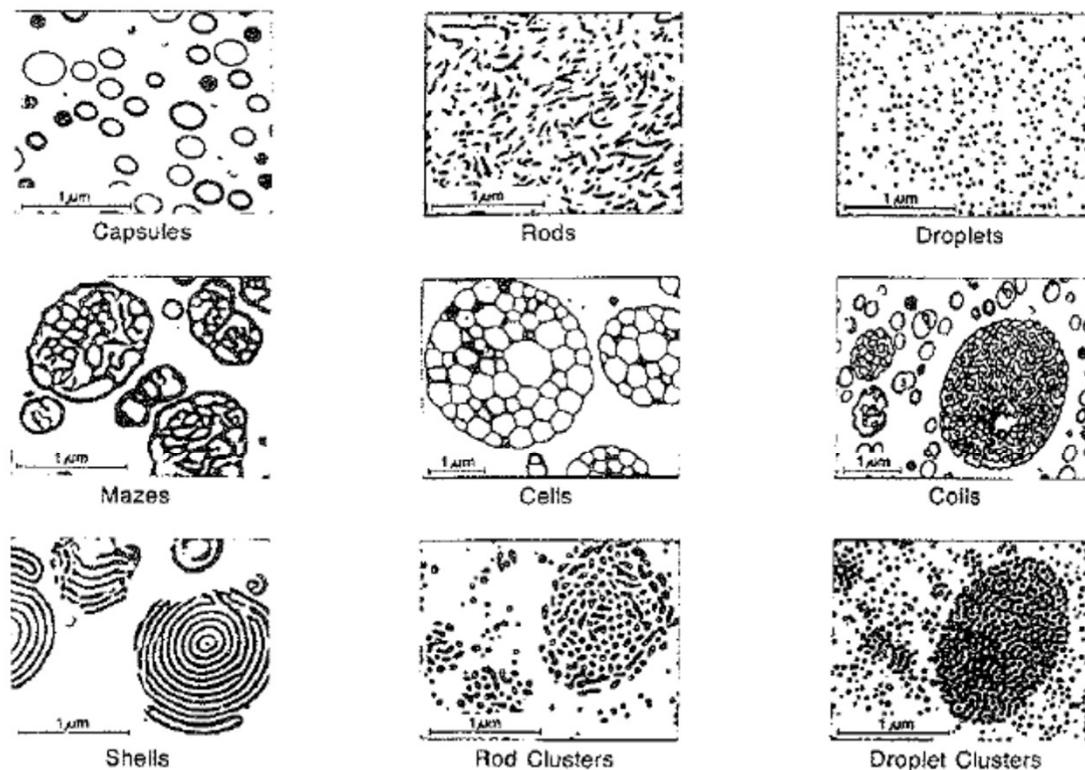


Figure 14. Particle structures observed in HIPS. (Reproduced with permission from ref. 32. Copyright 1982 Hanser.)

Typical properties of ABS and applications

Grade			Good Flow	Middle Impact	Heat Resistance	For Extrusion Standard	For Extrusion High Impact
Item	Unit	Test Method	UT61	MT81	GT-10	ET-70	ST-55
Rheologocal Properties							
Melt Flow Rate	cm ³ /10min	ISO 1133	35	23	20	9	15
Mechanical Properties							
Tensile Stress at Yield	MPa	ISO 527	50	48	52	43	49
Flexural Modulus	MPa	ISO 178	2,400	2,300	2,500	2,100	2,100
Flexural Strength	MPa	ISO 178	76	72	81	66	74
Charpy Notched Impact Strength	kJ/m ²	ISO 179	15	20	15	18	25
Rockwell Hardness	R Scale	ISO 2039	116	113	118	110	110
Thermal Properties							
Temperature of Deflection under Load	deg.C	ISO 75	81	78	85	81	82
Ball Pressure registration Temperature	deg.C	*1	90	90	95	-	-
Flammability	-	UL-94	HB	HB	HB	HB	HB
Other Properties							
Density	g/cm ³		1.05	1.04	1.05	1.05	1.04
Application	Housewares, Electrical appliances (injection)		←	Machinery Parts (Injection)	Sheets, Housing- related materials	←	

*1 : Electrical Appliance and Material Safety Law

HIPS Properties

Comparison of ABS and HIPS Mechanical Properties

Polymers	HIPS			ABS			PLA		
	OV	SD	SE \bar{x}	OV	SD	SE \bar{x}	OV	SD	SE \bar{x}
MFI (g/10 min)	7.5 ± 0.20	0.16	0.11	8.76 ± 0.16	0.13	0.09	13.52 ± 0.11	0.09	0.06
Young's modulus (MPa)	112.5 ± 0.12	0.09	0.06	175 ± 0.11	0.09	0.06	47.9 ± 0.10	0.08	0.05
Yield stress (MPa)	3.44 ± 0.21	0.17	0.12	0.49 ± 0.21	0.17	0.12	0.27 ± 0.16	0.13	0.09
Glass transition temp (°C)	100.41 ± 0.16	0.13	0.09	109.76 ± 0.2	0.16	0.11	62.57 ± 0.21	0.17	0.12
Peak load (N)	80.8 ± 0.11	0.08	0.06	207 ± 0.2	0.16	0.11	282.4 ± 0.20	0.16	0.11
Peak strength (MPa)	4.21 ± 0.16	0.13	0.09	10.78 ± 0.11	0.09	0.06	14.71 ± 0.16	0.13	0.09
Peak elongation (mm)	1.9 ± 0.20	0.16	0.11	4.75 ± 0.16	0.13	0.09	5.13 ± 0.16	0.13	0.09
Percentage elongation at peak (%)	3.0 ± 0.11	0.09	0.06	6.0 ± 0.15	0.12	0.08	7.0 ± 0.10	0.08	0.05

ABS is used in 3D Printing



HIPS is used in 3D Printing

Six HIPS color series

1.75mm 3D filament



Questions?



I may not be that funny or athletic or good looking
or smart or talented. . . . I forgot where I was going with this.

EMAC 276

Lecture 6: The Vinyl Chloride Family

Poly(Vinyl Chloride) - PVC

Polyvinylidene Chloride - PVDC

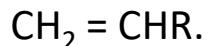
Chlorinated Poly(Vinyl Chloride) - CPVC

Andy Olah, Ph.D.

January 29, 2025

What is a “Vinyl” Type Polymer?

Vinyl polymers are the most common type of polymers derived from “vinyl-type” monomers having the general structure:



Where,

polystyrene – R = C₆H₅

polyvinyl chloride – R = Cl

polyvinyl acetate – R = O₂CCH₃

polyacrylonitrile - R = CN

Not to be confused with poly(vinyl chloride) (PVC) materials which have traditionally been identified as “Vinyls”; i.e., vinyl siding, vinyl records, etc.

Olefin polymers are a subgroup of vinyl monomers produced from alkenes having a C_nH_{2n} monomer structure:

polyethylene – R = H => CH₂ = CH₂; (n = 2) => C₂H₄

polypropylene – R = CH₃ => CH₂ = CH-CH₃; (n = 3) => C₃H₆

polybutylene – R = CH₂-CH₃ => CH₂ = CH-CH₂-CH₃; (n=4) => C₄H₈

History of Poly(Vinyl Chloride)

- 1838 Henri Victor Regnault (Fr): Photo-initiated polymerization of vinyl chloride monomer (VCM) when exposed to sunlight.
- 1872 Eugen Baumann (Gr): Photo-initiated polymerization of vinyl chloride monomer (VCM) when exposed to sunlight.
- 1913 Friedrich Heinrich August Klatte (Gr): First patent on the photo-initiated polymerization of VCM with sunlight.
- The US Patent was filed by Klatte on July 3, 1914 and issued on October 2, 1917; US 1,241,738
- With the publication of the patent the first industrial interest in PVC began:

UNITED STATES PATENT OFFICE.

FRITZ KLATTE AND ADOLF ROLLETT, OF SCHWANHEIM-ON-THE-MAIN, GERMANY,
ASSIGNEES TO THE FIRM OF CHEMISCHE FABRIK GREISHEIM-ELEKTRON, OF
FRANKFORT-ON-THE-MAIN, GERMANY, A CORPORATION OF GERMANY.

PLASTIC COMPOSITION AND PROCESS OF PRODUCING IT.

UNITED STATES PATENT OFFICE.

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ASSIGNORS TO THE FIRM OF CHEMISCHE FABRIK GREISHEIM-ELEKTRON, OF
FRANKFORT-ON-THE-MAIN, GERMANY, A CORPORATION OF GERMANY.**

PLASTIC COMPOSITION AND PROCESS OF PRODUCING IT.

1,241,738.

Specification of Letters Patent.

Patented Oct. 2, 1917.

No Drawing.

Application filed July 2, 1914. Serial No. 348,689.

"If instead of organic vinyl esters, vinyl halids, for instance vinyl chlorid, or vinyl bromid be ***polymerized masses are obtained which are not industrially utilizable***, they being opaque, porous, and chalk-like, and readily crumbling to a white powder."

"In accordance with this invention it is however possible to obtain from ***these valueless masses*** valuable products if the said masses be dissolved in the hereinbefore described manner and then be converted again to the solid state. By this treatment from the aforesaid masses products are obtained which are suitable for all purposes for which cellulose esters or celluloid have hitherto been used, namely a substitutes for horn, amber, or artificial resins or lacquers or for impregnating purposes and also for the production of films artificial threads and the like."

When PVC was Invented Polymer Science was in Transition

Science had a problem with plastics because it was the credo of chemistry that very large molecules cannot be stable. Until 1920 it was generally accepted that molecules can join together in large clusters and form colloids, but that they cannot really be big themselves. The basic concepts of today's viewpoint were expressed by a few visionaries between 1860 and 1920, but these remained individual opinions.



Polymers became Recognized as Macromolecules



Hermann Staudinger, 1917, in his laboratory in Zurich.

At the ETH in Zurich, Hermann Staudinger developed and taught a different vision: his work with polystyrene, polyoxymethylene and caoutchouc led him to believe the size of molecules was nearly limitless and they would form long chains. He published this concept for the first time in 1920 and coined the term «macromolecule» in 1926. The existence of such giant molecules met with a great deal of skepticism and only gradually began to find acceptance. Staudinger's experimental results were later explained by others in line with the laws of physics: notably Kurt H. Meyer and Hermann F. Mark, who in Ludwigshafen in 1928 shed light on the structure of cellulose, silk, chitin and caoutchouc via X-ray analysis, and Werner Kuhn, who in 1934 was the first to conclusively expound the viscosity of polymeric solutions and in Karlsruhe, then Kiel and then in Basel established the theoretical basis for rubber elasticity and the deformation of macromolecules.

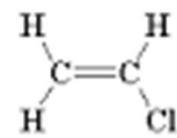
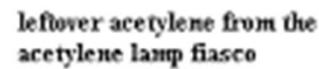
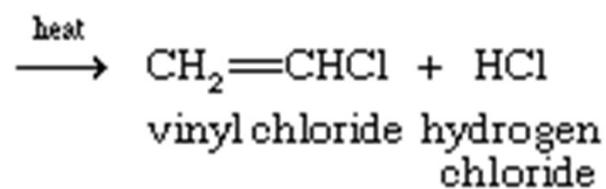
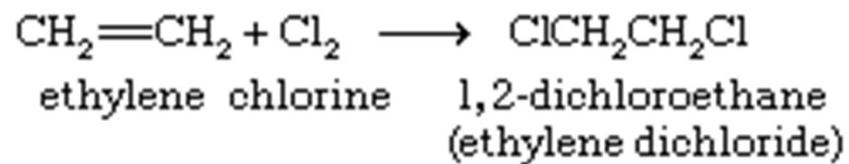
What is caotchouc?

caou·tchouc/*noun*

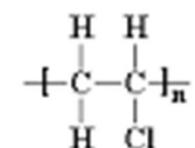
'kou,CHōok,-,CHōo(k)/*noun:*
unvulcanized natural rubber.



There are Two Pathways for Vinyl Chloride Monomer (VCM) Synthesis



vinyl chloride



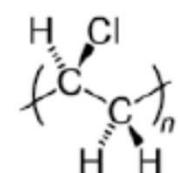
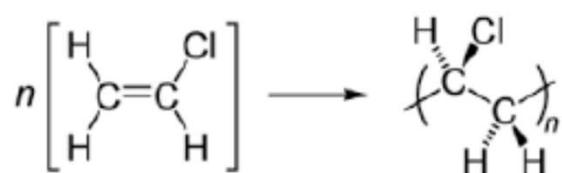
poly(vinyl chloride)

Health Effects of Vinyl Chloride Monomer

Chronic **effects** VCM is a known human carcinogen. Occupational overexposure has produced a specific cancer (angiosarcoma of the liver) and is associated with hepatocellular and cholangiocellular cancer.

In the 1960s, polyvinyl chloride (PVC) was shown to be associated with Raynaud's phenomenon and later with malignancies, including hemangiosarcoma of the liver. The **carcinogenicity** of PVC was established as a result of the review of all evidence in 1974 by the US Office of Technology Assessment and OSHA

The Structure of Poly(Vinyl Chloride)



Nearly 57% of the mass of poly(vinyl chloride)
is chlorine.

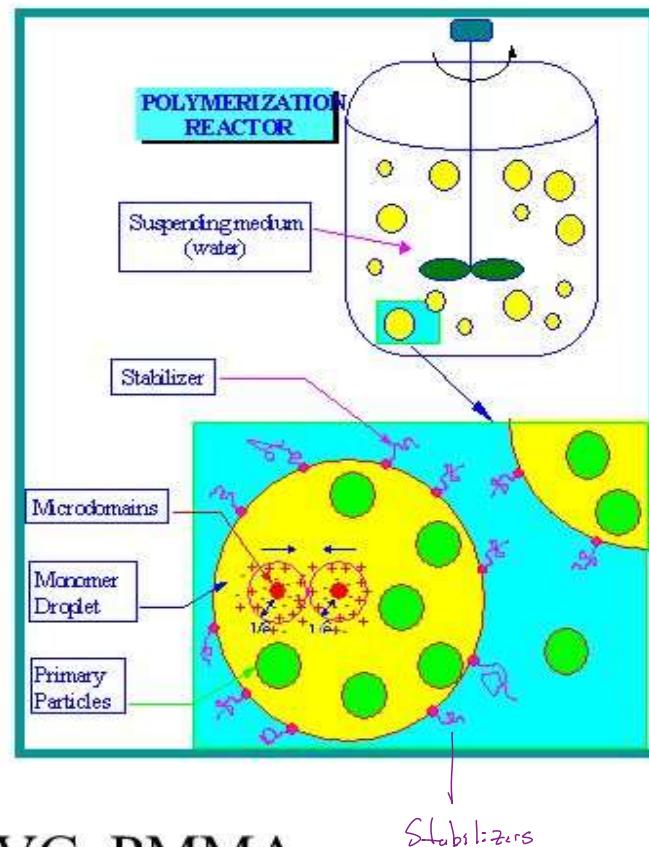


Suspension polymerization

- Disperse monomer droplets in a noncompatible liquid (e.g. H₂O)
- Polymerize the monomer by an initiator (soluble in the monomer)
- Stabilize the dispersion with a stabilizer (e.g. poly(vinyl alcohol) or methyl cellulose)
- Isolate granular bead products by filtration or spray drying
- Heat transfer is efficient and reaction is easily controlled
- Similar to bulk polymerization in kinetics and mechanism

Commercial uses

For making **granular polymers**, e.g. PS, PVC, PMMA



The Hierarchical Structure of Poly(Vinyl Chloride) when Suspension Polymerized

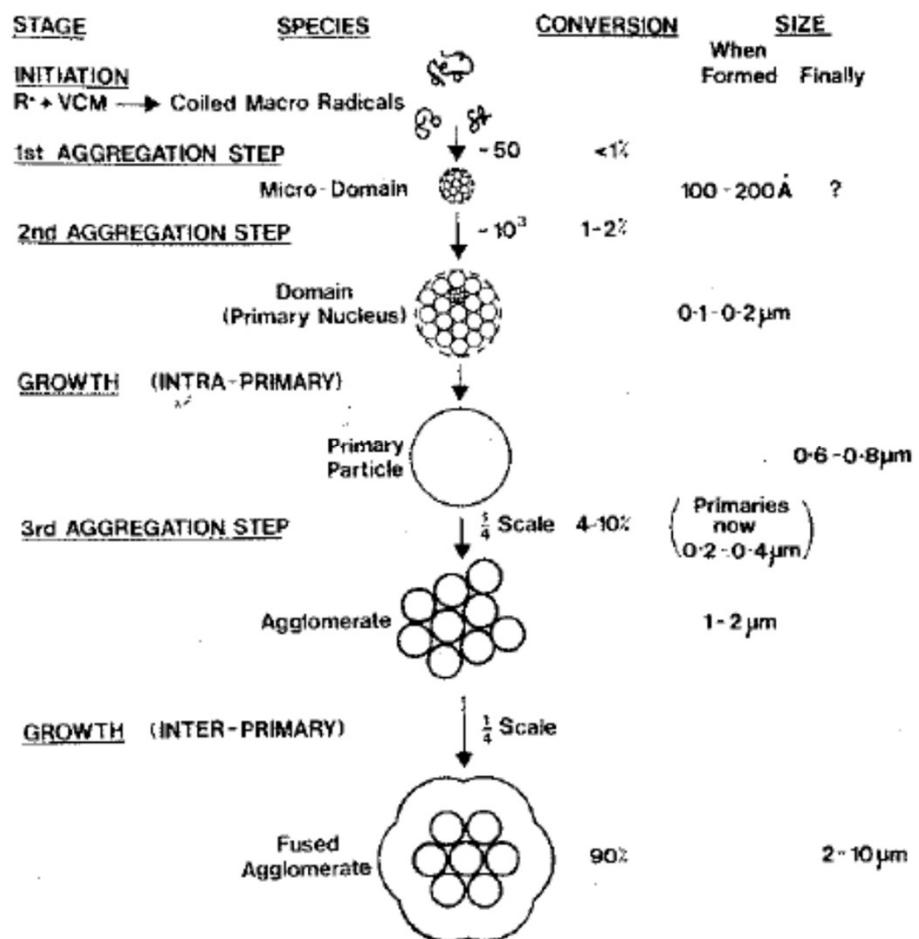


FIG. 7.27. Schematic representation of the mechanism of VCM polymerisation.

MORPHOLOGY OF PVC

181

<u>STAGE</u>	<u>SPECIES</u>	<u>CONVERSION</u>	<u>SIZE</u>
<u>INITIATION</u>	$R \cdot + VCM \rightarrow$ Coiled Macro Radicals		When Formed
<u>1st AGGREGATION STEP</u>	Micro-Domain	$\downarrow -50$ \downarrow	Finally $100-200\text{\AA}$?
<u>2nd AGGREGATION STEP</u>	Domain (Primary Nucleus)	$\downarrow -10^3$ \downarrow	$0.1-0.2\mu\text{m}$
<u>GROWTH (INTRA-PRIMARY)</u>	Primary Particle	\downarrow	$0.6-0.8\mu\text{m}$
<u>3rd AGGREGATION STEP</u>		$\downarrow \frac{1}{4} \text{ Scale}$ \downarrow	$(\text{Primaries now } 0.2-0.4\mu\text{m})$

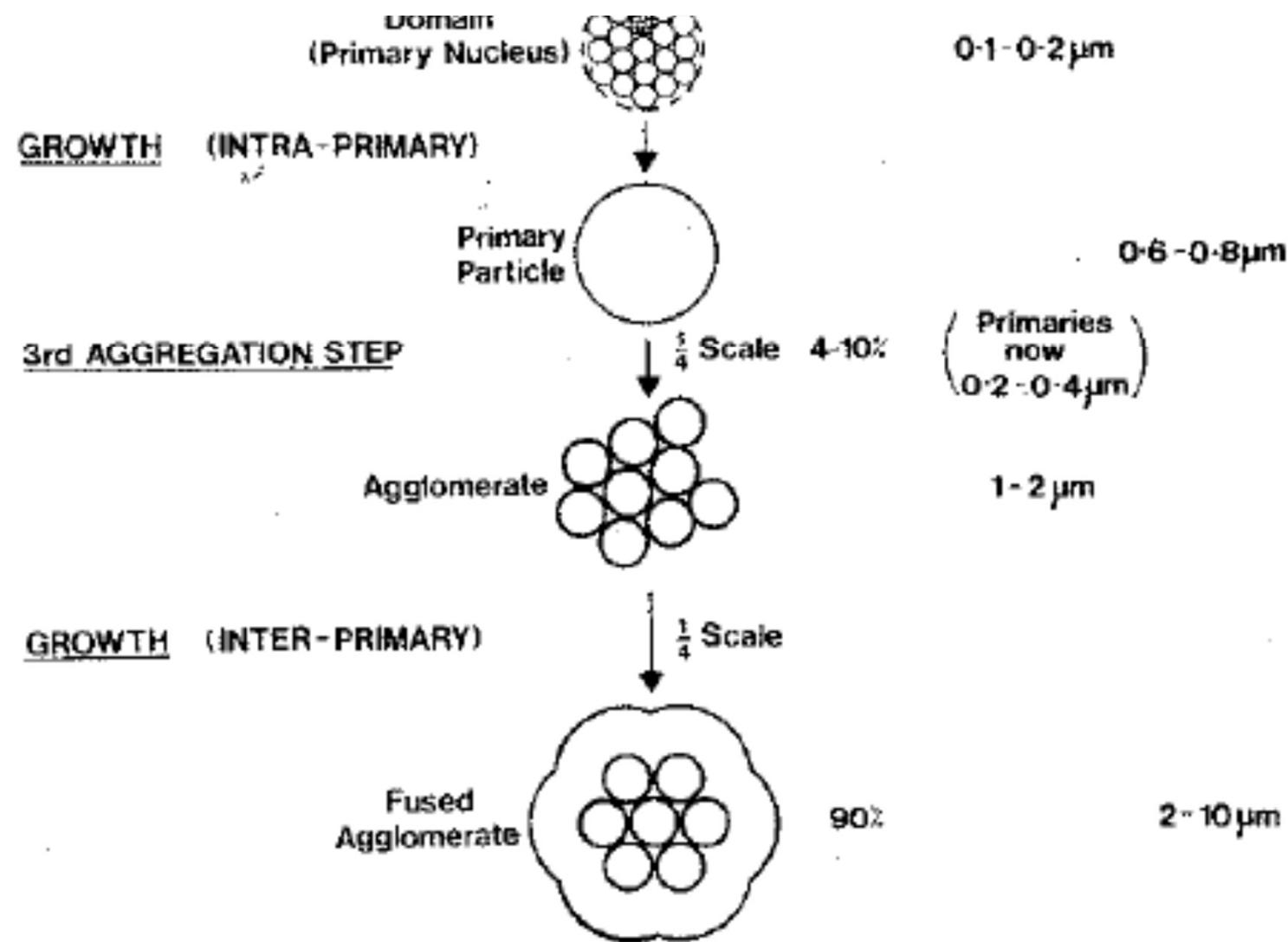


FIG. 7.27. Schematic representation of the mechanism of VCM polymerisation.

The Hierarchical Structure of Poly(Vinyl Chloride) when Suspension Polymerized

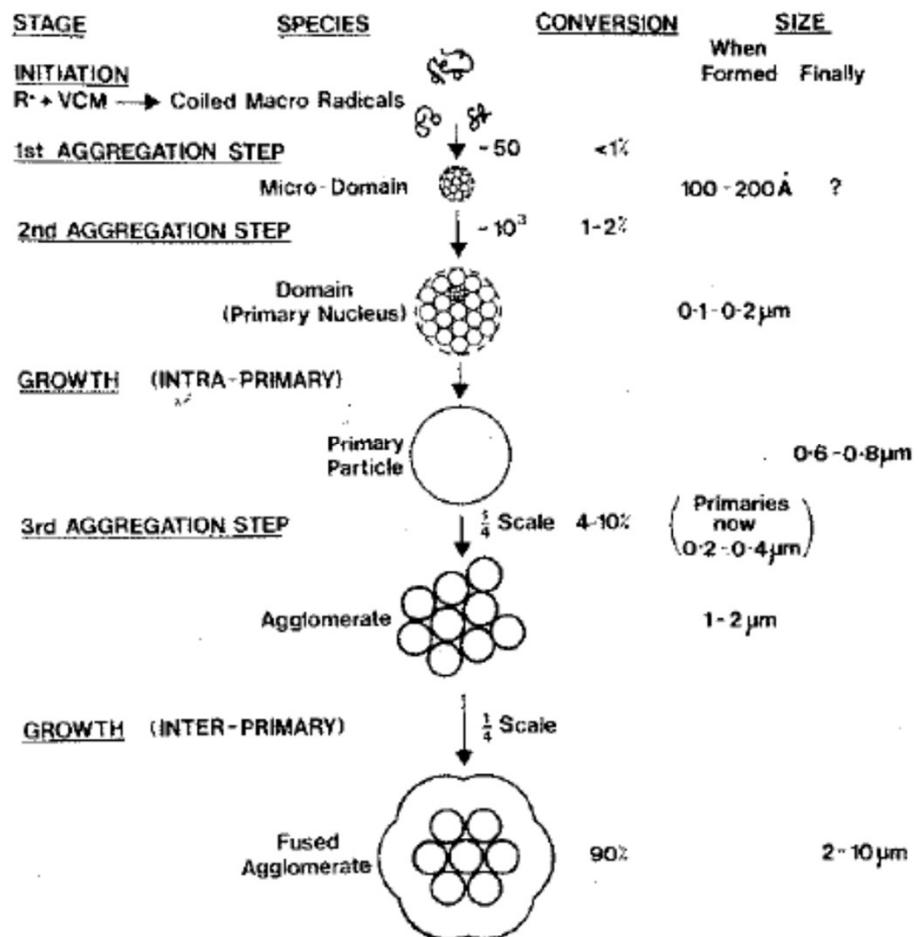
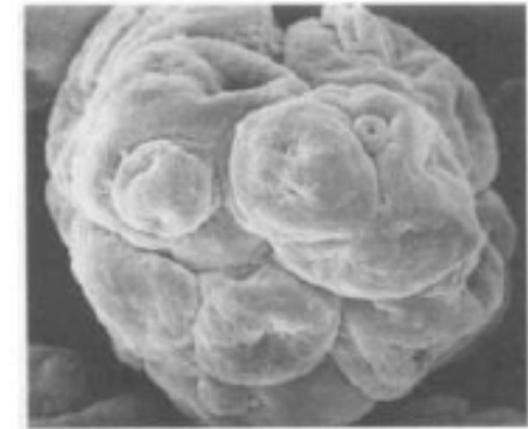


FIG. 7.27. Schematic representation of the mechanism of VCM polymerisation.

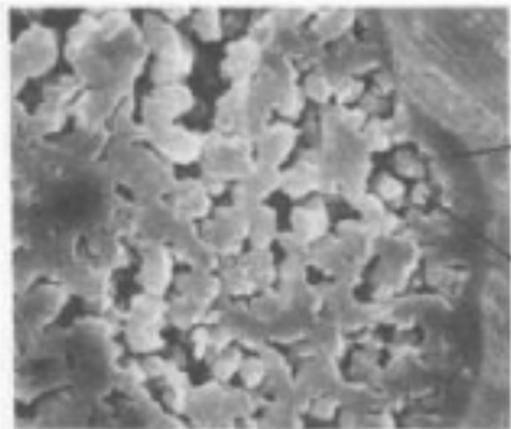
Downward Temp of PVC is T_g
 → Classified as amorphous like PS

Micrographs and Schematic of the Grain Structure of PVC

Summers, James W., J. Vinyl & Add. Tech., Vol 3(2) 130-139, 1997



Grain: 150 um dia.



Skin: 2 – 5 um thick

Primary Particles: 1 um dia.
*Can see hierarchical
Structure here*

Fig . 5 A PVC suspension grain showing the formation from monomer droplets and a cross section showing the skin and primary particles.

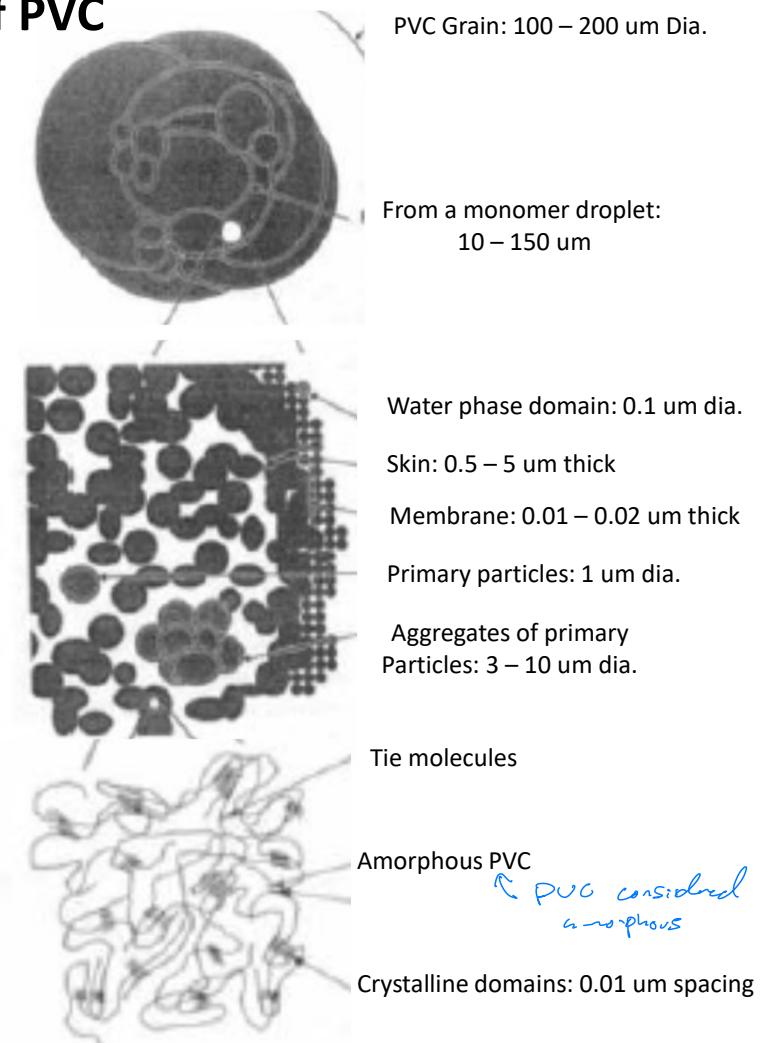
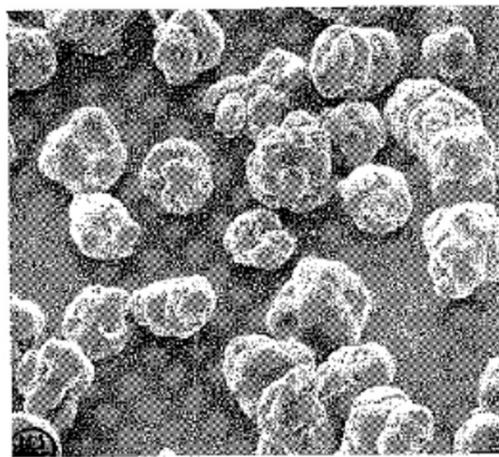


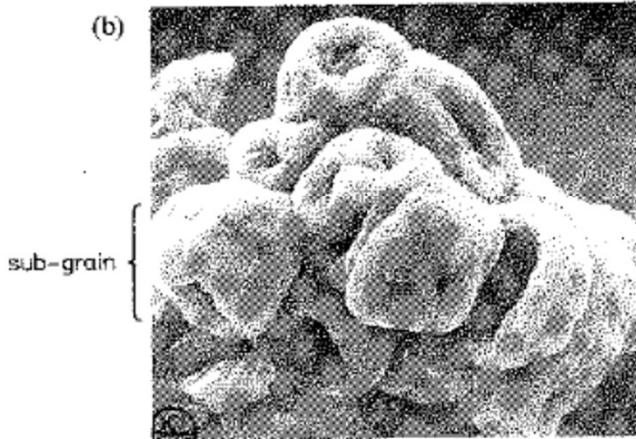
Fig. 6 The hierarchical structure of PVC

(a)

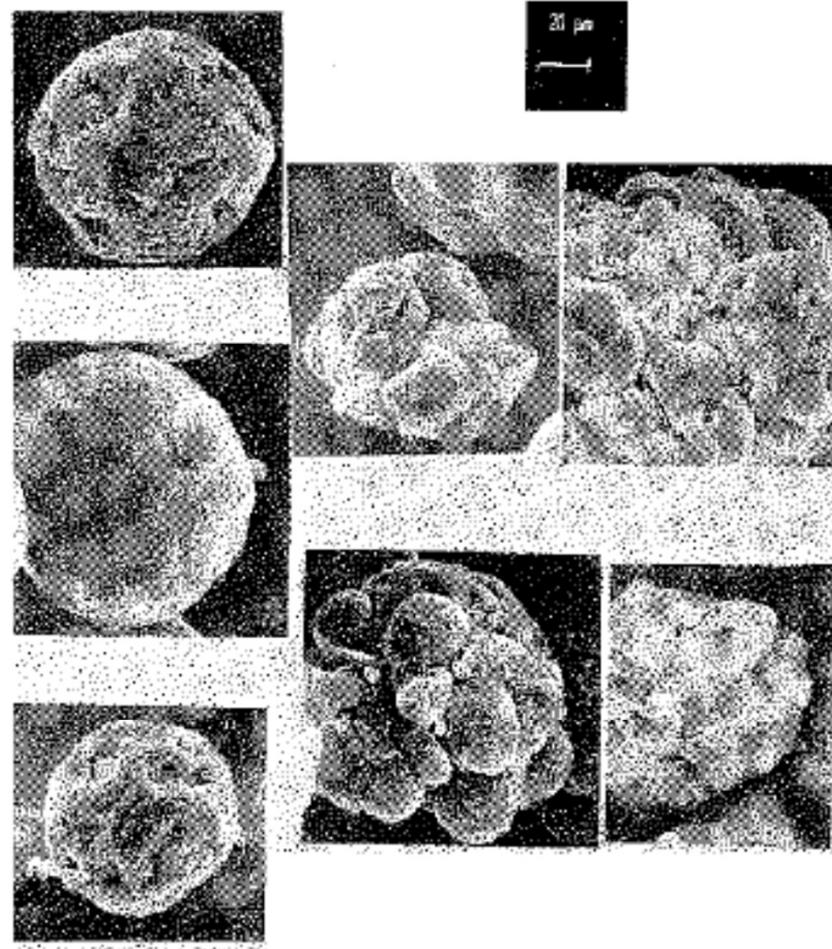


100 μm

(b)

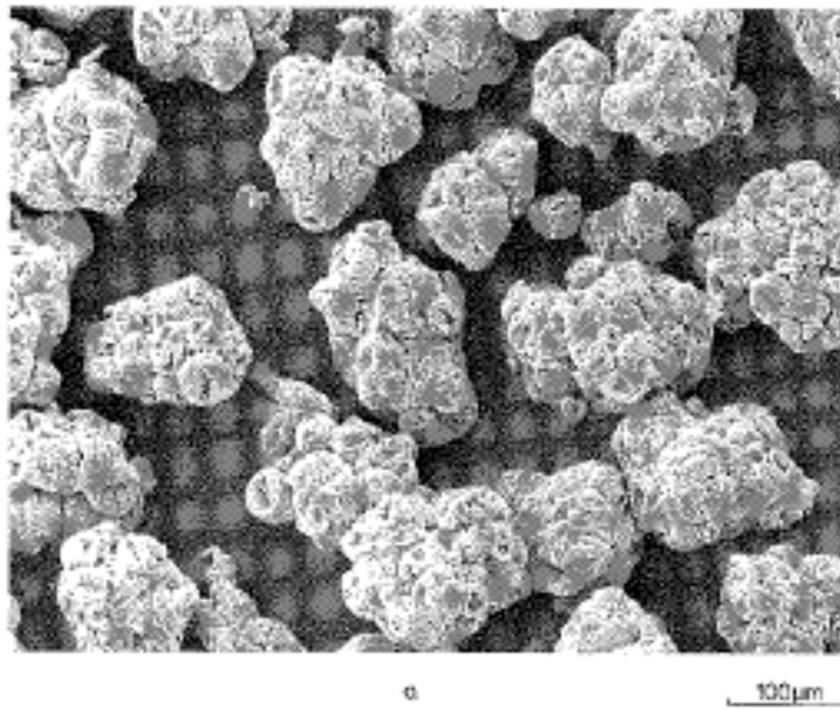


20 μm



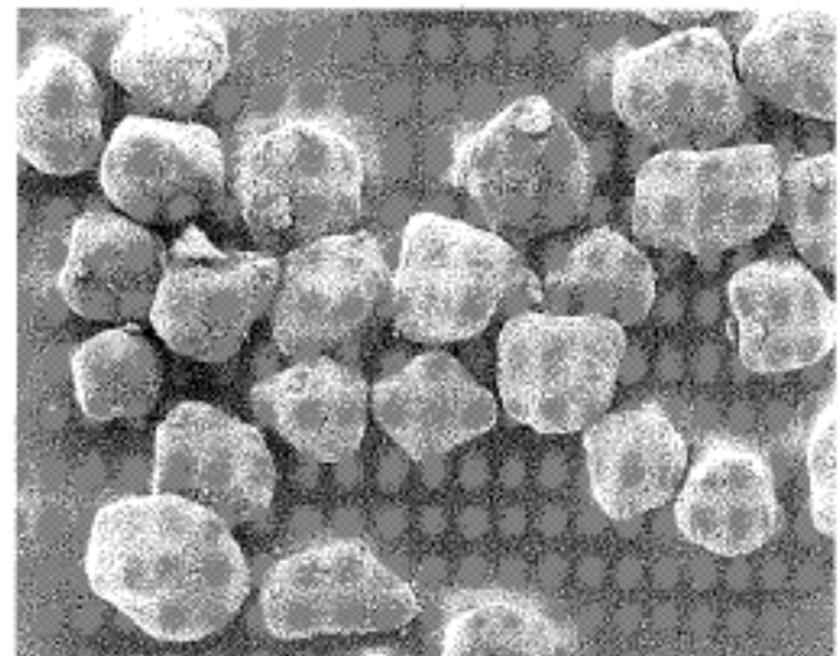
20 μm

Comparison of Suspension and Bulk Polymerized PVC



Suspension Polymerized

Aggregates of primary particles
as they grow



→ Not used today
Bulk Polymerized

Tries to prevent aggregation

Table 4. Quick Reference for Commercial PVC Molecular Weights.

Inherent Viscosity ASTM D1234	K Value 1% in Cyclohexanone	Number Average Molecular Weight $M_n (\times 10^{-3})$	Weight Average Molecular Weight $M_w (\times 10^{-3})$
0.42	45	15.0	30.0
0.47	48	18.0	36.0
0.52	50	20.0	40.0
0.57	53	22.5	45.0
0.62	55	25.0	50.0
0.67	57	27.5	55.0
0.73	59	30.5	61.0
0.78	61	33.0	67.0
0.83	63	36.0	72.0
0.88	65	38.5	78.0
0.92	67	41.0	82.5
0.98	69	44.0	89.5
1.03	70	47.0	95.0
1.08	72	50.0	101.0
1.13	74	52.5	107.5
1.21	76	57.0	117.0
1.30	79	62.5	128.5
1.40	82	68.5	141.0
1.60	87	81.0	166.0
1.80	92	93.5	195.0

Different Nomenclature Exists
for Describing the Molecular Weight
of Poly(Vinyl Chloride)

IV

K -Value

M_n

M_w

M_z } over 2
 M_{z+1} } distribution

PDI
 $M_w \approx 2 M_n$
 for all
 due to
 specific
 conditions

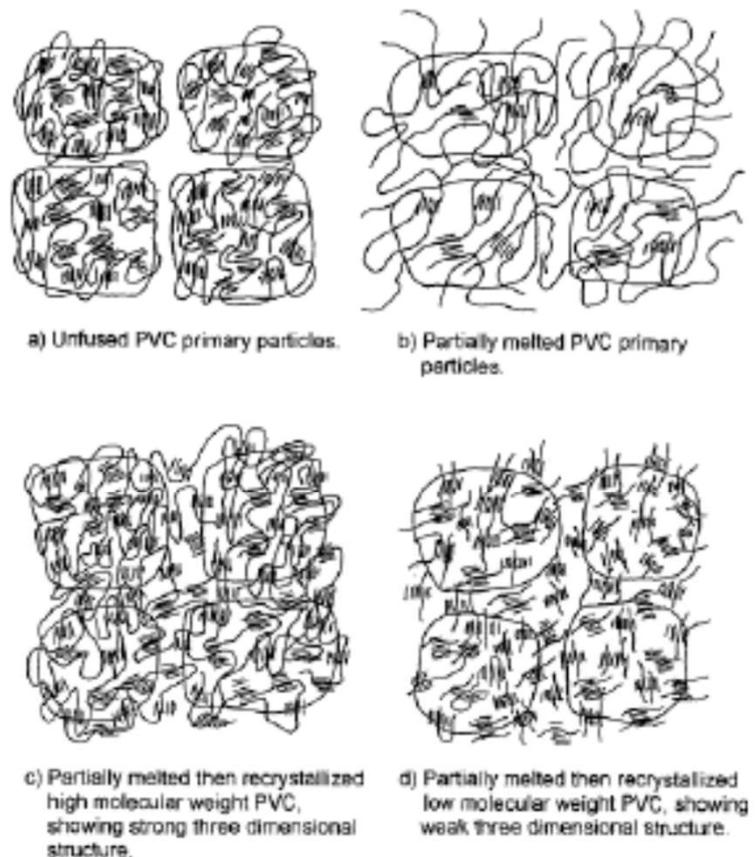
Basis for the Difficulty in Processing PVC

Must overcome primary particle memory
by heat and melt mixing during processing.

Fig. 12. Model for PVC fusion, accounting for molecular weight effects and processing temperature effects.

Initially PVC had Little or No End-Use Application

Poor contact
 \Rightarrow drop
in impact



Summers, James. W., J. Vinyl & Add. Tech.,
Volume 3(2), 130 – 139 (1997).

Patented Oct. 10, 1933

1,929,453

UNITED STATES PATENT OFFICE

1,929,453

SYNTHETIC RUBBER-LIKE COMPOSITION AND METHOD OF MAKING SAME

**Waldo L. Semon, Silver Lake Village, Ohio, as-
signor to The B. F. Goodrich Company, New
York, N. Y., a corporation of New York**

I claim:

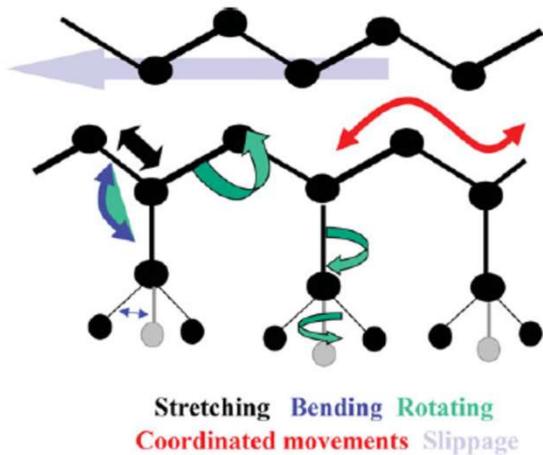
1. The method of manufacturing a resilient rubber-like composition, which comprises dissolving an insoluble polymerized vinyl halide at an elevated temperature in a composition which will dissolve the polymerized vinyl halide only at temperatures considerably above room temperature, in such proportions as to form a stiff, resilient position to gel by cooling it.

Waldo Semon Plasticized PVC

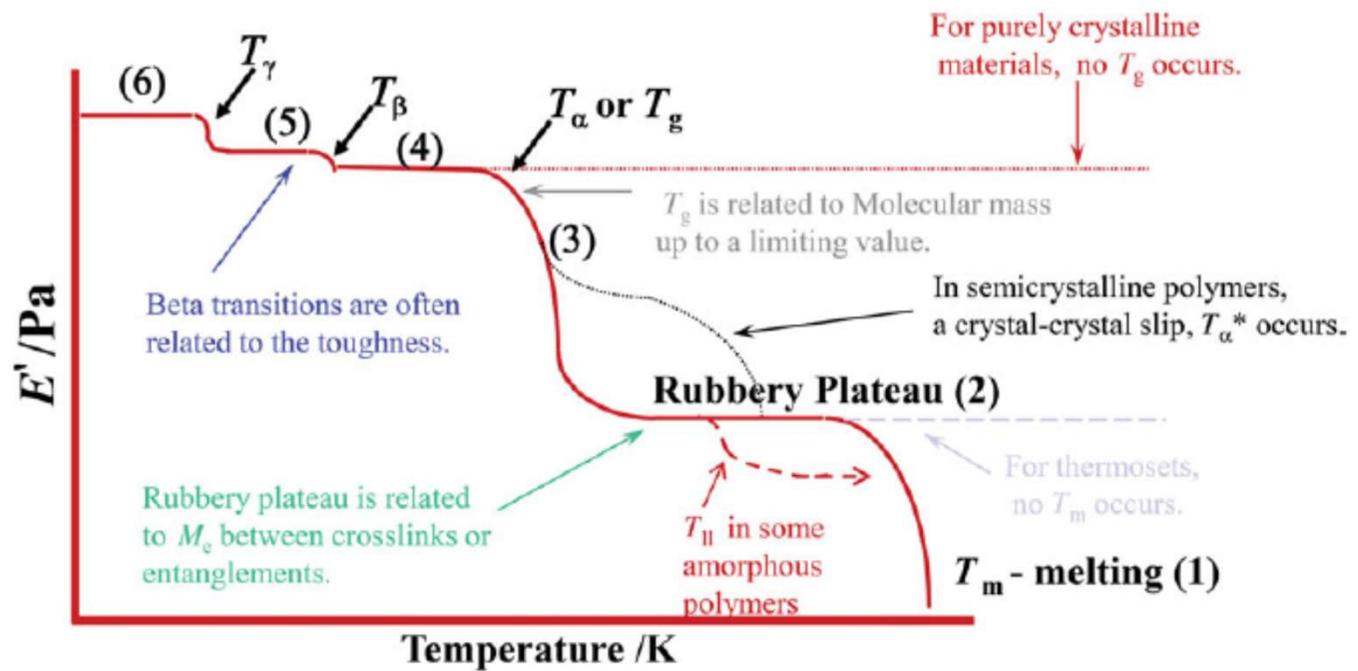


Assigned at Goodrich to develop methods for prolonging the integrity of rubber, Semon's curiosity led him to conduct experiments with vinyl polymers, then considered a waste product in the industrial production of rubber. He discovered that by mixing PVC powder in a solvent and heating it, he could produce a malleable gel that would retain its shape when cooled. With capital in short supply after the stock market crash of 1929, there was little enthusiasm for investing in Semon's PVC compound at the company, whose principal product was tires. Semon nonetheless persisted in exploring the compound, perfecting practical applications suited to its qualities. Waterproof, fire-resistant, and nonconductive, "vinyl," as it eventually became known to the public, proved an inexpensive, functional fabric for umbrellas, raincoats, shoe heels, shower curtains, automobile seats, and dozens of other commonly used objects. Semon patented the process in 1933--it is one of 116 U.S. patents.

Thermal Transitions in Amorphous Polymers



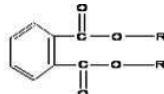
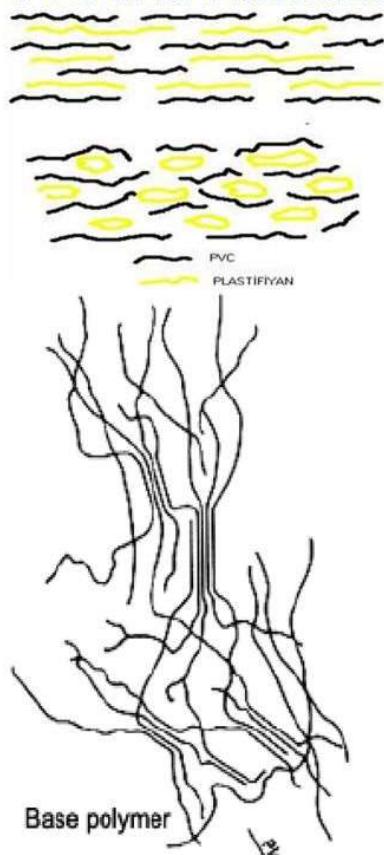
The Crankshaft Model of
Polymer Molecular Motions



(6)	(5)	(4)	(3)	(2)	(1)
Local motions and stretch	Bend	Side groups	Gradual main chain	Large-scale chain	Chain slippage

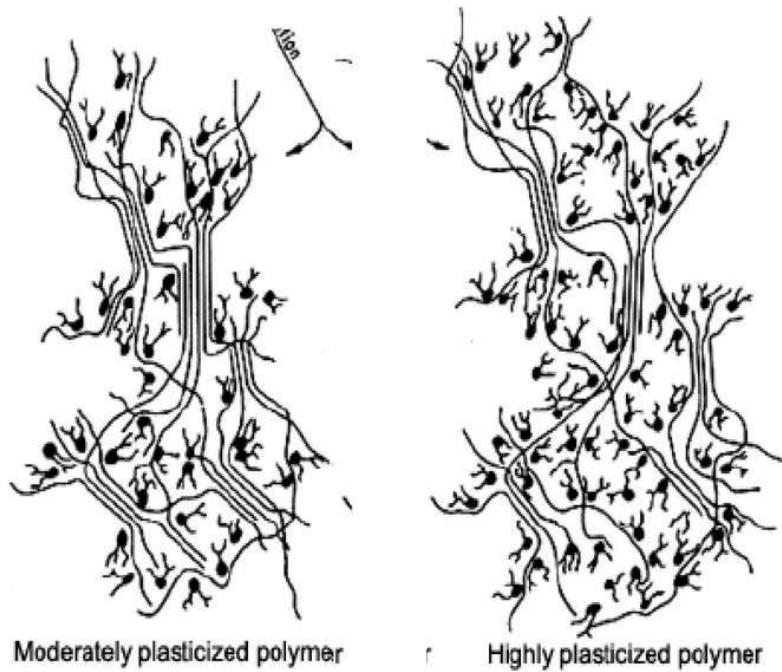
Fundamental Function of a Plasticizer

PVC and Plasticizers



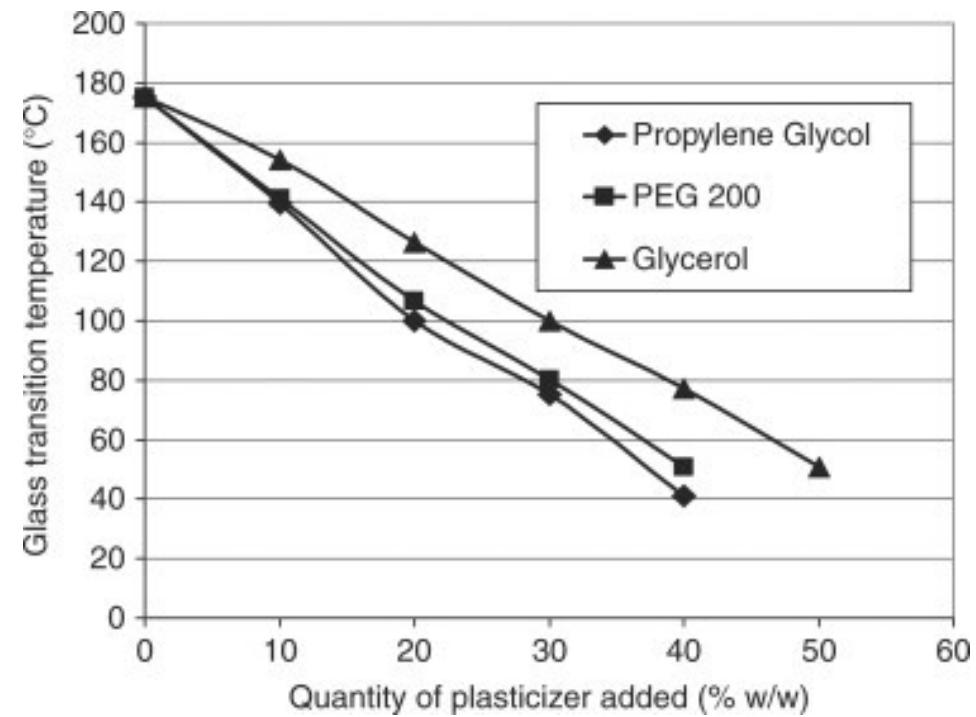
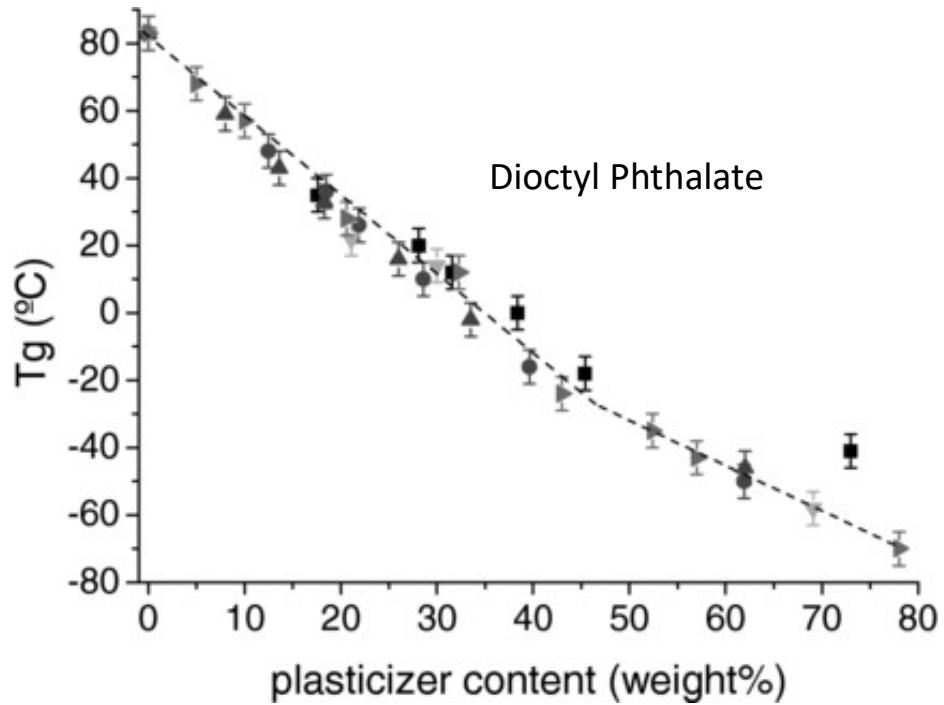
Chemical Formula of DOTP, DIDP, DINP,
and DOP.

*Orthophthalates: R'=alcohol; for DOP R'=2-ethyl
hexanol; for DIDP R'=isodecyl alcohol; for DINP
R'=isononyl alcohol*

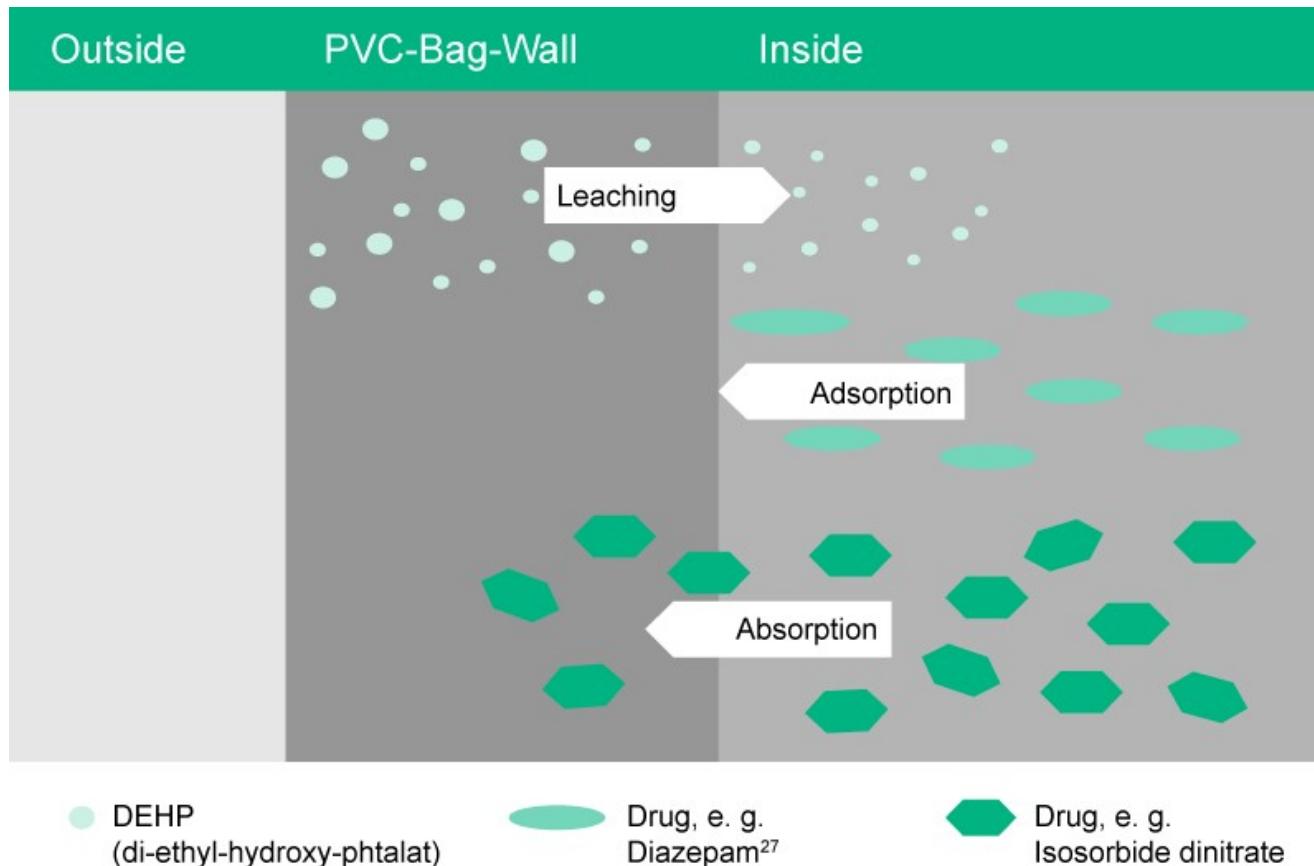


Plasticizers usually possess long alkyl chains which have the effect of screening the long polymer chains from each other, thereby, preventing them from reforming the chain-chain interactions which gives the unplasticized polymer its rigidity.

Influence of the Plasticizer Concentration on T_g



Be Aware of the Mechanism of Plasticizer Leaching



Certain Phthalates are Known to have Health Effects

Plastic dolls from Disney's smash hit *Frozen* franchise are being recalled over safety fears.

The Elsa and Anna dolls are said to contain potentially toxic materials which could harm children's reproductive systems and livers.

"The plastic material of the dolls contains an excessive amount of bis(2-ethylhexyl) phthalate (DEHP), di-'isononyl' phthalate (DINP) and dibutyl phthalate (DBP) (measured values up to 1% by weight, 1% by weight and 0.15% by weight respectively).

It said the products were made in outside the US and were most commonly sold online.

- Carcinogen
- Mutagen
- Teratogen
- Endocrine Disruptor



Health Effects Influence

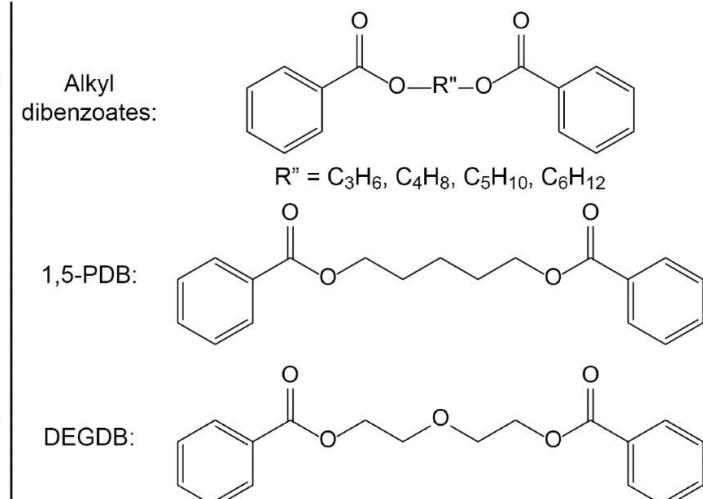
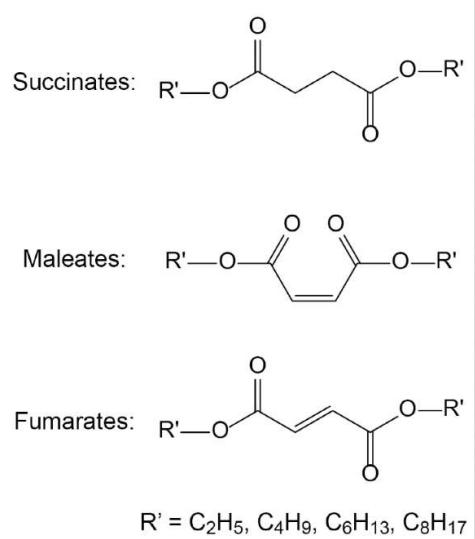
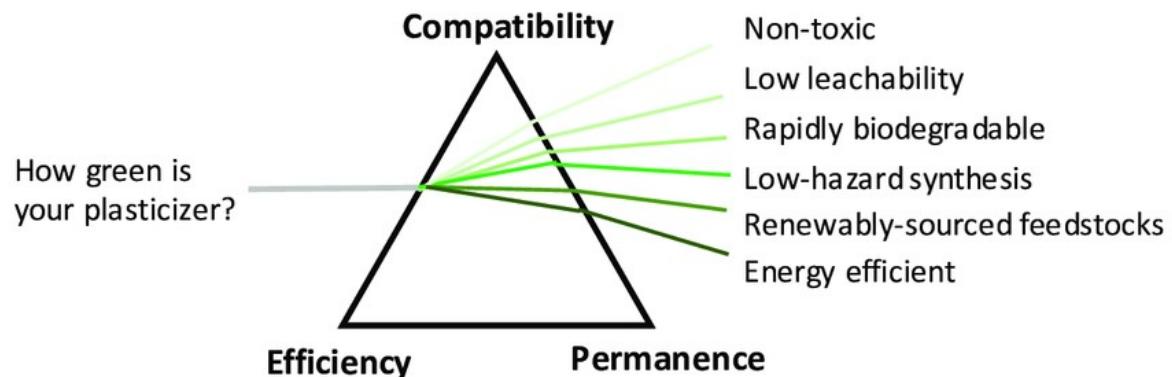
A **carcinogen** is any substance, radionuclide, or radiation that promotes carcinogenesis, the formation of cancer. This may be due to the ability to damage the genome or to the disruption of cellular metabolic processes.

Teratogen: Any agent that can disturb the development of an embryo or fetus. *Teratogens* may cause a birth defect in the child. Or a *teratogen* may halt the pregnancy outright. The classes of *teratogens* include radiation, maternal infections, chemicals, and drugs.

In genetics, a **mutagen** is a physical or chemical agent that changes the genetic material, usually DNA, of an organism and thus increases the frequency of mutations above the natural background level.

Endocrine disruptors are chemicals that can interfere with **endocrine** (or hormonal) systems at certain doses. These disruptions can cause cancerous tumors, birth defects, and other developmental disorders. Any system in the body controlled by hormones can be derailed by hormone **disruptors**.

A New Generation of Plasticizers for Poly(Vinyl Chloride)



Since Certain Plasticizers May Migrate, Be Careful when Using these Materials in Analytical Testing

This **plastic tubing** is made of **Tygon** formulation E-3603 polyvinyl chloride (**PVC**) and is for use with peristaltic and vacuum pumps in lab applications. ... This **plastic tubing** is rated as very flexible as it bends more easily than flexible or rigid **tubing**.



Certain Products Relative to Plasticizer Level

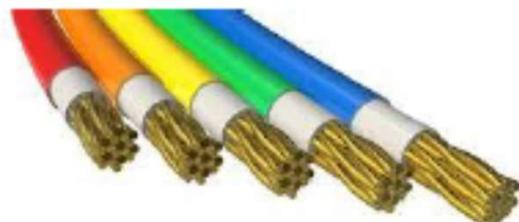
DINP = Di-isobutyl Phthalate

Table 5.3 Typical Properties of General Purpose Vinyl Plastic Products

	Rigid	Semirigid	Flexible	Very flexible	Extremely flexible
DINP, phr	0	34	50	80	600
Wt% of composition	0	25	33	44	86
<i>Typical properties</i>					
Specific gravity, 20/20 °C	1.40	1.26	1.22	1.17	1.02
Hardness Durometer A, 15 s	—	94	84	66	< 10
Flexural stiffness ^a at 23 °C					
MPa	> 900	69	12	3.4	—
psi	> 130,000	10,000	1,700	500	—
Tensile strength ^b					
MPa	> 41	31	21	14	—
psi	> 6,000	4,500	3,100	2,000	—
Elongation (%) ^b	< 15	225	295	400	—
Brittleness ^c					
°C	> 23	-16	-32	-47	—
°F	> 73	+3	-26	-53	—
<i>Examples</i>					
	Bottles, pipe, siding, records	Shades, shoe heels, thin films, produce wrap	Wall-cover- ing, book- binders, produce upholstery, garden hose	Boots, gloves, water beds	Fishing lures

Do not drink out of garden hose - plasticizers

Examples of Plasticized PVC Products



Plasticization was first
tried to make use of PVC
but came at health costs

Other than Plasticizing Poly(Vinyl Chloride) was Still an Unusable Material

Frazier Groff – Charleston, West Virginia - 1933

"By experimentation I have discovered that a preferred type of vinyl resins are those resulting from the conjoint polymerization (by which is meant polymerization of two or more compounds while in mutual contact of a vinyl halide, such as vinyl chloride, and an oxygen-containing vinyl compound, by which is meant particularly the vinyl esters of aliphatic acids, of which ester vinyl acetate is typical. The proportion of these substances in the original monomeric mixture is a controlling factor upon the resin produced. I prefer to use more than about 70% by weight of the vinyl halide and 30% or less by weight of the vinyl ester of an aliphatic acid."

"The resin must further possess a high fusion point, low solubility, and it must be tough and uniform in regard to all of these properties."

Example I

100 parts of vinyl resin
60 parts of ground barytes*
40 parts of rottenstone**
1 part of carnauba wax
1 part of calcium stearate
1 part of lime

* barite – predominantly barite sulfate

** rottenstone – weathered siliceous limestone used as a powder

Reactivity Ratios for Free Radical Polymerization (Vinyl Chloride and Vinyl Acetate)

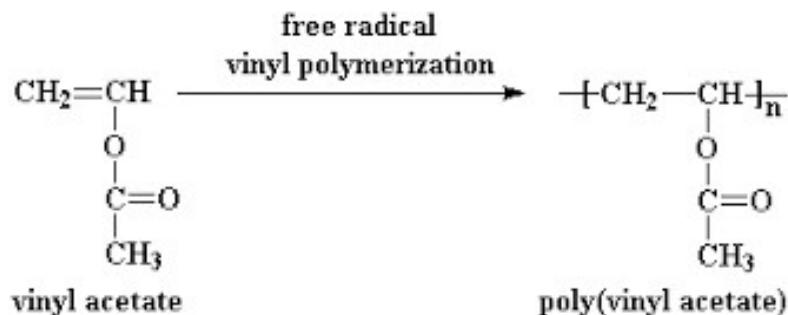
Products of Monomer Reactivity Ratios in Copolymerization

Copolymer Composition (r ₁ , r ₂)								
Monomer	r ₁	r ₂	Copolymer	r ₁	r ₂	Copolymer	r ₁	r ₂
Butadiene								
1.0			Styrene					
0.71	0.55		Vinyl Acetate					
0.30	0.34	0.39	Vinyl Chloride					
0.19	0.24	0.30	1.0	Methyl Methacrylate				
0.10	0.16	0.12	0.96	0.61	Vinylidene Chloride			
0.04	0.14	0.90	0.75	0.96	0.80	Methyl Acrylate		
0.02	0.02	0.25	0.13	0.24	0.34	0.84	Acrylonitrile	

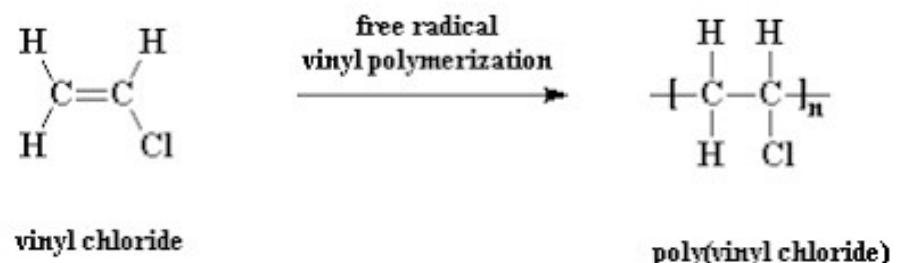
$$r_1 * r_2 = 0.39 < 1 \Rightarrow \text{Alternating Copolymer}$$

Copolymerization of Vinyl Chloride and Vinyl Acetate

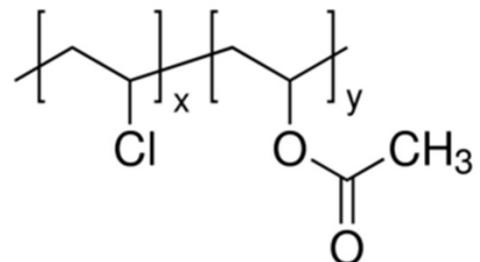
Vinyl Acetate Monomer and Homopolymer



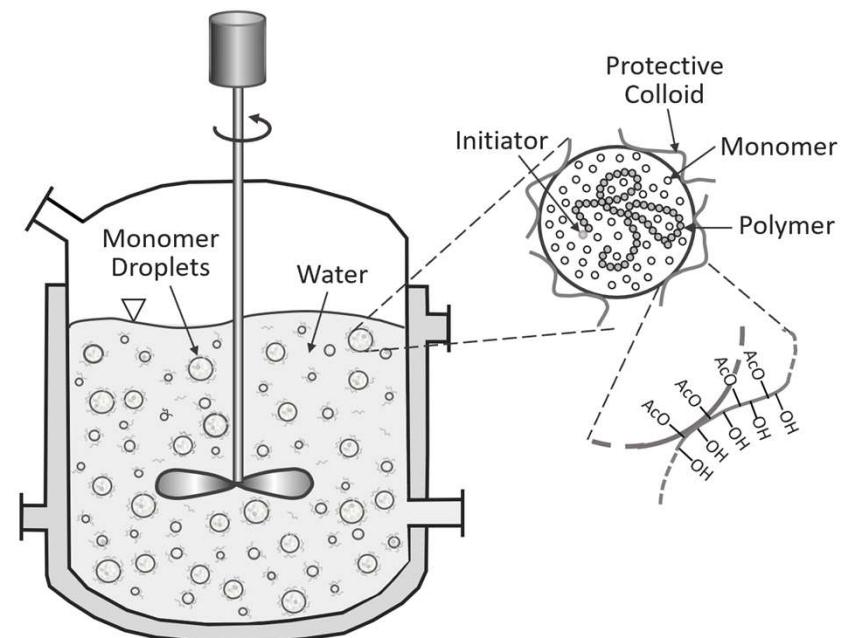
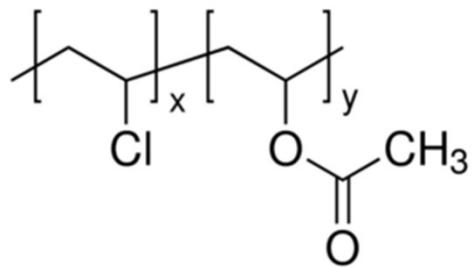
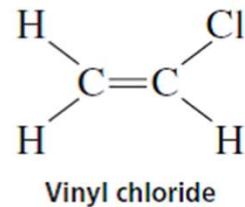
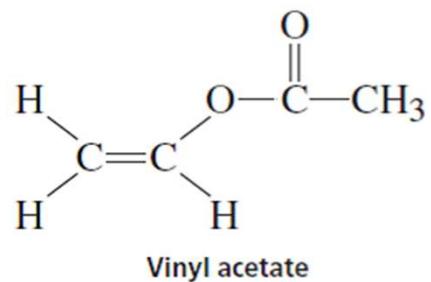
Vinyl Chloride Monomer and Homopolymer



Poly (Vinyl Chloride-co-Vinyl Acetate) Copolymer



Suspension Polymerization is the Common Process for Producing Poly(Vinyl Chloride-co-Vinyl Acetate)



Patented: October 31, 1933

US 1,932,889

United States Patent Office

US 1,932,889

RECORD

**Frazier Groff, Charleston, W. Va., assignor to
Carbide and Carbon Chemicals Corporation, a
Corporation of New York**

**Do Drawing. Application August 10, 1931
Serial No. 556,299**

I claim: -

1. A record having a reproducing surface formed from a composition containing a vinyl resin identical with that resulting from the conjoint polymerization of a vinyl halide and a vinyl ester of an aliphatic acid in the proportions of at least 70% of the vinyl halide and which is less than about 30% soluble in toluene at 20 deg to 30 deg C, said record being characterized by a low surface noise level, resistance to needle wear, slight wear on the needle, toughness, and water resistance.

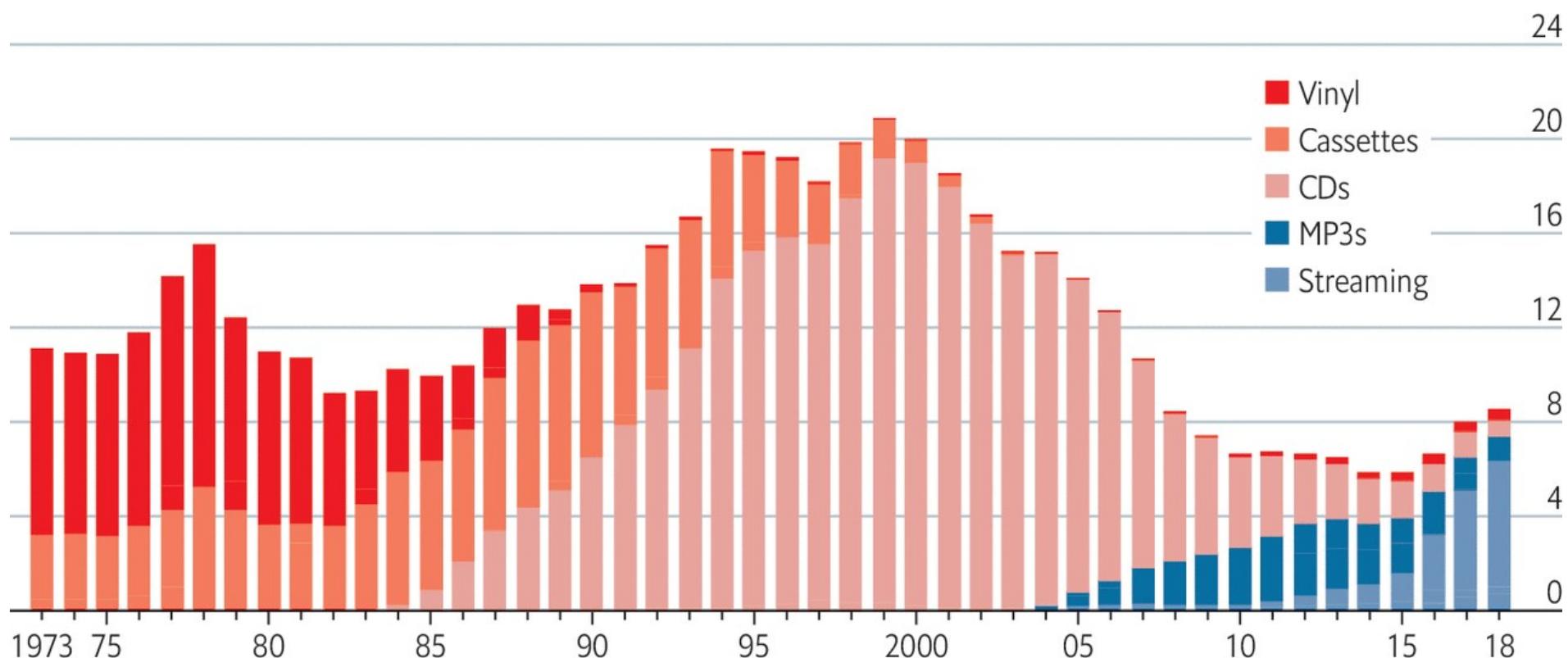


History of Voice Reproduction

- 1878 – Edison's First Recorder Patent
- 1887 – Berliner's First Patent
- 1895 – Berliner's Record Patent
- 1925 – Last Edison Cylinder Record Produced
- 1933 – First PVC (vinyl) Record Patent
- 1978 – Peak of Vinyl Record Production
- 1982 – End of 8-Track Era
- 2002 – End of Cassette Era
- 2018 – Best Buy Stopped Selling CD's
- 2020 – Vinyl Records Expected to Outsell CD's

Track records

United States, recorded-music revenues by format, 2018 \$bn



Source: Recording Industry Association of America

The Economist

Vinyl Records Outsell CDs for First Time Since 1987

Music lovers in the United States bought 41 million vinyl albums
and 33 million CDs in 2022

by Sarah Kuta, Smithsonian Magazine, March 16, 2023

In 2022, listeners purchased 41 million vinyl records, compared to just 33 million CDs.

Vinyl sales grew by 17 percent last year, bringing in \$1.2 billion in revenue. CDs made \$483 million, a drop of 18 percent.

Even so, both records and CDs made up only a small fraction of the music industry's revenue in 2022. **The majority—roughly 84 percent—came from streaming services, per the RIAA.**

There are Nontraditional Uses for Vinyl Records



Poly(Vinyl Chloride) is Highly Sensitive to Thermal Degradation

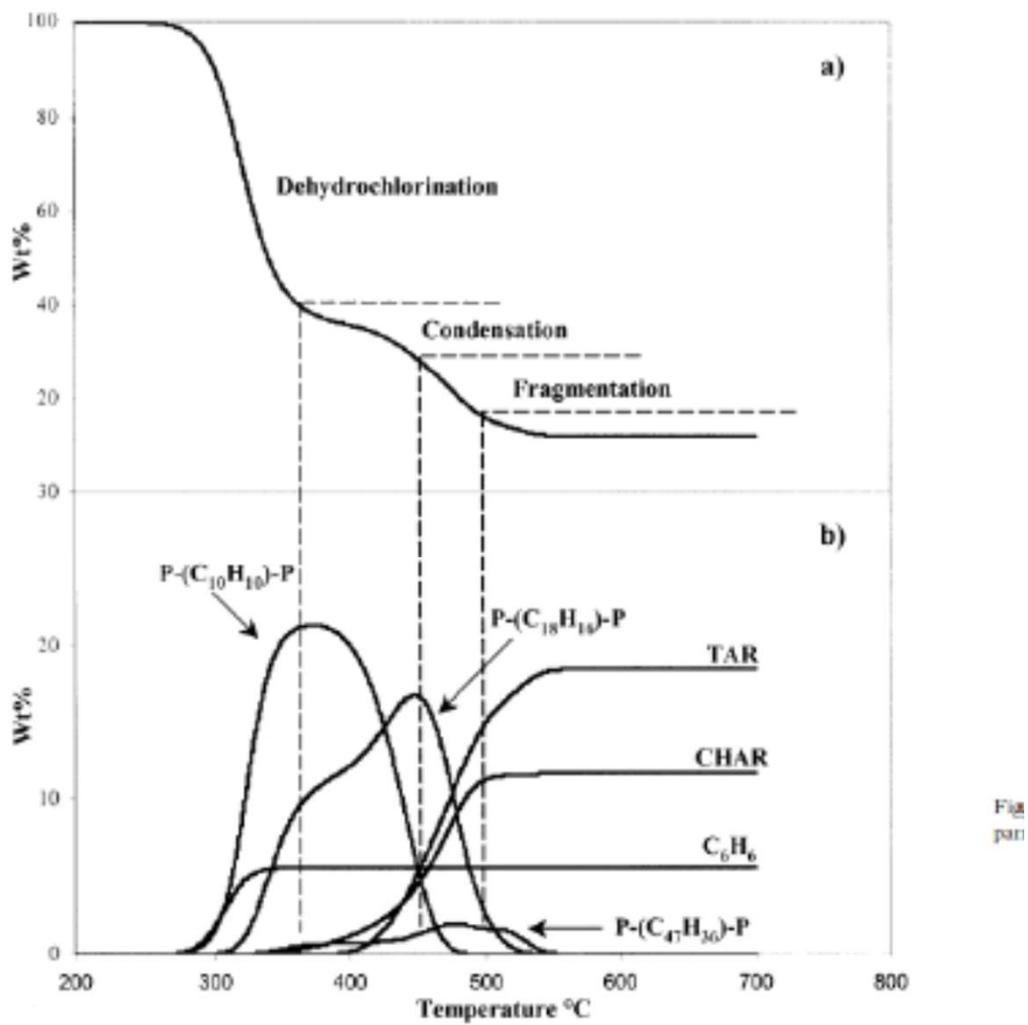


Fig. 1. Predicted dynamic TGA with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$; panel (a) residue (wt.%) behavior and identification of the main thermal decomposition phases panel (b) benzene, PAH and char formation profiles. The TAR fraction represents the total amount of volatile aromatics.

Lesson 6: The Vinyl Chloride Family

Questions?



Dr. Andy Olah, amo5@case.edu, O: 216-368-0606, C: 216-272-0505

We all get heavier as we get older . . . because there's a lot more information in our heads.

That's my story and I'm sticking to it.

EMAC 276

Lesson 7: The Vinyl Chloride Family; PVC, Part 2

Poly(Vinyl Chloride) - PVC

Polyvinyldine Chloride - PVDC

Chlorinated Poly(Vinyl Chloride) – CPVC

Poly (1,2 Dichloroethylene)

Andy Olah, Ph.D.

January 31, 2025

There will be a quiz on Monday, February 10th



* From the Hitchhikers Guide to the Galaxy – Douglas Adams

EMAC 276 - Homework Assignment #2

Due: Friday, February 14, 2025

Dr. Olah

During our classes we identified several common polymers that when initially discovered were described as “value-less”, “impossible to process”, “a useless mass”, etc. We also identified several methods (“tricks”) that were subsequently utilized to develop these polymers into successful products; many which are still with us today.

Your exercise is to select one polymer (either from our in-class discussion or from outside our class discussion) and describe 1) the polymer and the initial performance deficiency, 2) the action taken to overcome this deficiency, and, 3) the ensuing product(s) developed from this modification.

If you choose to use an “in class” example your maximum score will be 10.

If you choose to use an “outside the class” example your maximum score will be 12. (i.e., final score +2)

Your answer shall be short comprising between one-half to one page.

Your answer is shall be structured accordingly:

Paragraph #1: Identify and describe the polymer and it's initial deficiency **(3 Points)**

Paragraph #2: Identify the modification or “trick” which was utilized to overcome this deficiency. **(5 Points)**

Paragraph #3: Identify the commercial product or products resulting from this modification. **(2 Points)**

Poly(Vinyl Chloride) is Highly Sensitive to Thermal Degradation

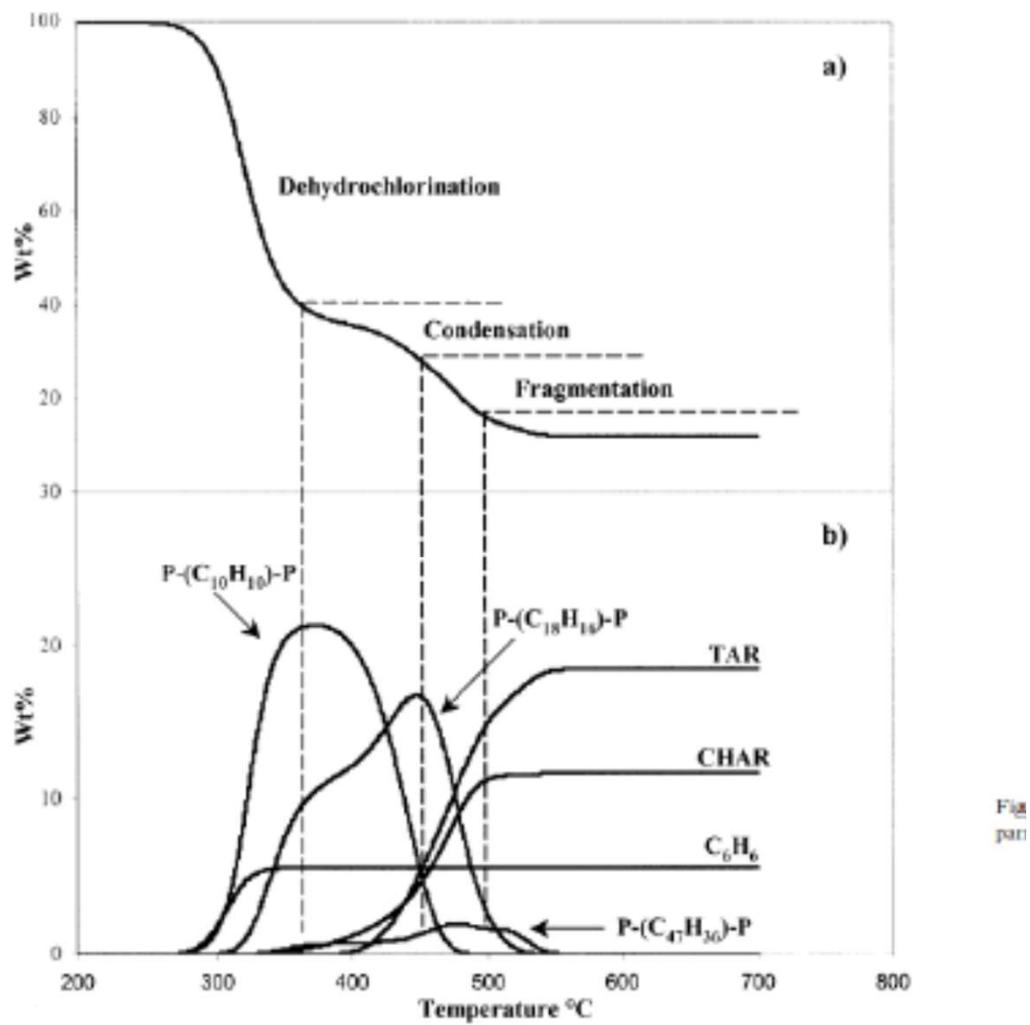
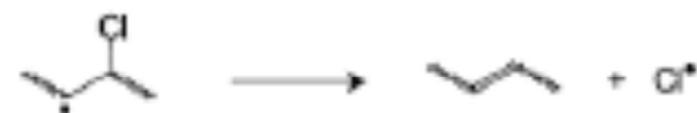


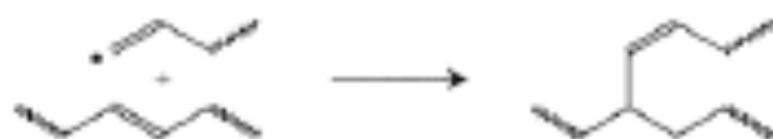
Fig. 1. Predicted dynamic TGA with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$; panel (a) residue (wt.%) behavior and identification of the main thermal decomposition phases panel (b) benzene, PAH and char formation profiles. The TAR fraction represents the total amount of volatile aromatics.

a) Dehydrochlorination



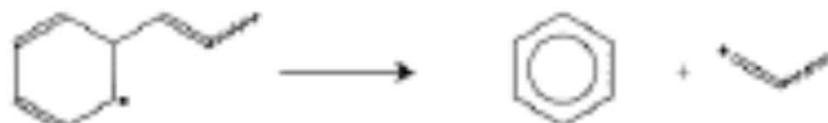
Dehydrochlorination

b) Condensation



Condensation

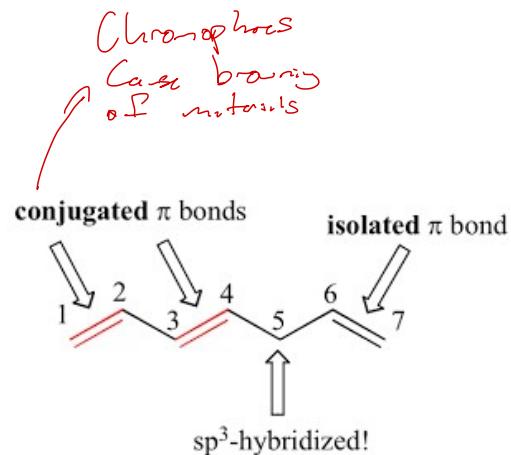
c) De-alkylation



De-alkylation

Fig. 2. Sketched mechanisms of the main radical chain propagation steps: panel (a) dehydrochlorination; panel (b) condensation; panel (c) de-alkylation.

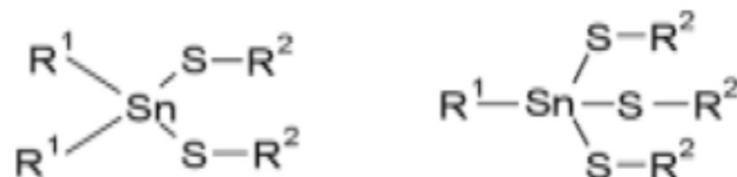
Discoloration Arising from an Increase in Conjugated Double Bonds



No.	Different PVC formulations ^c		Degradation time at 180 °C (min)									
	Ca/Na/Zn-AMMA	CaSt ₂ /ZnSt ₂	0	5	15	25	35	45	55	65	75	120
No.13	0 g	0 g										
No.14	3 g	0 g										
No.15	2 g	0 g										
No.16	1 g	0 g										
No.17	0 g	3 g										
No.18	0 g	2 g										
No.19	0 g	1 g										

^cVarious quantities Ca/Na/Zn-AMMA were added to 100 g PVC/50 g DOTP. The mass ratio of Ca-AMMA : Na-AMMA : Zn-AMMA is 45 : 3 : 2(g : g : g). The mass ratio of CaSt₂ : ZnSt₂ is 4:1(g : g).

The Most Common Stabilizers for Poly(Vinyl Chloride) are Organo-Tin Based

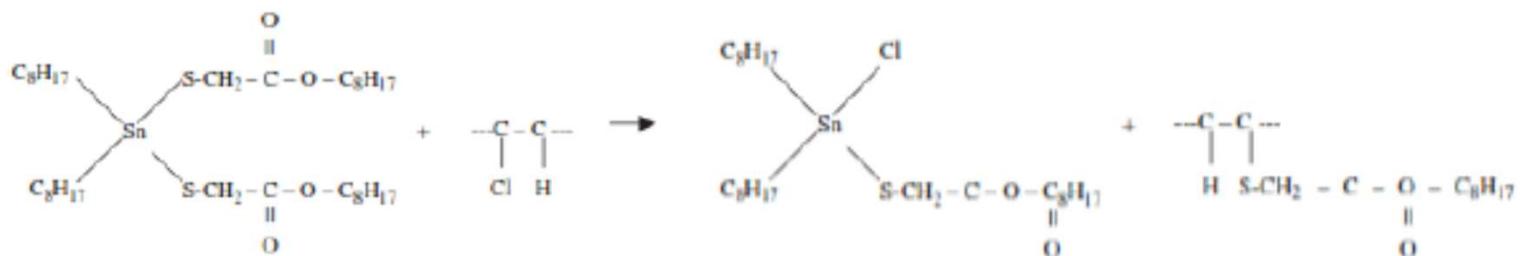


Sn- R¹ S- R²

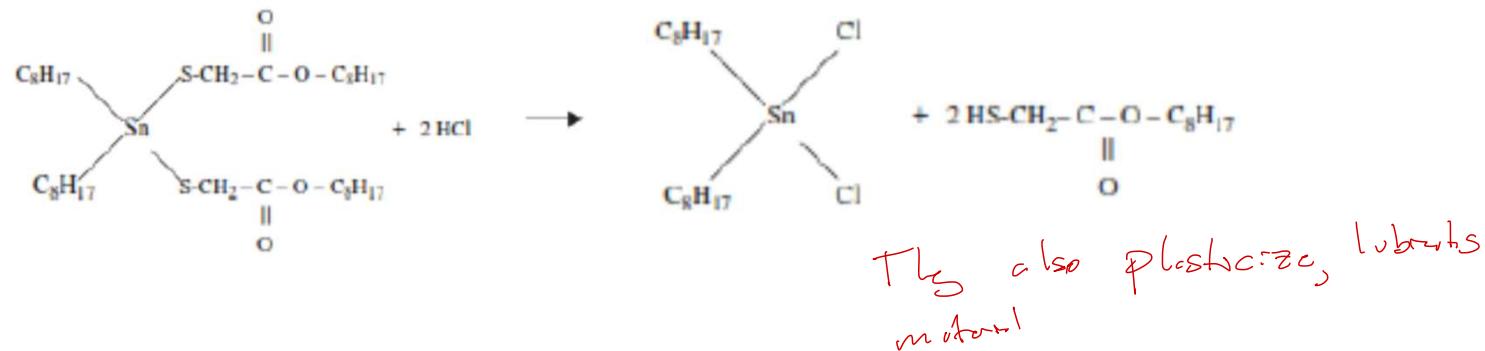
CH ₃ -/	Methyltin -S-CH ₂ -CO-O-alkyl	thioglycolates (alkyl is mostly ethylhexyl or iso-octyl)
n-C ₄ H ₉ -	Butyltin -S-CH ₂ -CH ₂ -CO-O-alkyl	mercaptopropionates
n-C ₈ H ₁₇ -	Octyltin -S-CH ₂ -CH ₂ -O- CO alkyl -S-alkyl -S-	mercaptoethanol esters (so-called reverse esters) alkylmercaptides sulfides

Tin Stabilizers are Unique Since they Perform Multiple Functions

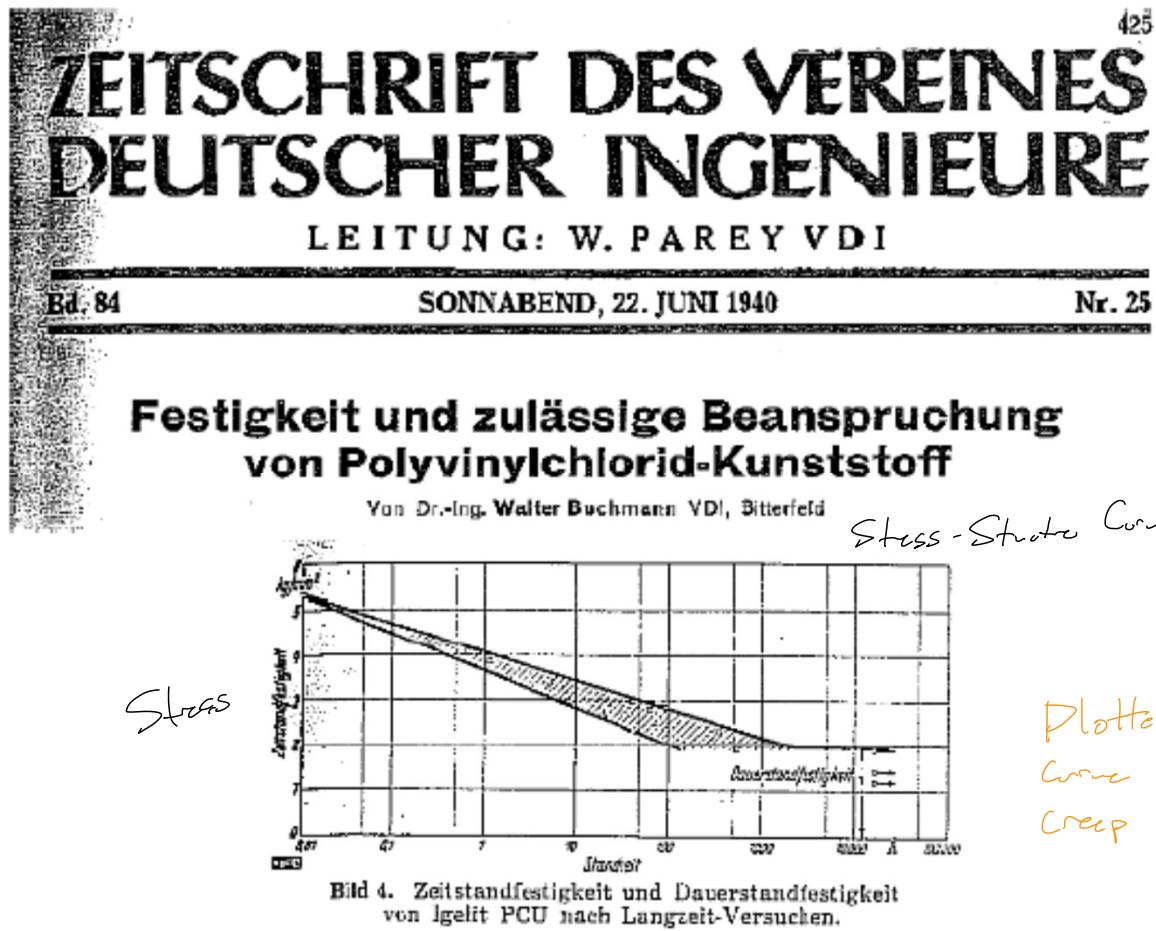
1. Labile chlorine atoms are substituted by S atoms and conjugated double bond formation is prevented:



2. HCl which is evolved as a result of PVC degradation and speeds up the conjugated double bond formation, enters into the reaction by scavenging.



Development of Rigid PVC Pipe and Fitting Compounds



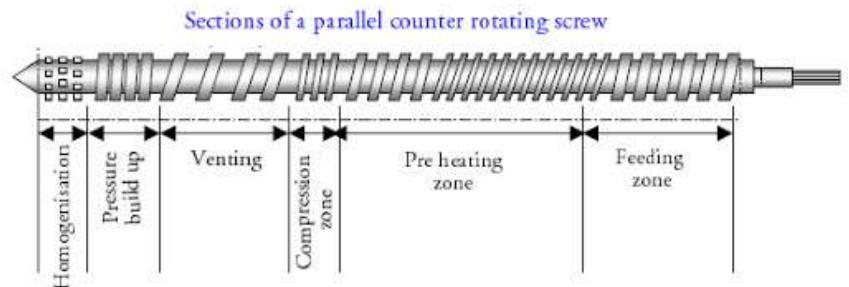
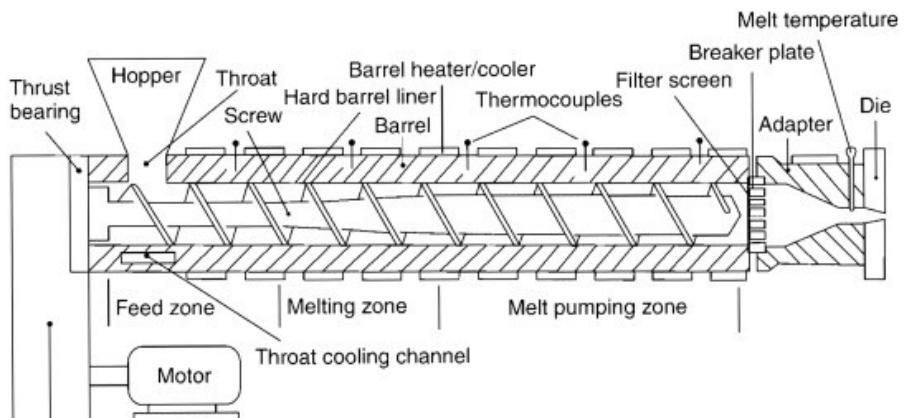
PVC pipe was first produced in Germany Between 1936 and 1939.

Plotted on log
curve today due to
Creep

T_{inc}

Compound Development and Extrusion Engineering and Design Allowed for Rigid PVC Processing

Material	PHR (Parts by weight per hundred parts of resin)
PVC resin ($k = 60$)	100.0
Stabilizer (butyl tin)	1.5
Acrylic processing aids/impact modifier	6.0 <i>\leftarrow Much higher not needed for PS</i>
Internal lubricant (calcium stearate., etc)	1.0
External lubricant (ester group)	1.2
Filler (CaCO_3)	3.0
Color pigments (metal oxides)	3.0
Chemical foaming agents (azodicarbonamide)	0.5
Recycled PVC	0.0

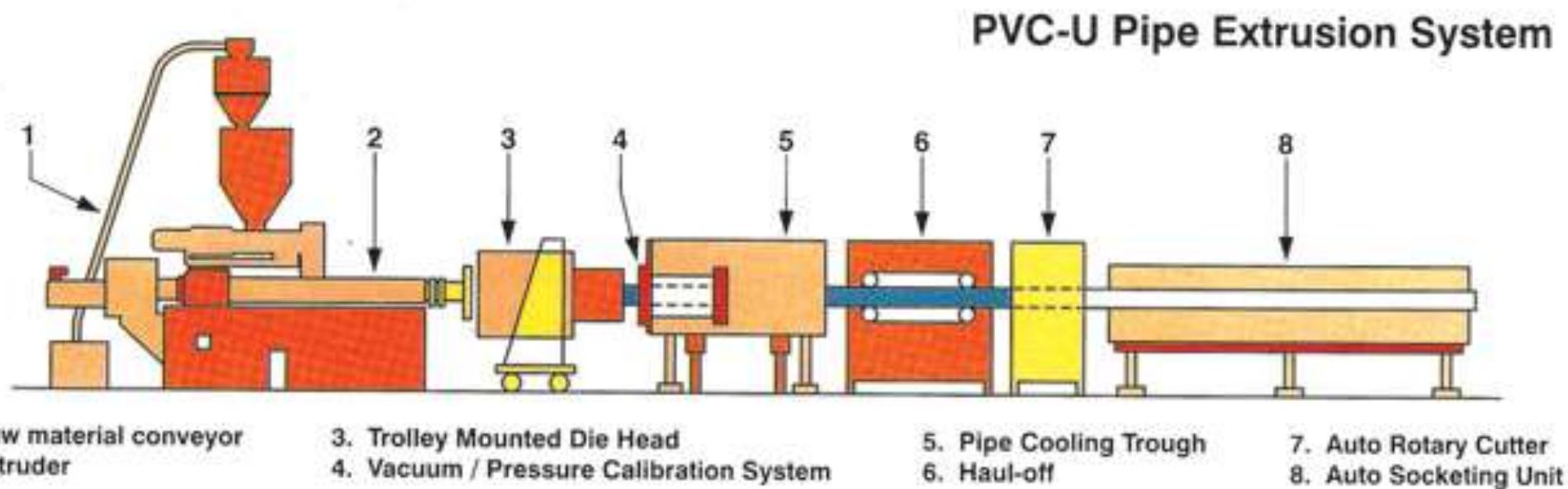


Standardization of PVC Rigid Compound - 1985

TABLE I
PPI PVC RANGE COMPOSITION FOR LISTING AT 73°F (23°C)

<u>Ingredient</u>	<u>Qualification Requirements</u>	<u>Allowable Content Range (in parts per hundred parts of resin)</u>
PVC Resin	Compliance to B.1 and Listing by PPI	100
Heat Stabilizer	Compliance to B.2 and Listing by PPI	0.3 - 1.0
Calcium Stearate	Compliance to A.2	0.4 - 1.5
Paraffin Wax	Compliance to A.3	0.6 - 1.5
Polyethylene Wax	Compliance to A.4	0.0 - 0.3
Titanium Dioxide	Compliance to A.5	0.5 - 3.0
Calcium Carbonate	Compliance to A.6	0.0 - 5.0
Process Aid	Compliance to B.2 and Listing by PPI	0.0 - 2.0
Colorant	Compliance to B.2 and Listing by PPI, or compliance to TR-3 Part D.1 Listing By PPI	See Table 9
Combination and Functional Equivalent		

Extrusion Process for PVC Pipe Manufacturing



Die Tooling Design for Plastic Pipe Manufacturing

Design Parameters

CTS Copper tube size

IPS iron pipe size

Pipe Die

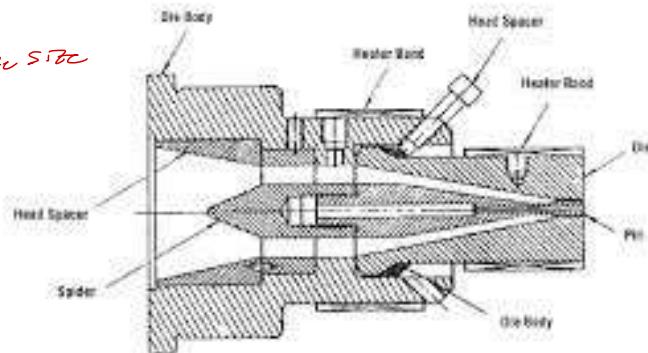
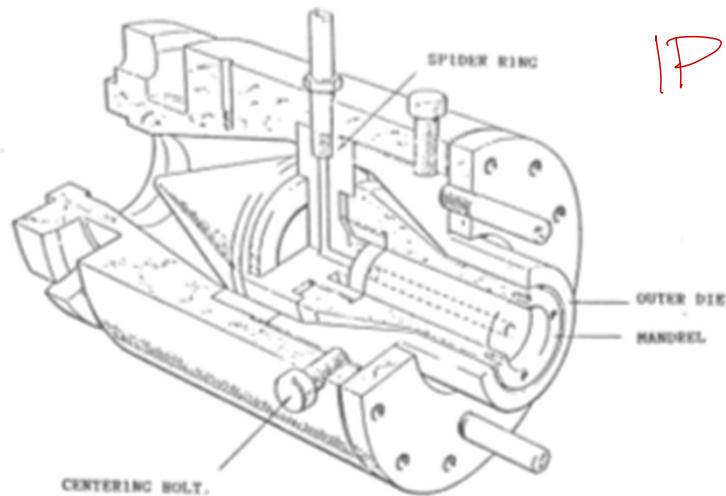
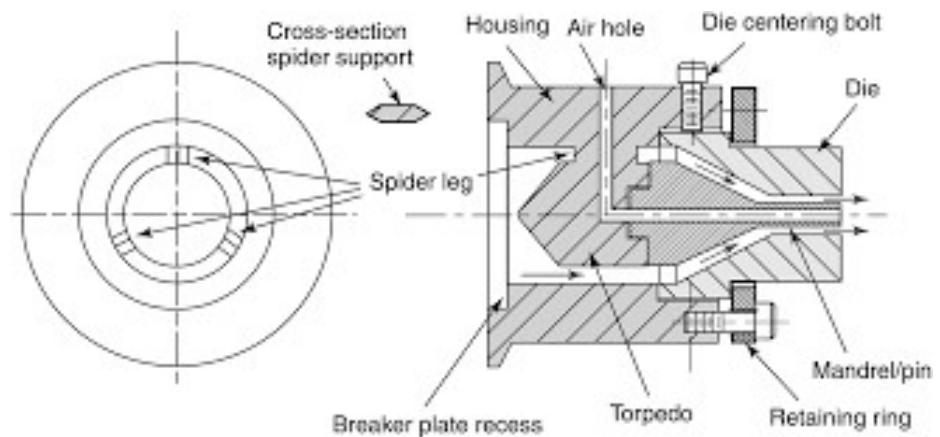
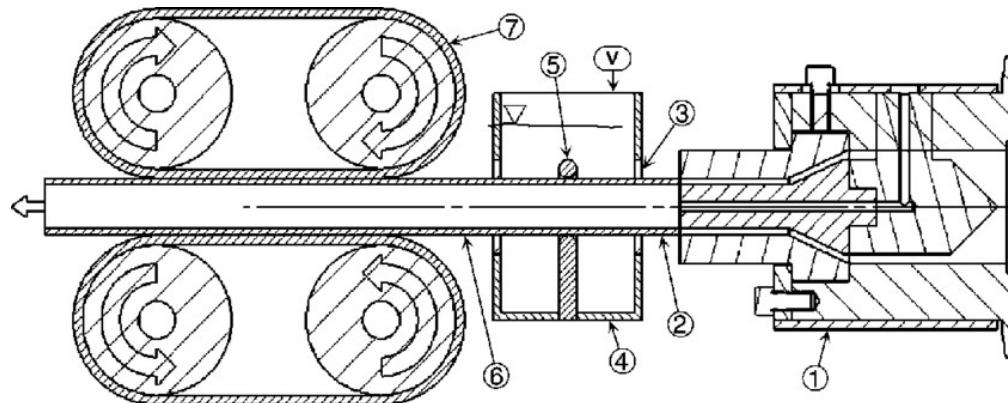


Figure 30. Pipe Die



How to Accurately Size the Pipe (OD & Wall)



Calibrators or Sizing Sleeves to accurately Specify the OD of the pipe.

Wall thickness is sized by increasing or decreasing the rate of the puller.

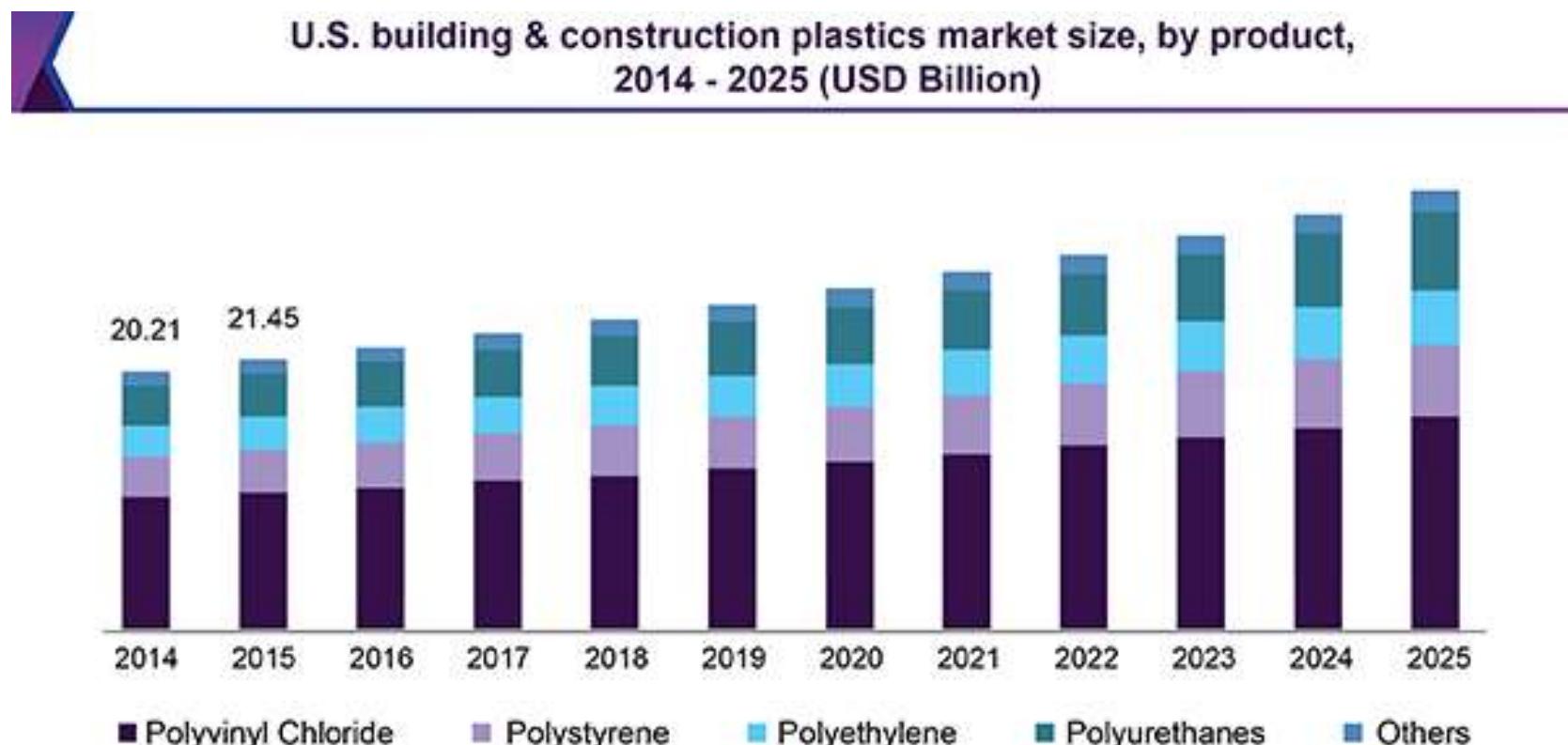
PVC Pipes are Produced in Various Sizes



The Future of PVC Pipe

The PVC pipe market is expected to reach an estimated \$51.5 billion by 2024 with a CAGR of 5.8% from 2019 to 2024. The major drivers for this **market** are growth in residential and non-residential construction activities and replacement of aging pipelines.

PVC Position in the Building and Construction Market Segment



Source: www.grandviewresearch.com

Further Development of PVC Rigid Compounds Resulted in Vinyl Siding

Patented: February 21, 1967

US 3,304,676

United States Patent Office

US 3,304,676

SIDING CONSTRUCTION

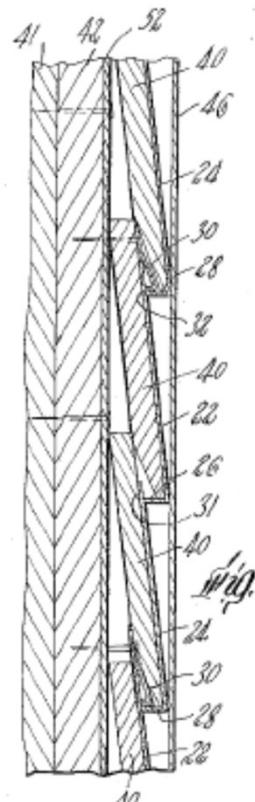
Stanley H. Sallie, Mansfield, and Norman D. Olson

Sherborn, Mass., assignors to Bird & Son, inc., East

Walpole, Mass., a corporation of Massachusetts

Filed Jan. 29, 1964, Serial No. 340,917

"To accomplish some of its objects, the invention provides a multiple paneled plastic siding unit of organic plastic material of a uniform color throughout its cross-section and its surfaces. Each siding unit is adapted to interlock with adjacent units above and below it as well."



Why was PVC Siding Originally Produced Only in Pastel Colors?



SUZANNE DECHILLO/THE NEW YORK TIMES/SHUTTERSTOCK



Double 4"



Double 5"



Double 4" Dutch Lap



Beaded



Insulated

The Problem was that Heat Distortion Occurred with Darker Colors – Both Temporary and Permanent



New Technology was Developed to Produce Dark Colors What Changed?



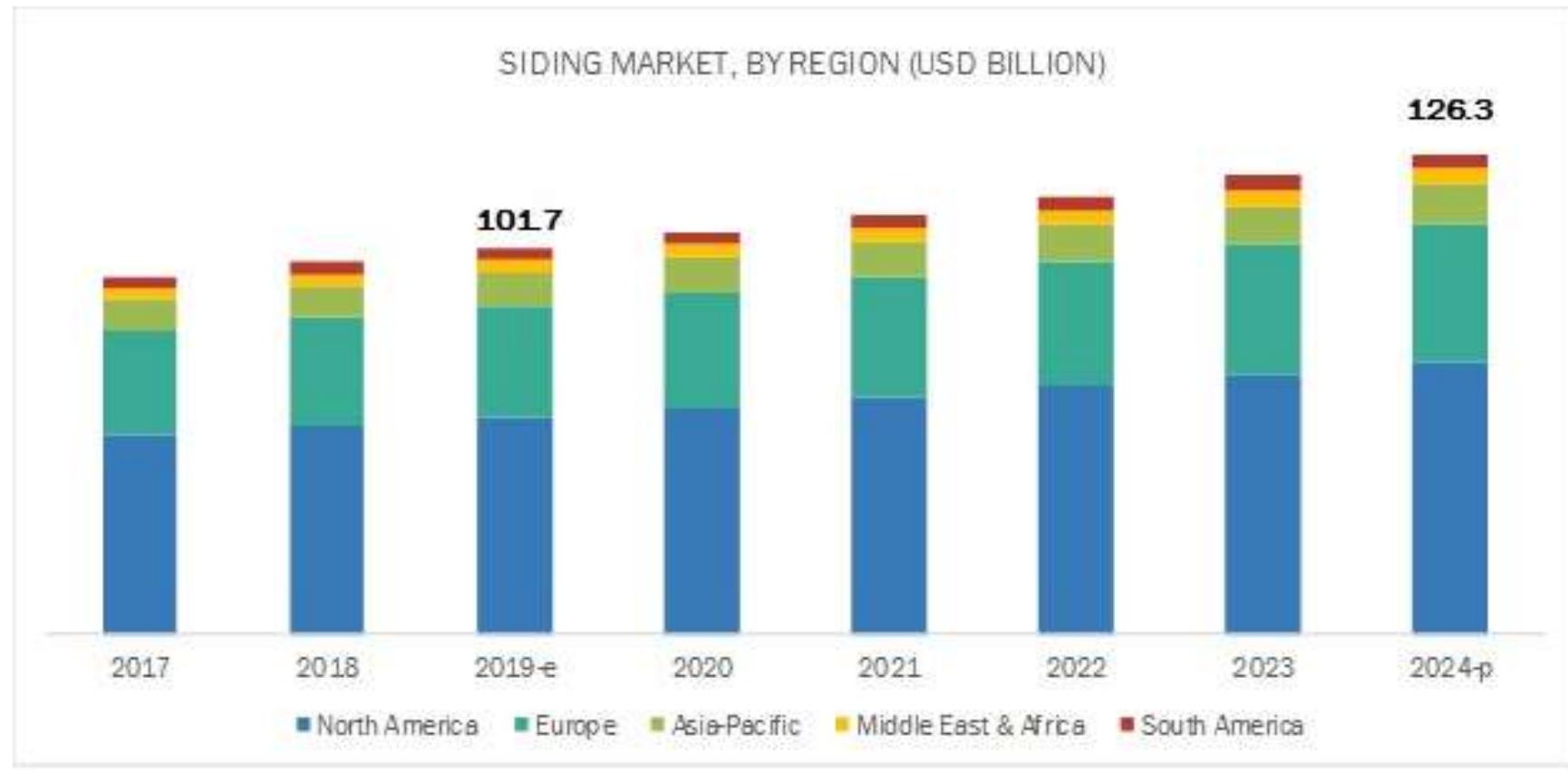
What Changed?

Several New Technologies have been Introduced:

- Profile Foam Backed Siding
 - Reinforce
 - Insulate
- Reflective Surfaces/Paint
 - Dissipation of Heat
- Use of Multilayer Profile
 - CPVC Substrate with PVC & Acrylic



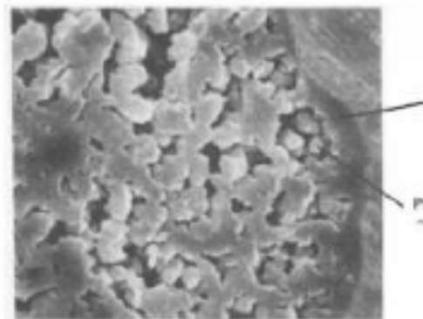
The Vinyl Siding Market Continues to Grow



Micrographs and Schematic of the Grain Structure of Poly(Vinyl Chloride)



Grain
~150 μm dia.



Skin
~2 - 5 μm thick

Primary particles
~1 μm dia.

primary particles.

Summers, James. W., J. Vinyl & Add. Tech., Volume 3(2), 130 – 139
(1997).

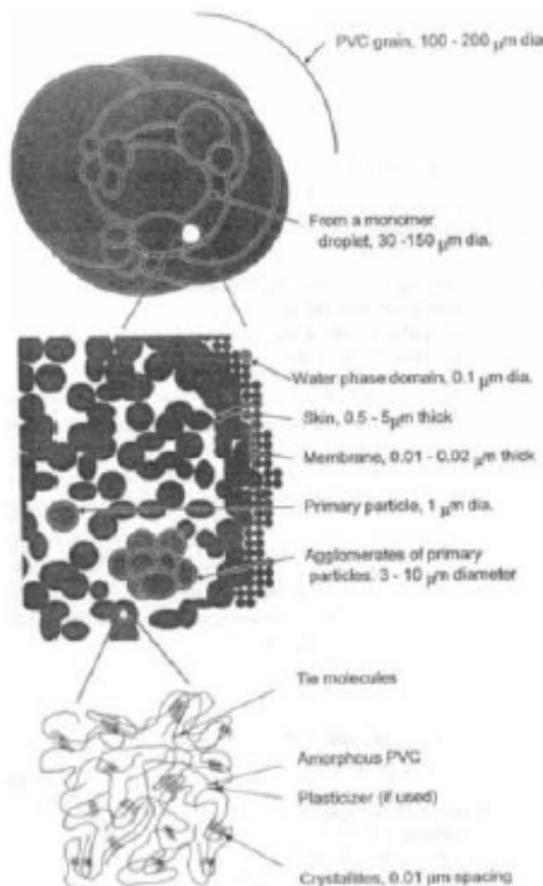


Fig. 1. The microstructure of PVC.

First Patent for Chlorinated Poly(Vinyl Chloride) CPVC

December 4, 1934

US 1,982,765

United States Patent Office

US 1,982,765

ARTIFICIAL MASS

Curt Schonburg, Bittenfeld, Germany assignor to

I. G. Farbenindustrie Aktiengesellschaft,
Frankfurt-on-the-Main, Germany

1. The process which comprises treating polymerized vinyl chloride in the presence of an organic solvent or swelling agent with chlorine.
2. The process which comprises treating polymerized vinyl chloride in the presence of a chlorinated aliphatic hydrocarbon with chlorine.
3. The process which comprises treating polymerized vinyl chlorine in the presence of an organic solvent or swelling agent with chlorine until the dried polymerization product contains 64 to 66 percent of chlorine.

Patented: November 1, 1980

US 4,412,898

United States Patent Office

US 4,412,898

**PROCESS FOR CHLORINATION OF PVC IN
WATER WITHOUT USE OF SWELLING AGENTS**

**Alan J. Olsen, Westlake, Robert G. Vielhaber, Doylestown, both of Ohio
assignor to The B.F. Goodrich Company, Akron, Ohio**

United States Patent Office

US 4,412,898

PROCESS FOR CHLORINATION OF PVC IN
WATER WITHOUT USE OF SWELLING AGENTS

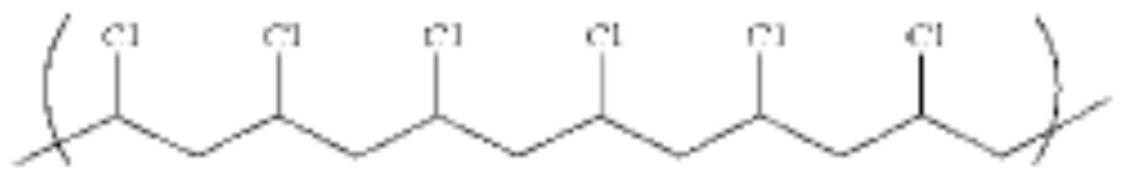
Alan J. Olsen, Westlake, Robert G. Vielhaber, Doylestown, both of Ohio
assignor to The B.F. Goodrich Company, Akron, Ohio

1. A process for producing chlorinated poly(vinyl chloride) resin having a density within the range from about 1.50 to 1.65 g/cc at 25° C., comprising:

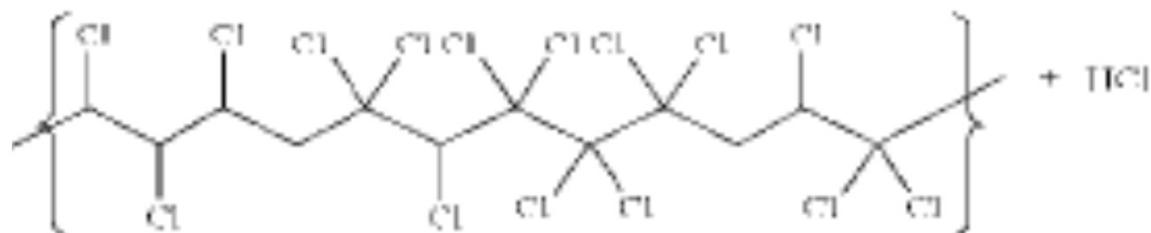
- (a) introducing an aqueous suspension of poly(vinyl chloride) containing from about 15 to about 35% by wt poly(vinyl chloride) into a reactor operable under elevated pressure;
- (b) removing essentially all oxygen from said suspension and reactor;
- (c) introducing chlorine into the reactor until the pressure therewithin is in the range from about 10 psig to about 100 psig;
- (d) soaking the poly(vinyl chloride) under said pressure for a period of from about 1 minute to about 45 minutes at a "soak" temperature in the range from about 60° C. to about 85° C.;
- (e) irradiating the poly(vinyl chloride) with ultraviolet light at a relatively high and constant intensity in the range from about 2 watts to about 50 watts per gallon of said aqueous suspension;
- (f) increasing the temperature of said suspension by at least 5° C.

- (f) increasing the temperature of said suspension by at least 5° C. autogenously from said soak temperature to a finishing temperature in the range from about 80° C. to about 120° C.;
- (g) maintaining a finishing temperature in the range from about 80° C. to about 120° C. during chlorination;
- (h) continuing to introduce chlorine into the reactor as the reaction proceeds, so that the pressure in the reactor is maintained substantially constant within said range of pressure;
- (i) stopping flow of chlorine into the reactor when sufficient chlorine has been added to produce a suspension of chlorinated poly(vinyl chloride) having said density upon completion of the reaction; and,
- (j) separating solid macrogranular chlorinated poly(vinyl chloride) from said suspension of chlorinated poly(vinyl chloride) product characterized by having a heat distortion temperature measured by ASTM Test Method D648 which is in the range from about 100° C. to about 135° C.

The Production of CPVC from PVC



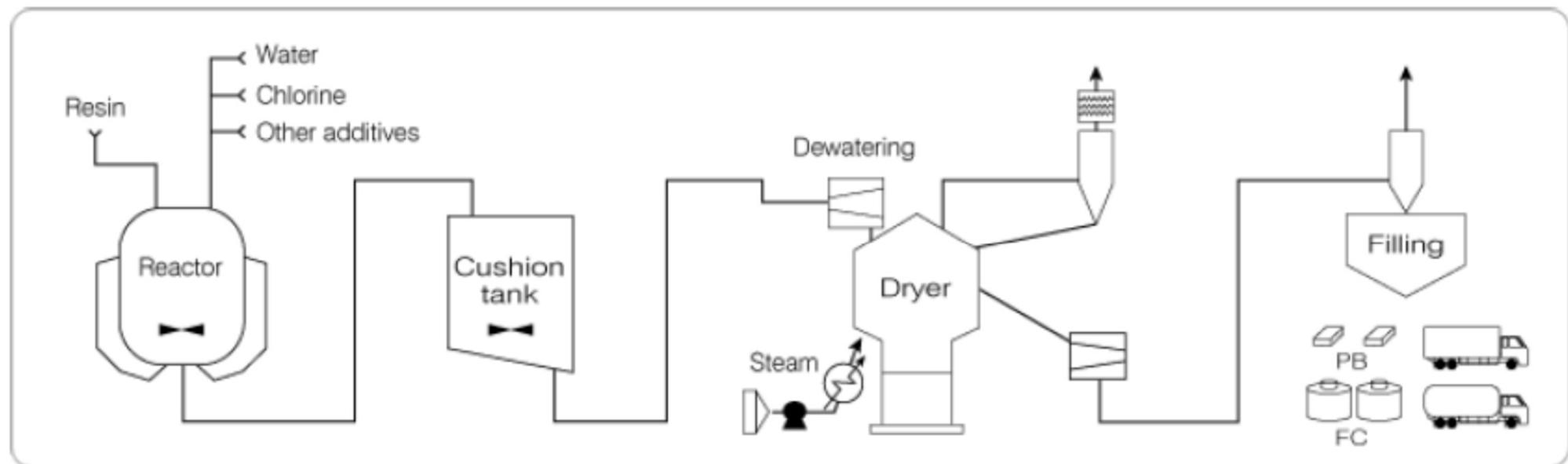
PVC Powder in a Water Slurry
Vacuum + Liquid Chlorine
Ultraviolet Light



Neutralize the HCl and Dry

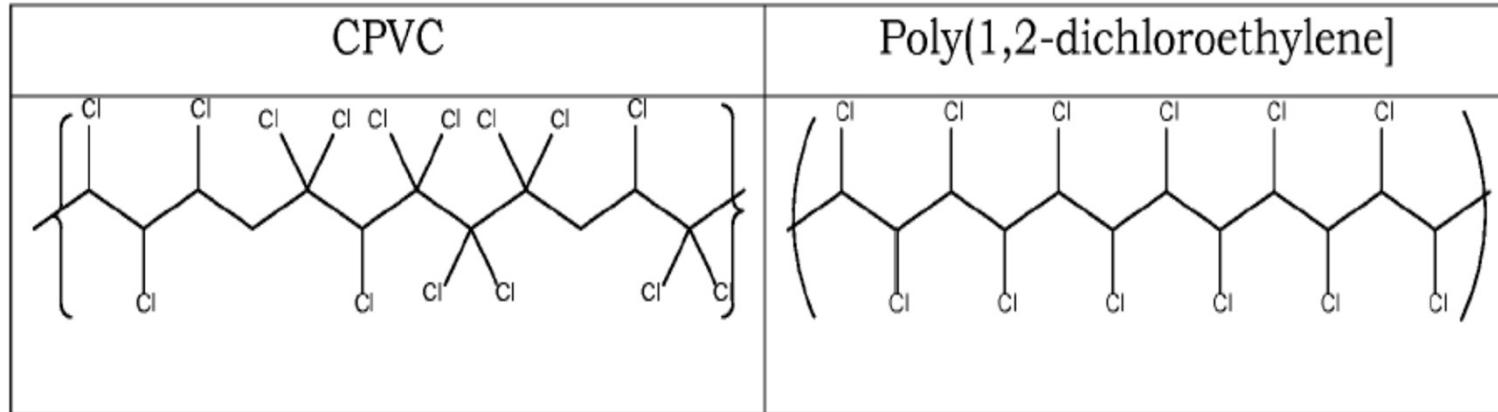
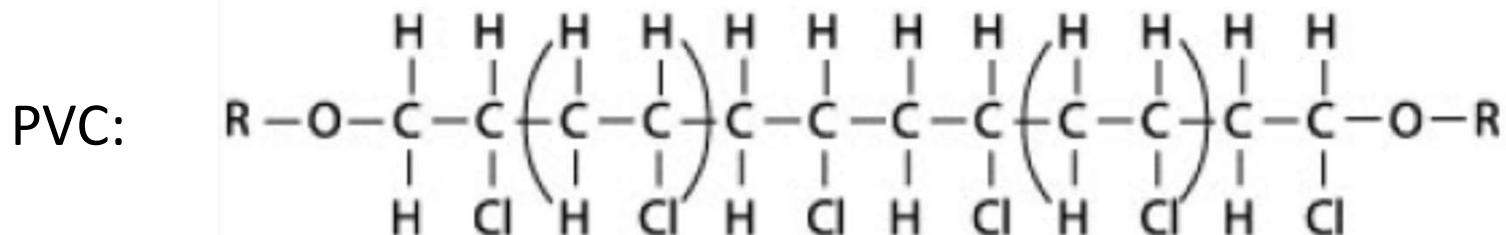
Compound

Production Scheme for Chlorinating Poly(Vinyl Chloride)



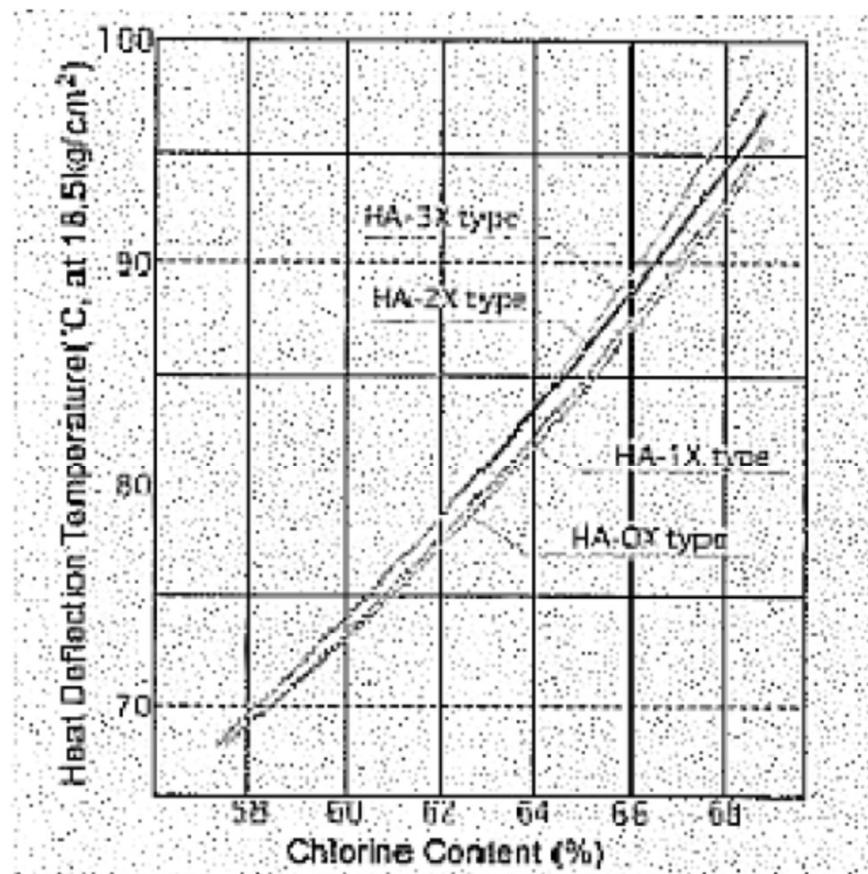
Due to the high acid level (HCl) during chlorination all reactors were titanium.

Understanding the Structure of CPVC



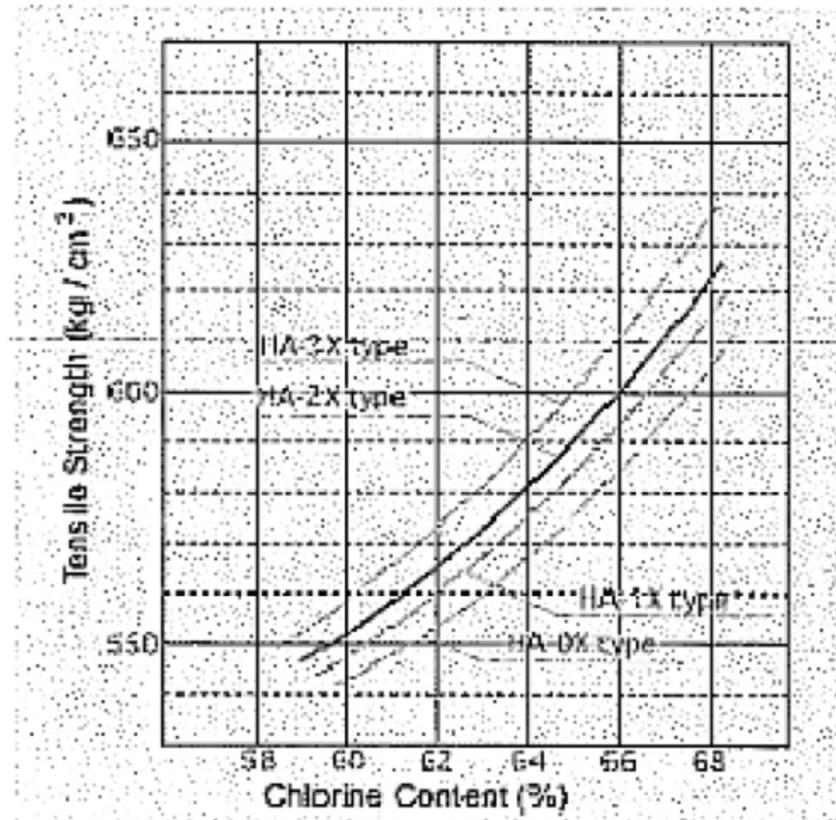
Chlorination of PVC was based on the need to approach the structure of Poly(1,2-dichloroethylene)

Influence of Chlorine Content upon the Heat Deflection Temperature of CPVC



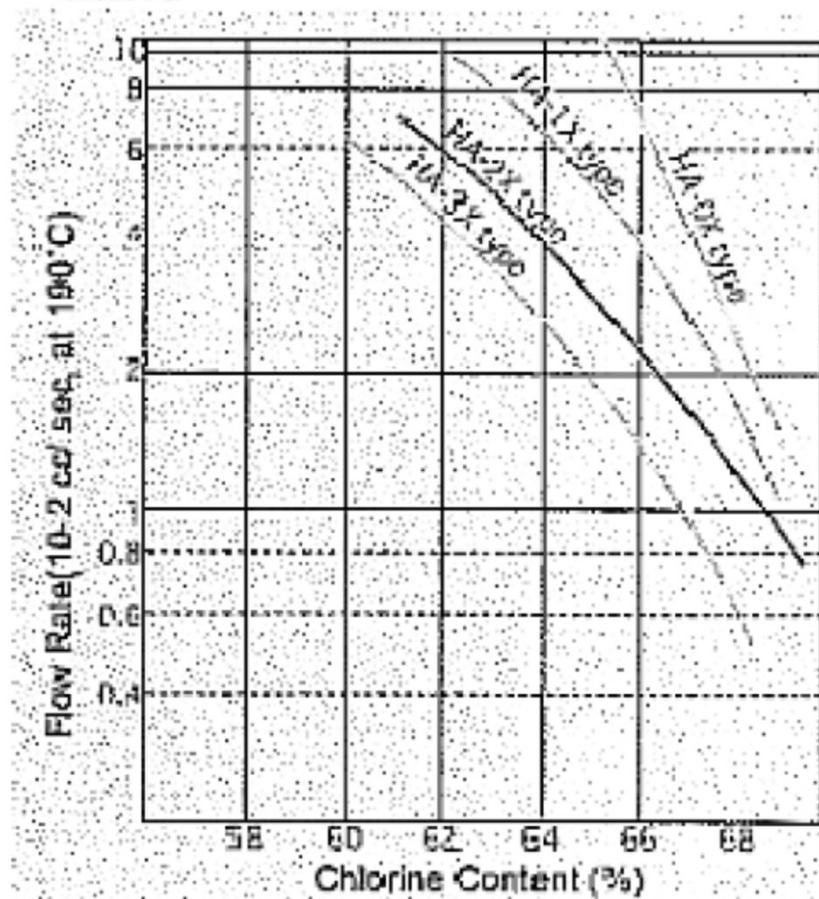
Influence of Chlorine Content upon the Tensile Strength of CPVC

Chart 3



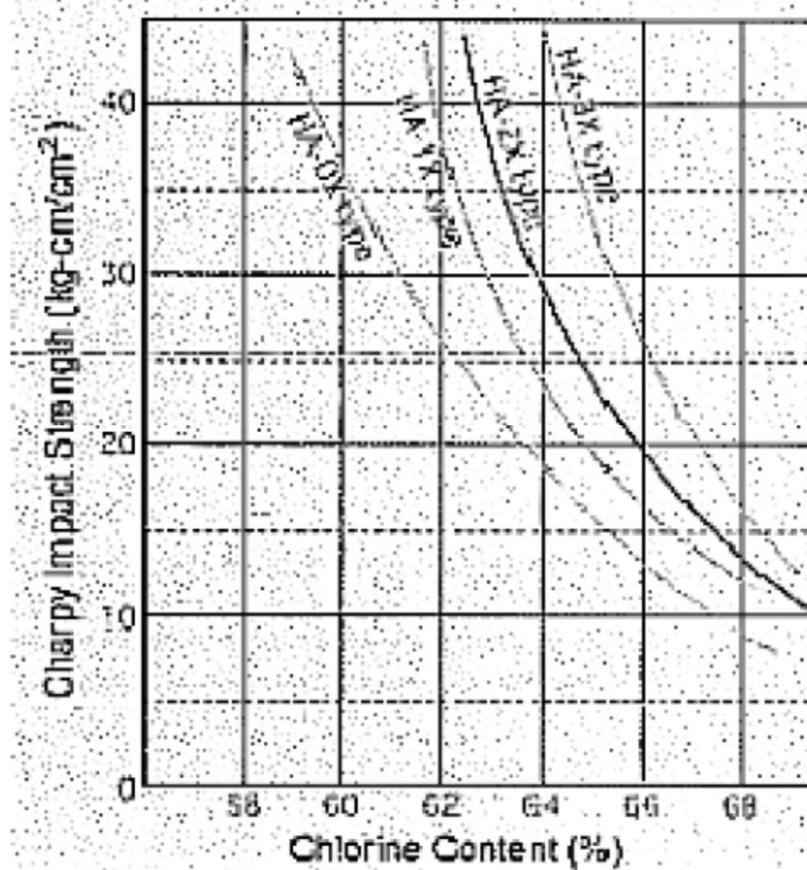
Influence of Chlorine Content upon the Flow Rate of CPVC

Chart 2



Influence of Chlorine Content upon the Charpy Impact Strength of CPVC

Chart 4



CPVC Applications are Primarily in Fluid Handling



CPVC Applications do Extend Into Higher Arenas



Why?



Discovery of Polyvinylidene Chloride Product

Ralph Wiley accidentally discovered polyvinylidene chloride in 1933. He, then, was a college student who worked part-time at Dow Chemical lab as a dishwasher. While cleaning laboratory glassware, he came across a vial he could not scrub clean. Dow made this material into a greasy, dark green film, first called "Eonite" and then "Saran".

Ralph Wiley went on to become one of Dow Chemical's research scientists and invent and develop many plastics, chemicals and production machines.

June 6, 1939

2,160,931

United States Patent Office

US 2,160,931

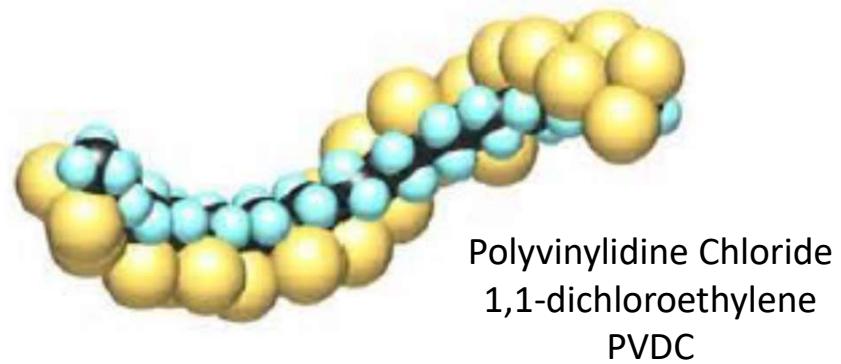
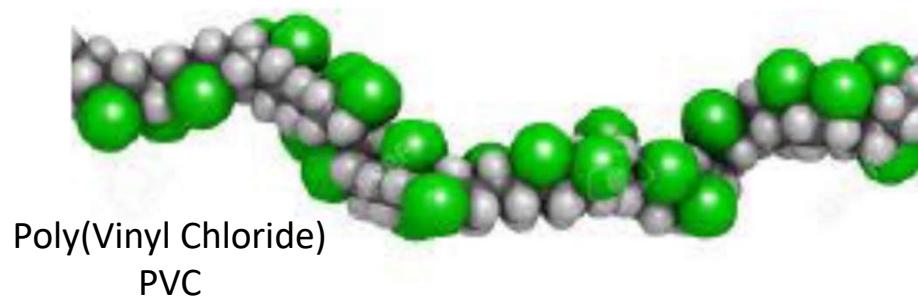
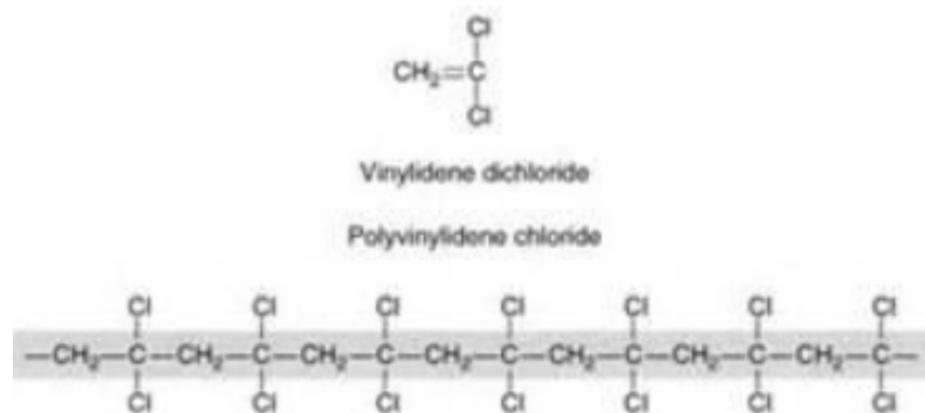
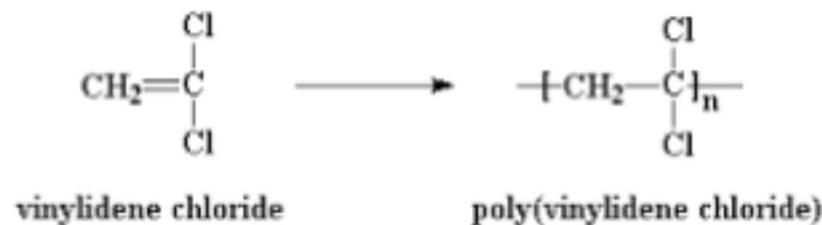
CO-POLYMERIZATION PRODUCTS

**Ralph M. Wiley, Midland, Mich., assignor to
The Dow Chemical Company, Midland, Mich.,**

Application July 1, 1934

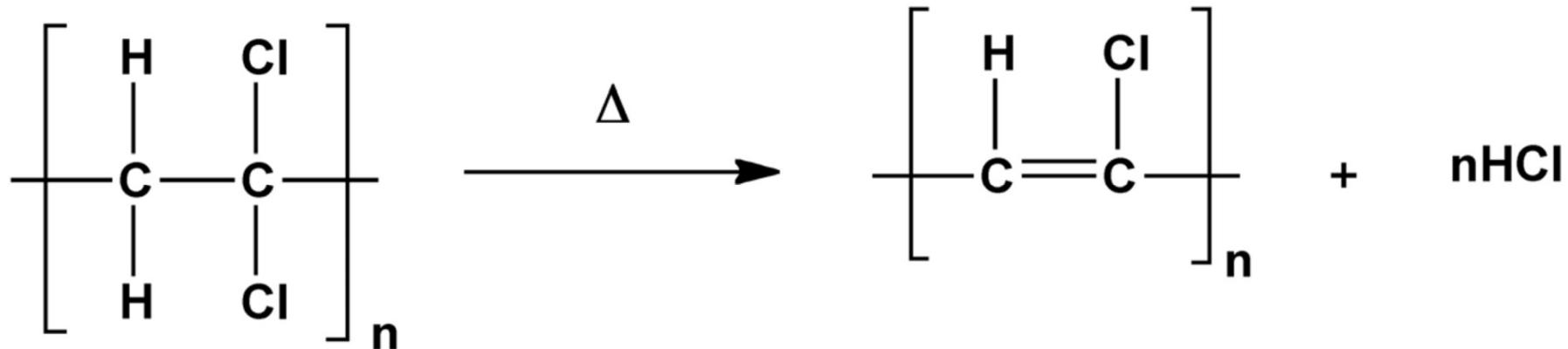
In a process for preparing a plastic, the step which consists in reacting 1,1-dichloroethylene with not more than an equal amount of vinyl chloride to produce polymeric bodies containing between about 5 and about 30 percent by weight of the vinyl chloride co-polymerized with said 1,1 dichloroethylene.

Polyvinylidene Chloride, 1,1-Dichloroethylene (PVDC)



Polyvinylidene Chloride is an Unstable Polymer

- Vinylidene chloride polymers undergo thermal decomposition in two distinct stages. The first occurs at very modest temperature ($120\text{-}160\text{ }^{\circ}\text{C}$) and corresponds to the elimination of hydrogen chloride. This initial degradation corresponds to the loss of hydrogen chloride uncomplicated by other processes.
- The dehydrogenation is a radical chain process with distinct initiation, propagation, and termination steps. Both initiation and propagation reflect first-order loss of hydrogen chloride. It is this initial degradation step that is of concern for the processing of these polymers.

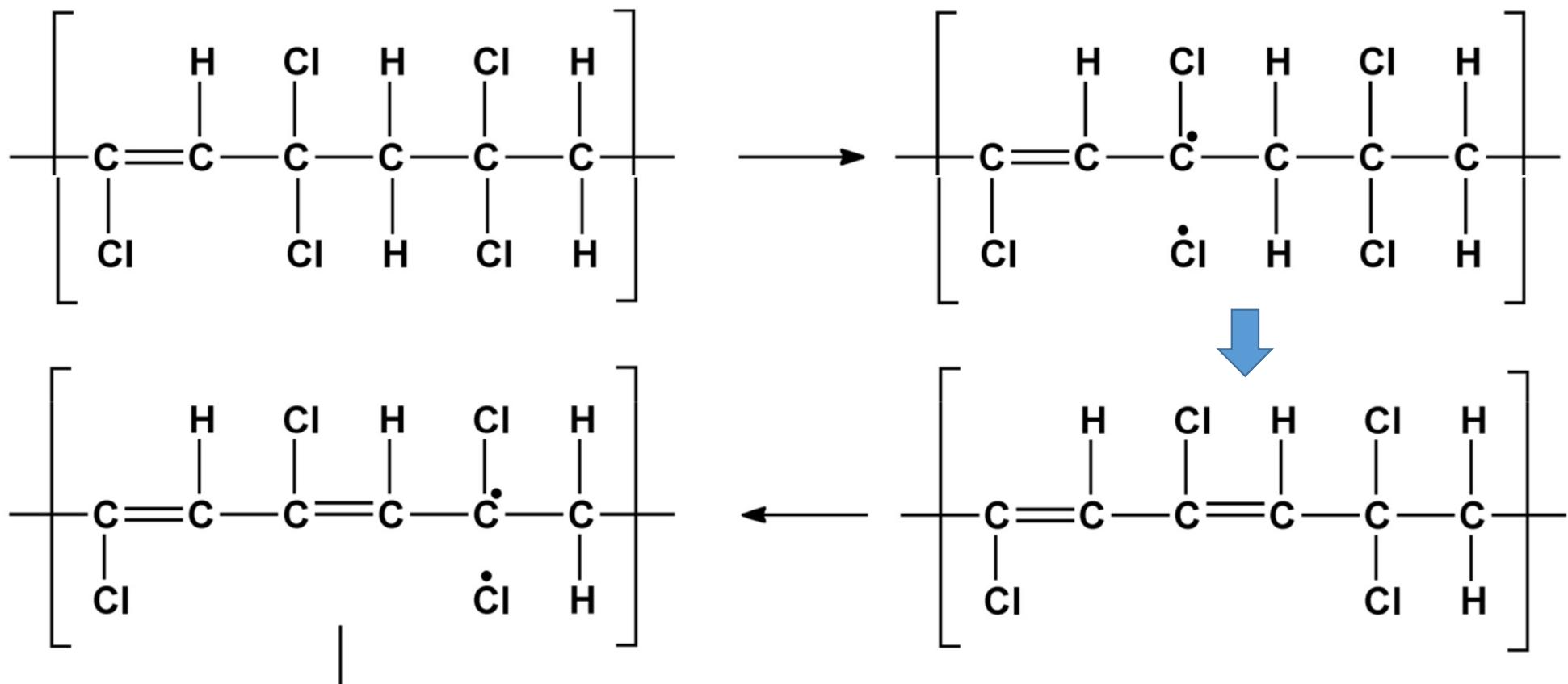


Polyvinylidene Chloride is an Unstable Polymer

- When exposed to ultraviolet light, poly(vinylidene chloride) copolymers undergo a similar release of hydrogen chloride resulting in the formation of polyene sequences in the polymer backbone. Crosslinking between polymer chains may also occur when these double bonds undergo Diels-Alder condensations. PVDC properties are therefore strongly affected by UV-treatment: it will indeed lead to coloration and an increase of the permeability and the polymer gel content. Moreover, as already mentioned previously, double bonds created by pre-treatment of PVDC by UV radiation play the role of activating sites for the polymer thermal degradation.

Polyvinylidene Chloride is an Unstable Polymer

- At higher temperatures, the unsaturated materials generated by initial degradation undergo extensive cross-linking via cycloaddition reactions to form aromatic structures and ultimately a highly porous, strongly absorptive carbon.



Reactivity Ratios for Free Radical Polymerization (1,1-Dichloroethylene and Vinyl Chloride)

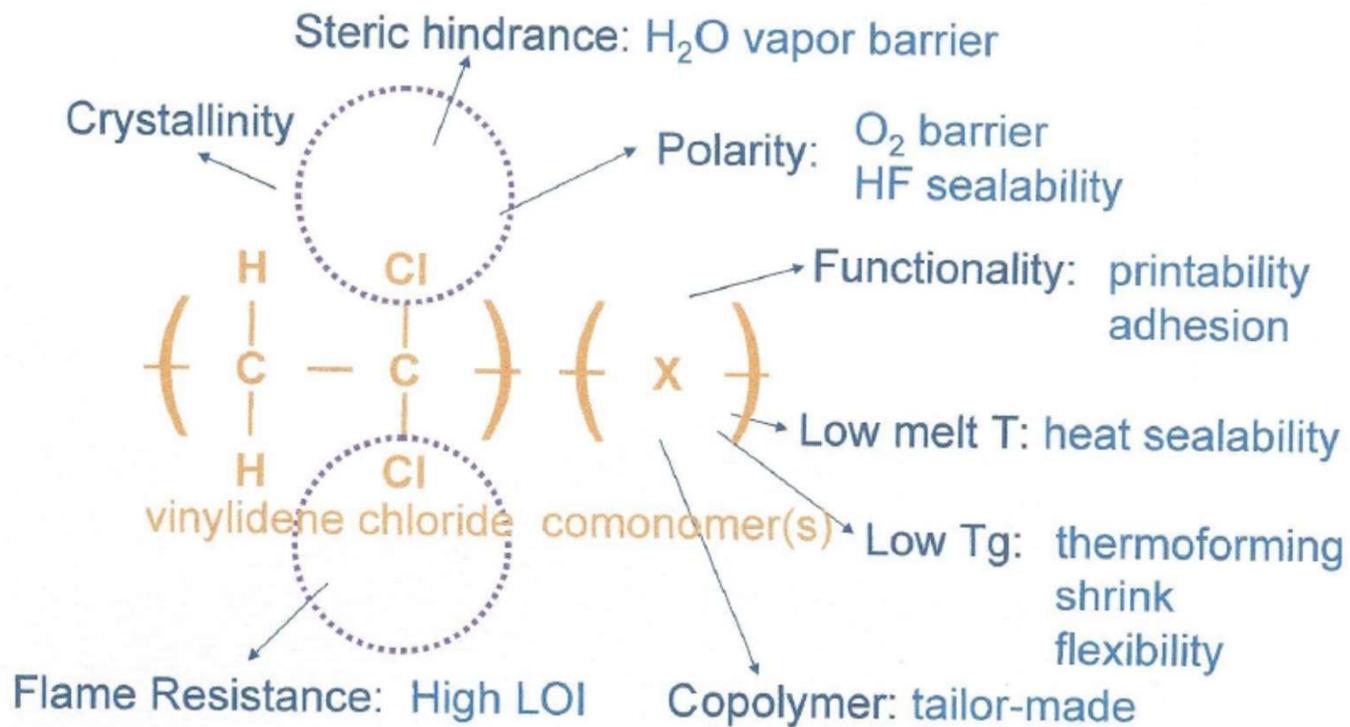
Products of Monomer Reactivity Ratios in Copolymerization

Butadiene								
1.0		Styrene						
0.71	0.55		Vinyl Acetate					
0.30	0.34	0.39		Vinyl Chloride				
0.19	0.24	0.30	1.0		Methyl Methacrylate			
0.10	0.16	0.12	0.96	0.61		Vinylidene Chloride		
0.04	0.14	0.90	0.75	0.96	0.80		Methyl Acrylate	
0.02	0.02	0.25	0.13	0.24	0.34	0.84		Acrylonitrile

$r_1 * r_2 \sim 1 \Rightarrow$ Random Copolymer – A A B B B A A A B A B A A A

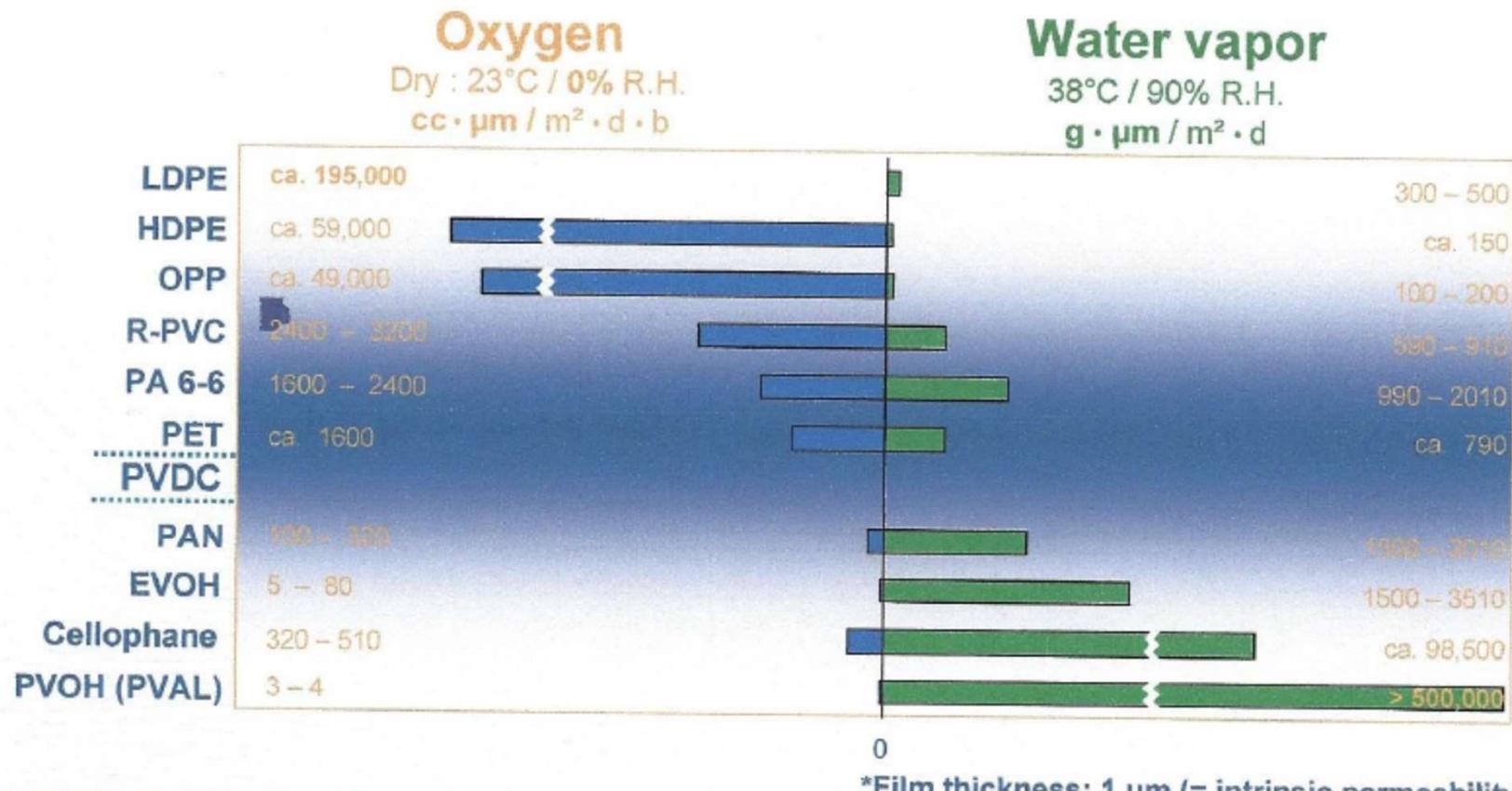
Commercial Benefits of Polyvinylidene Chloride in Packaging

What is PVDC?



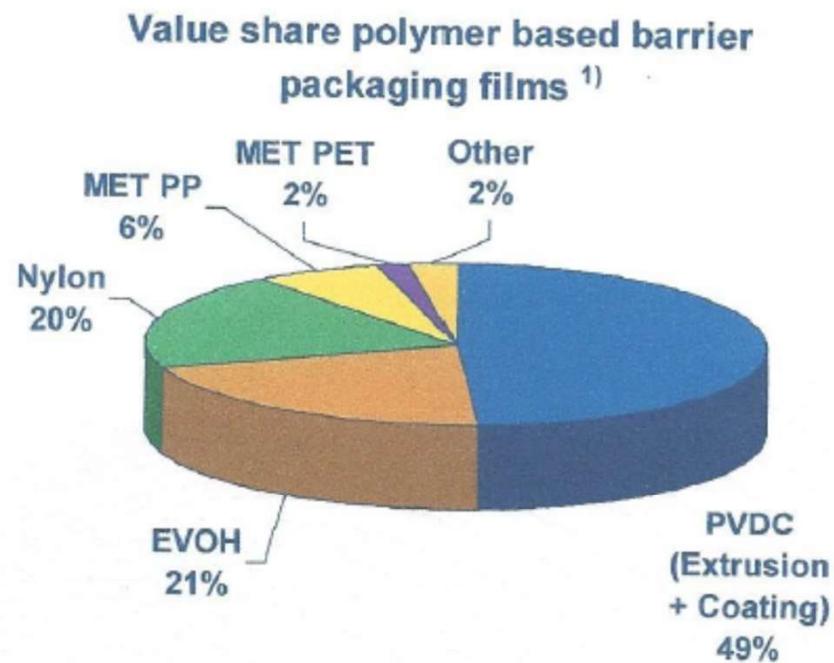
Commercial Benefits of Polyvinylidene Chloride in Packaging

Permeability of various polymers*



Commercial Benefits of Polyvinylidene Chloride in Packaging

- PVDC remains the leading barrier polymer in high performance packaging films



¹⁾ Source: [2] Kline & Company, High-Performance Barrier Packaging Films USA 2005

Commercial Benefits of Polyvinylidene Chloride in Packaging

- PVDC prevents :
 - Moisture loss or gain
 - Oxidation of ingredients
 - Aroma and odor transfer
 - Oil and fat permeation
- PVDC provides:
 - Seal integrity (heat, HF, ultrasonic)
 - Consumer appeal
 - Transparency and gloss
 - Antimist
 - Printability
 - Scratch resistance
- Regulatory compliance for direct pharmaceutical and food contact



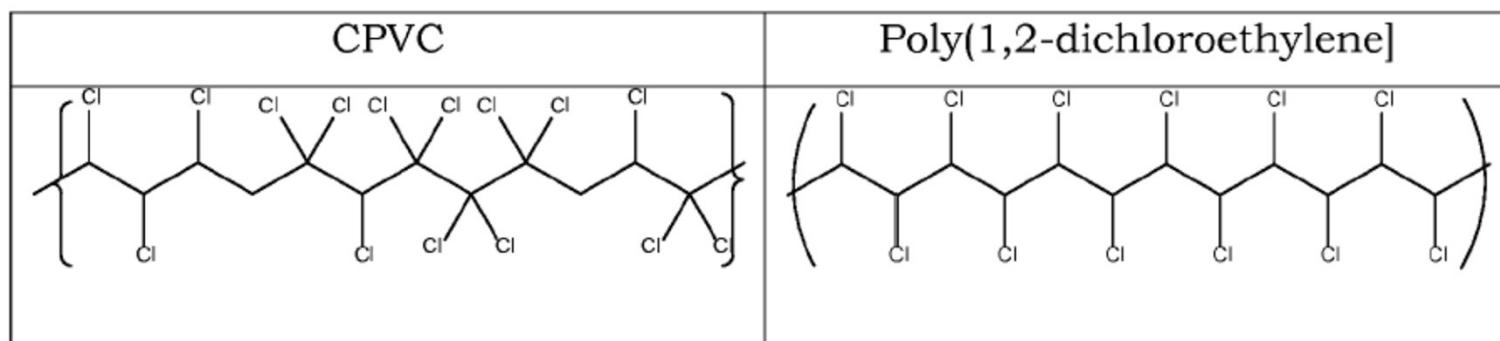
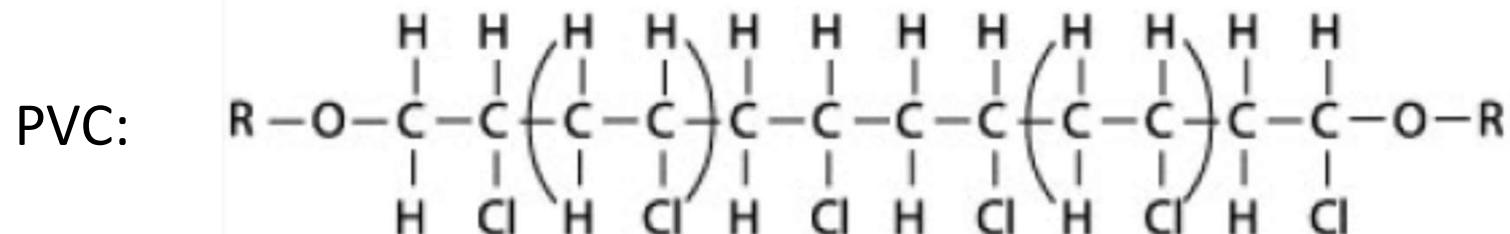
The Introduction of the Product Saran

In 1943, John Reilly (Ralph Wiley's boss) and Ralph Wiley of The Dow Chemical Co. completed the final work needed for introduction of PVDC, which had been invented in 1939.

The word "Saran" was coined by a combination of John Reilly's wife's and daughter's names, Sarah and Ann Reilly. In 1949, Dow introduced **Saran Wrap**, a thin, clingy **plastic wrap** that was sold in rolls and used primarily for **wrapping** food. It quickly became popular for preserving food items stored in the refrigerator.

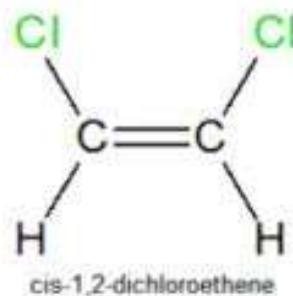
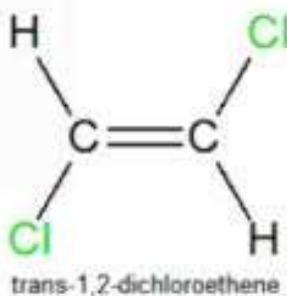


The Pursuit of Poly(1,2-dichloroethylene) Continued

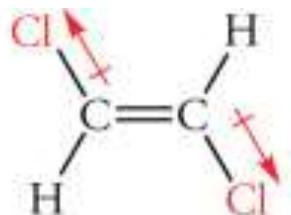


Chlorination of PVC was based on the need to obtain the structure close to Poly(1,2-dichloroethylene)

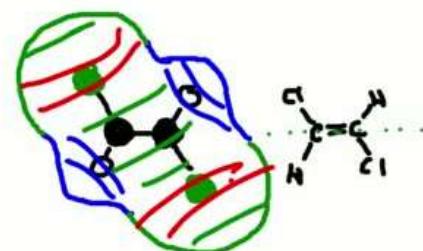
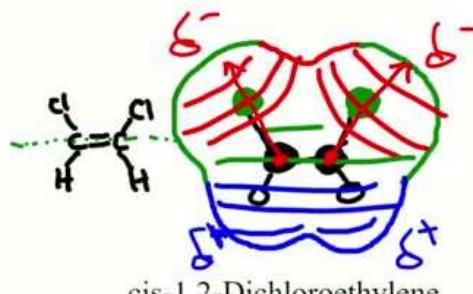
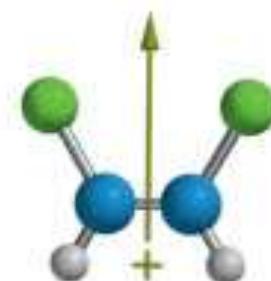
The Problem



cis-1,2-dichloroethene



trans-1,2-dichloroethene



The Four Approaches to Produce Poly(1,2-dichloroethylene) B.F. Goodrich - 1992

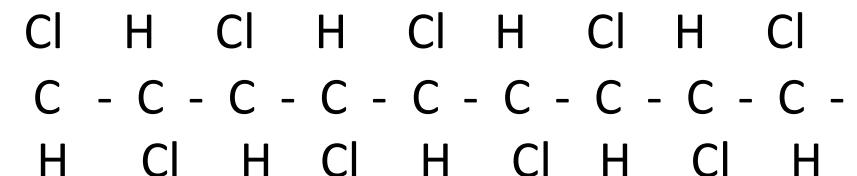
- Replicate the Dow Chemical Company Patent
US 3,367,925: 2-6-1968, Gordon Liu & **Coleman Bryan**
- High Pressure Free Radical Polymerization
Lou Cohen: BFG – Avon Lake, OH
- Metallocene Polymerization Methods – New Catalysts
Dr. Bryan Goodall: BFG – Brecksville, OH
- Novel Chlorination Method
BFG: Private Lab: Avon Lake '92–'93 & Brecksville '93 -'18

Projects to Produce Poly(1,2-dichloroethylene)

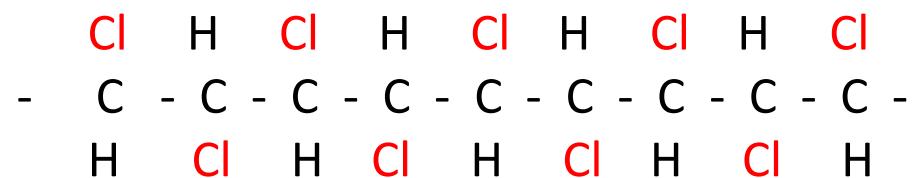
1. Replicate the Dow Chemical Company Patent
Failed to Produce Polymer
2. High Pressure Free Radical Polymerization
Failed to Produce Polymer
3. Metallocene Polymerization Methods – New Catalysts
Failed to Produce Polymer
4. Novel Chlorination Method
???????????

Novel Chlorination Method Basis

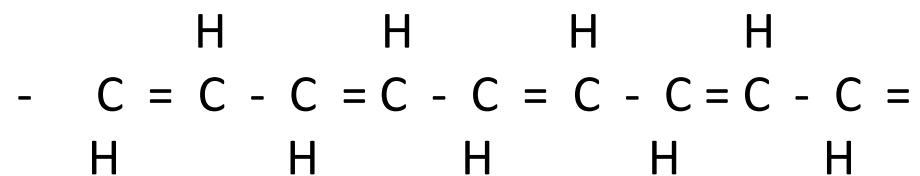
1st Draw Structure of Poly(1,2-dichloroethylene)



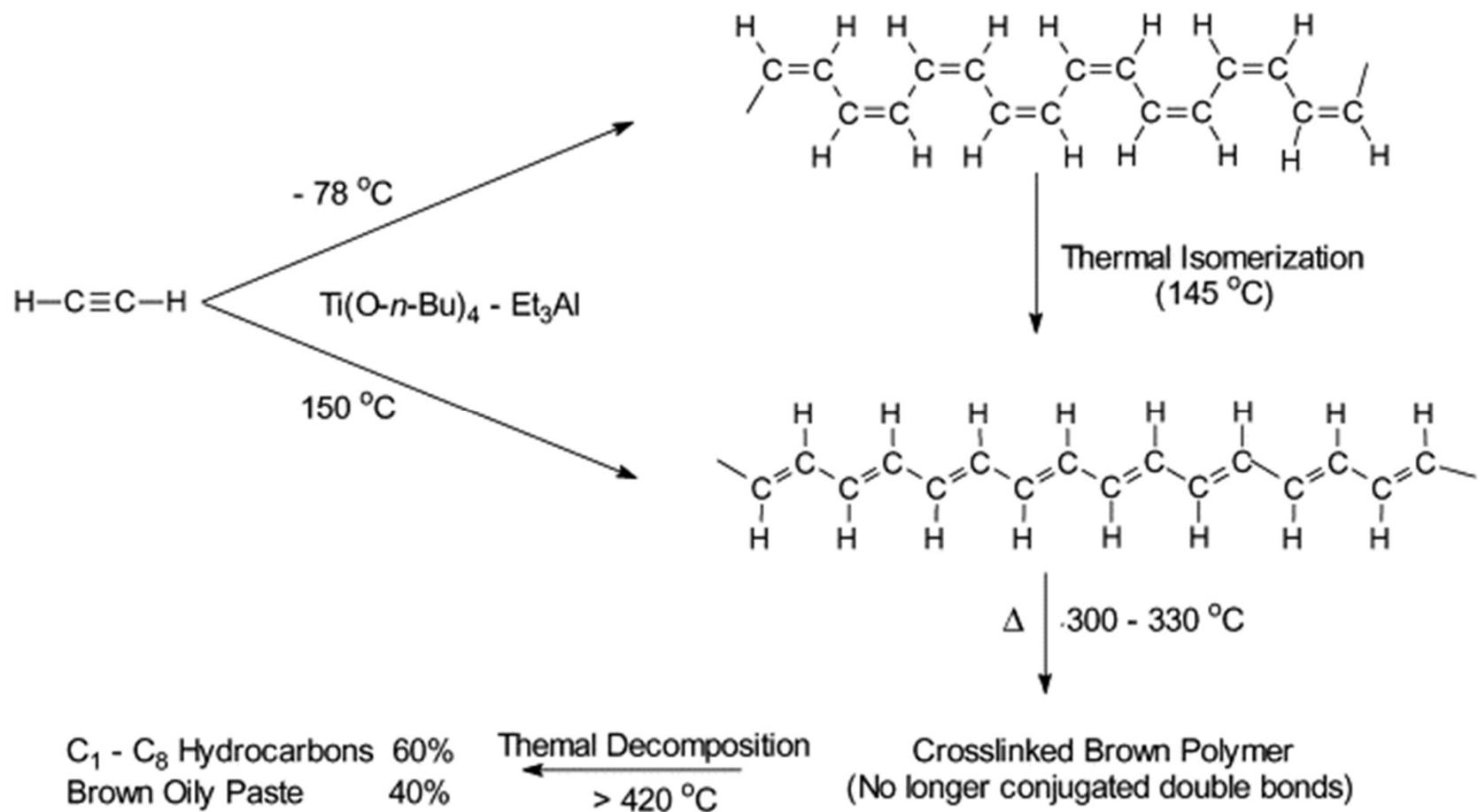
2nd Identify and Remove all Chlorines



3rd Identify Resulting Structure



Polyacetylene



Development Time-Line

- First done in 1997-98: Slurry polymerization and chlorination in an aromatic solvent.
 - Polyacetylene in slurry is a very dark (cobalt blue) slurry
 - Upon chlorination in solution changes to a white powder then clear solution.
 - Precipitates to a white powder; identified as 95% poly(1,2 DCE) w/ Tg > 200 C
 - Downside, carryover of chlorinated organic solvents.
 - Project stalled Needed to transition to gas phase.
- BFG became Noveon, Inc. (2001) – Privately held.
 - Sold project to CEO (2003)
 - Needed to develop gas phase technology
- Noveon became Lubrizol (2004)
 - Project stalled due to acquisition.
 - Resold to new CEO as a corporate funded project 2007.
 - Added new members Fields, Burrington.

(12) **United States Patent**
Fields et al.

(10) **Patent No.:** US 9,279,026 B2
(45) **Date of Patent:** Mar. 8, 2016

**POLYACETYLENE AND CHLORINATED
POLYACETYLENE AND PRODUCTION
PROCESSES THEREOF**

Applicant: **Lubrizol Advanced Materials, Inc.,**
Cleveland, OH (US)

Inventors: **Garry L. Fields**, Richfield, OH (US);
James D. Burrington, Gates Mills, OH
(US); **Andrew M. Olah**, Spencer, OH
(US)

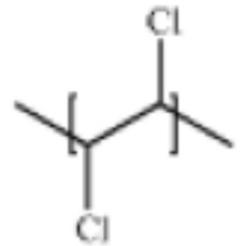
Assignee: **Lubrizol Advanced Materials, Inc.,**
Cleveland, OH (US)

Provisional application No. 61/549,370, filed on Oct.
20, 2011.

Indirect Pathway to Poly(1,2-dichloroethylene)

What is Claimed is:

1. A polymer composition comprising polyacetylene of formula $(C_2H_2)_n$ wherein n is greater than 10, and wherein the polymer composition is in the form of a granular solid.
12. Chlorinated polyacetylene (CPA) comprised primarily of repeat units equivalent to 1,2-dichloroethylene and repeat units equivalent to acetylene, wherein the CPA is in the form of a granular solid.
2. The polymer composition of claim 19 wherein the chlorinated polyacetylene exhibits an Mw as measured by GPC of at least 30,000.



Indirect Pathway to Poly(1,2-dichloroethylene)



Te□	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9
Wt % Cl (NMR) (CHCl/HC=CH)	70.0 11.6	68.0 7.0	68.1 7.1	69.3 9.6	68.0 7.0	67.4 6.2	66.7 5.5
Mol % CHCl	92.06	87.50%	87.65%	90.57	87.50%	86.11%	84.62%
DSC (Tg)	203.7	174.9	187.0	188.7	141.0	188.2	191.8
Rx (Al/Ti)	0.27	0.30	0.22	0.244	0.244	0.325	0.27
(Rx Temp (F.))	(90-110)	(85-105)	(78-90)	(77-120)	(77-120)	(78-83)	
Max Temp	113 F.	119 F.	93 F.	126 F.	126 F.	100 F.	
GPC							
Mw	39718	30446	67566	33791	4065	33996	69155
Mn	9661	7183	9157	7243	1911	6208	11774
M _p	9837	9093	8016	8325	2200	7003	10643
Mw/Mn	4.11	4.24	7.38	4.67	2.13	5.48	5.87

Lesson 7: PVC, CPVC, PVDC, 1,2 DCE

Questions?



Dr. Andy Olah, amo5@case.edu, O: 216-368-0606, C: 216-272-0505

"Just remember, once you're over the hill you begin to pick up speed."

EMAC 276

Lecture 9 : The Polyolefin Family

Polyethylene – PE: Part 1

Polypropylene - PP

Poly(1-butene) – Polybutylene – PB

Andy Olah, Ph.D.

February 10, 2024

EMAC 276 - Homework Assignment #2

Due: Friday, February 14

Dr. Olah

During our classes we identified several common polymers that when initially discovered were described as “value-less”, “impossible to process”, “a useless mass”, etc. We also identified several methods (“tricks”) that were subsequently utilized to develop these polymers into successful products; many which are still with us today.

Your exercise is to select one polymer (either from our in-class discussion or from outside our class discussion) and describe 1) the polymer and the initial performance deficiency, 2) the action taken to overcome this deficiency, and, 3) the ensuing product(s) developed from this modification.

If you choose to use an “in class” example your maximum score will be 10.

If you choose to use an “outside the class” example your maximum score will be 12. (i.e., final score +2)

Your answer shall be short comprising between one-half to one page.

Your answer is shall be structured accordingly:

Paragraph #1: Identify and describe the polymer and it's initial deficiency **(3 Points)**

Paragraph #2: Identify the modification or “trick” which was utilized to overcome this deficiency. **(5 Points)**

Paragraph #3: Identify the commercial product or products resulting from this modification. **(2 Points)**

What is a “Olefin” Type Polymer?

Vinyl polymers are the most common type of polymers derived from “vinyl-type” monomers having the general structure:



Where,

polystyrene – R = C₆H₅

polyvinyl chloride – R = Cl

polyvinyl acetate – R = O₂CCH₃

polyacrylonitrile - R = CN

Not to be confused with poly(vinyl chloride) (PVC) materials which have traditionally been identified as “Vinyls”; i.e., vinyl siding, vinyl records, etc.

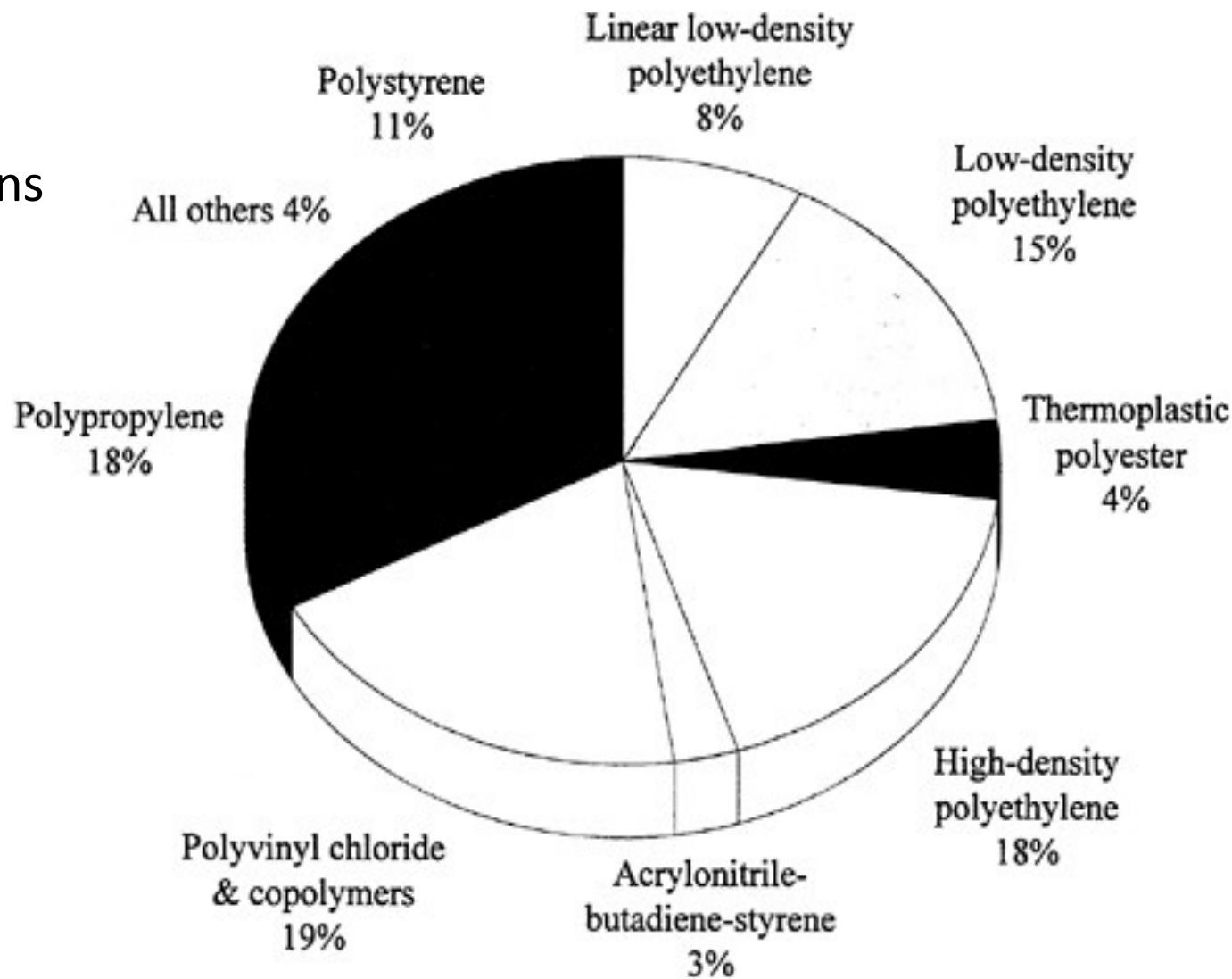
Olefin polymers are a subgroup of vinyl monomers produced from alkenes having a C_nH_{2n} monomer structure:

polyethylene – R = H => CH₂ = CH₂; (n = 2) => C₂H₄

polypropylene – R = CH₃ => CH₂ = CH-CH₃; (n = 3) => C₃H₆

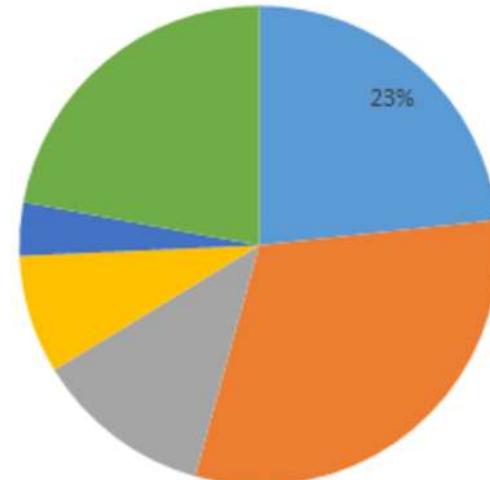
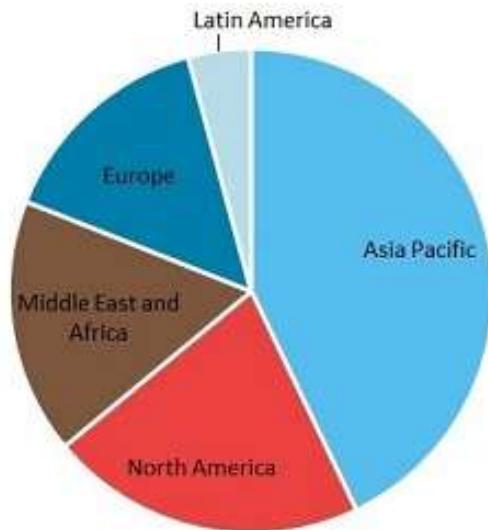
polybutylene – R = CH₂-CH₃ => CH₂ = CH-CH₂-CH₃; (n=4) => C₄H₈

The Polyolefin Resins Represent the Largest Volume of Polymer Resins in the Global Market Comprising 59%



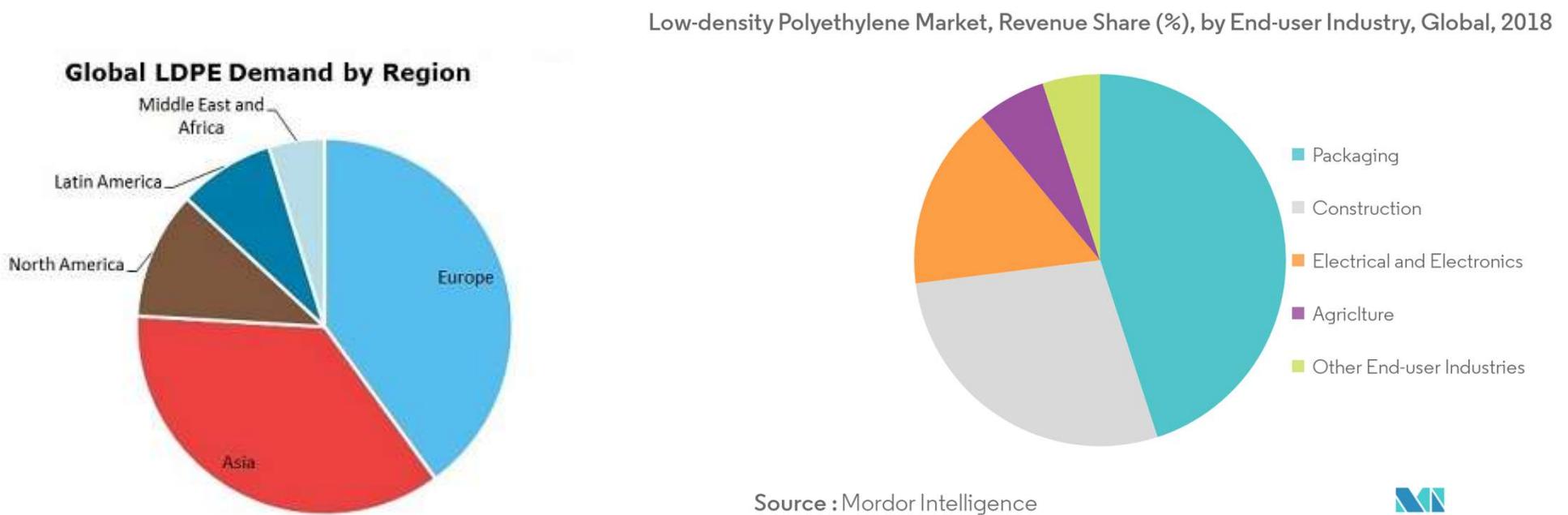
Global HDPE Production and Market

Global HDPE Capacity by Region



- Injection Molded
- Blow Molded
- HDPE Pipes
- HDPE Films
- Colored HDPE
- Others

Global LDPE Demand and Market



Early History of Polyethylene Polymerization

1894 - Accidentally discovered by Hans von Peckmann by decomposition of diazomethane producing a white powder. Analysis indicated it was simply made up of carbon and hydrogen with repeat units of (– CH₂ –).

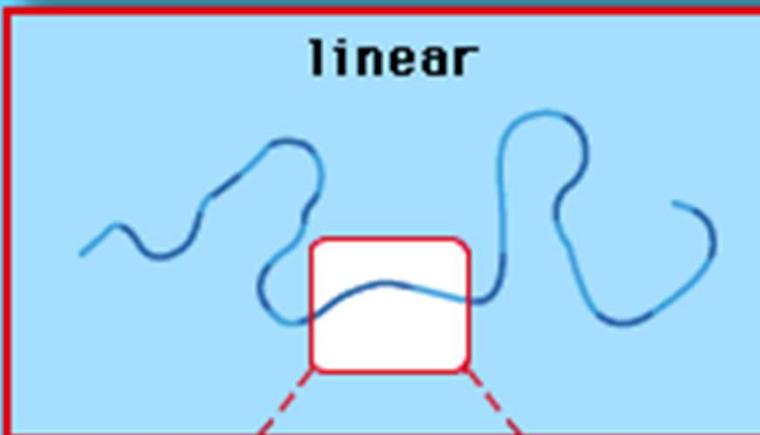
1929 - Friedrick and Marvil produced a low molecular weight material by reacting ethylene with n BuLi.

1933 – Eric Fawcett and Reginald Gibson at Imperial Chemical Industries (ICI) studying ethylene and benzaldehyde at high temperatures. A white waxy material was produced. The reaction was caused by free radicals produced by retained oxygen in the system.

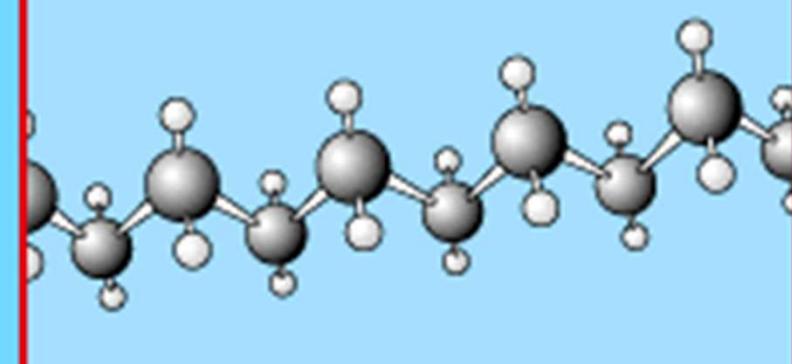
1939 – Michael Perrin at ICI was able to produce large quantities of polyethylene by the high pressure polymerization method which allowed commercial production to ensue.

Polyethylene is a Very Basic Polymer

linear



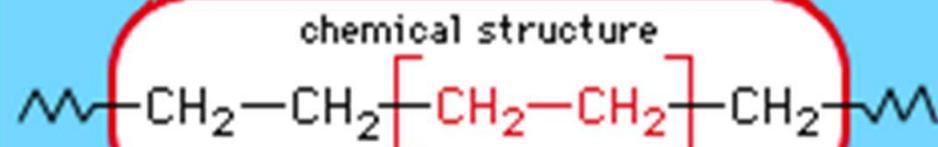
molecular structure



high-density polyethylene (HDPE)

● carbon (C)

● hydrogen (H)



The Simplest of Molecular Structures Can Lead to a Large Diversity of Structure and Morphology

Three fundamental features of polyethylene leading to the diversity of structures and in turn performance are:

- a. Short chain and long chain branching.
- b. Co-monomer content and distribution.
- c. Molecular weight and molecular weight distribution.

These Variations of Polyethylene Lead to a Diversity of Products

Linear Versions:

- High density polyethylene (HDPE)
- Ultra-high molecular weight polyethylene (UHMWPE)

Branched Versions:

- Low-density polyethylene (LDPE)
- Linear low density polyethylene (LLDE)
- Medium-density polyethylene (MDPE)
- Very-low-density polyethylene (VLDPE)
- High-molecular-weight polyethylene (HMWPE)
- Ultra-low-molecular-weight polyethylene (ULMWPE)
- Chlorinated polyethylene (CPE)

Bimodal and Trimodal Polyethylene

Cross-linked polyethylene (PEX): four forms (PEX-a, PEX-b . . etc)

The Variance of Most Polyethylene Products is Based on Branching



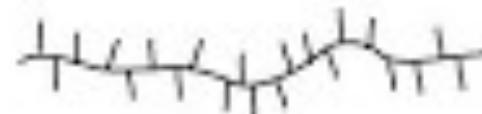
High-Density Polyethylene (HDPE)
 $X_c \sim 55\text{-}77\%$ $T_m \sim 125\text{-}132^\circ\text{C}$



Low-Density Polyethylene (LDPE)
 $X_c \sim 30\text{-}54\%$ $T_m \sim 98\text{-}115^\circ\text{C}$

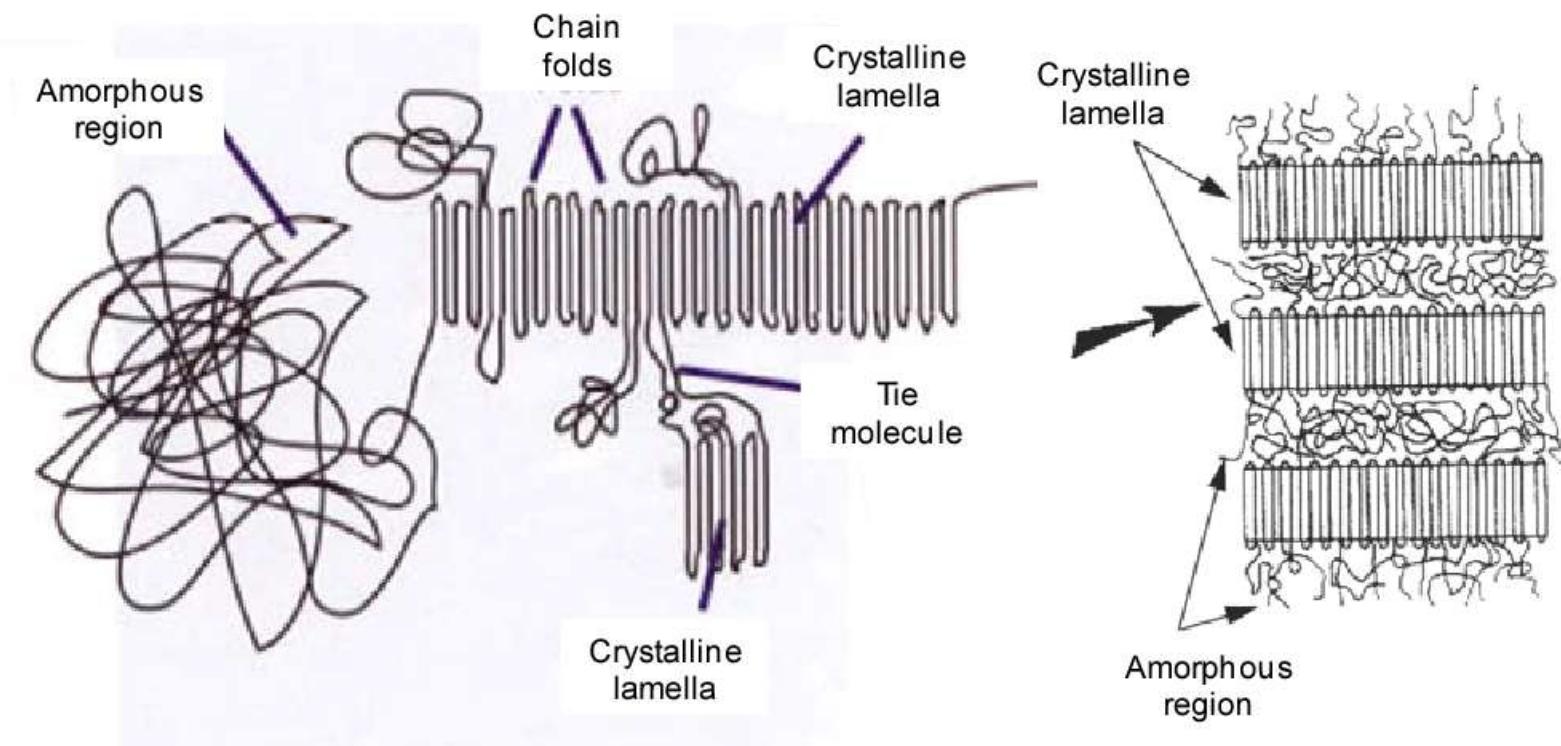


Linear Low-Density Polyethylene (LLDPE)
Branching density ~ 25-100 C atoms
 $X_c \sim 22\text{-}55\%$ $T_m \sim 100\text{-}125^\circ\text{C}$

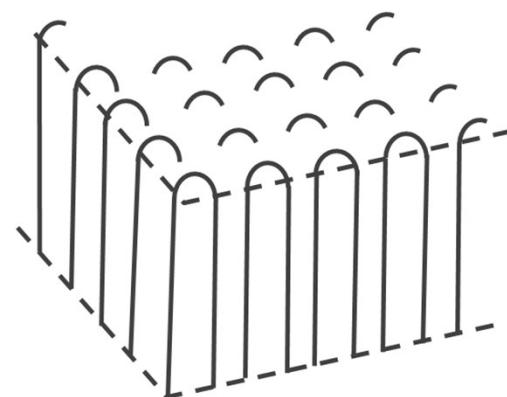
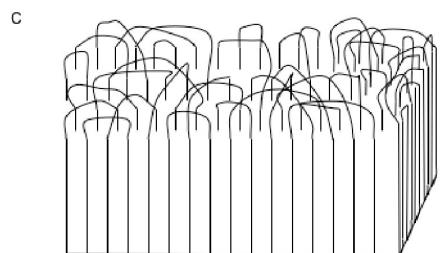
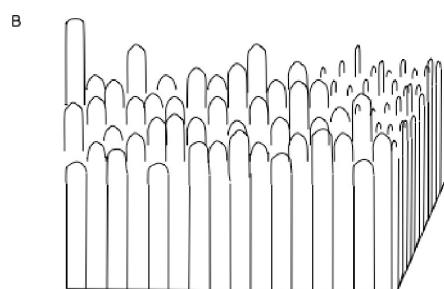
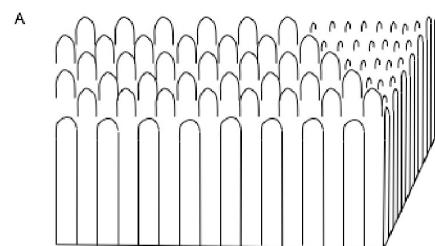


Very Low-Density Polyethylene (VLDPE)
Branching density ~ 7-25 C atoms
 $X_c \sim 0\text{-}22\%$ $T_m \sim 60\text{-}100^\circ\text{C}$

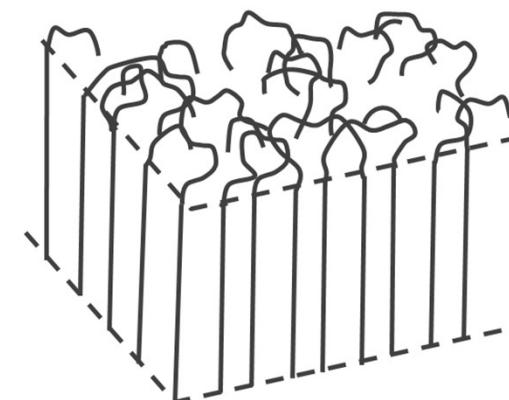
Polyethylene is a Semi-crystalline Material having both Amorphous and Crystalline Regions



The Polyethylene Molecules in the Crystalline Domains are Chain Folded



Adjacent Re-entry Model

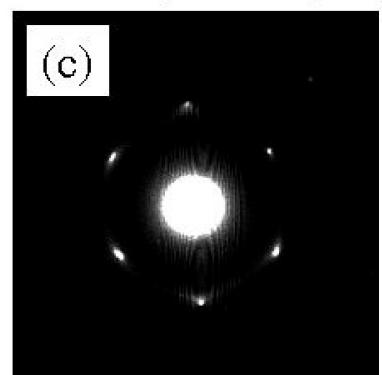
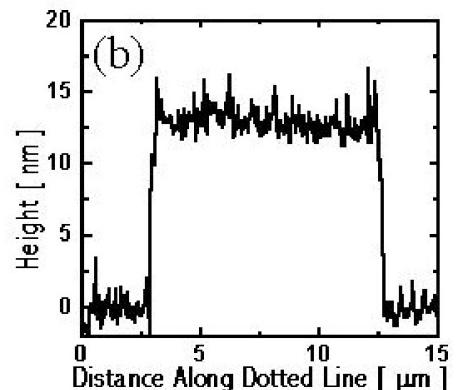
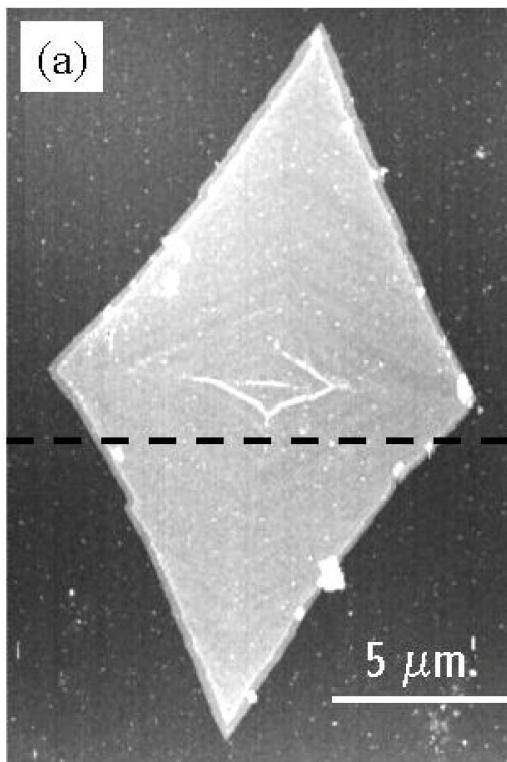
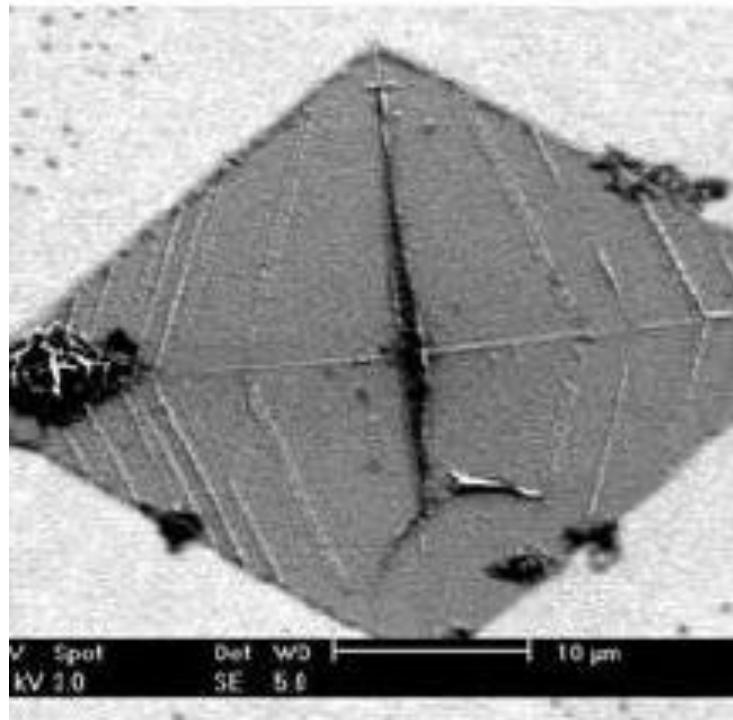


Switchboard Model

Polyethylene Single Crystal Growth from Solution

- Polyethylene was of $M_w=32,100$ and $M_w/M_n=1.11$ (32 K fraction), and of $M_w=119,600$ and $M_w/M_n=1.19$ (120 K fraction).
- From octane and hexadecane solutions, single crystals were obtained by isothermal crystallization at 94.0 and 99.0 °C, respectively. After the crystallization, the dispersion of single crystals was dropped on an aqueous solution of poly(vinyl alcohol) (PVA). Aqueous solution was 7 wt%. After drying PVA at room temperature, the single crystals distributed on the surface of PVA were observed with an atomic force microscope in a dynamic force mode in air.

Results of Growing a Polyethylene Single Crystal from Solution



Schematic Representation of a Polyethylene Single Crystal Grown from Solution

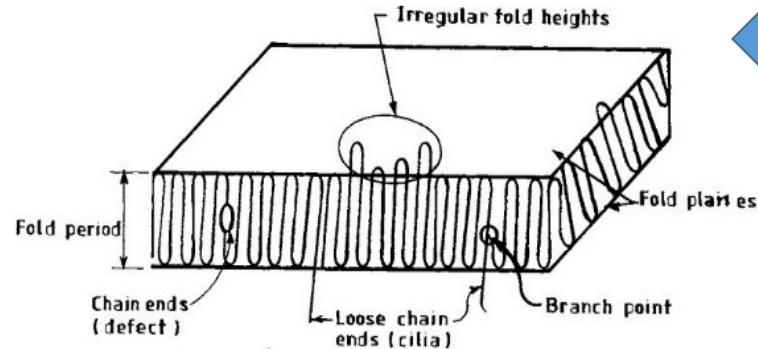


Figure 3.16 Schematic diagram of chain folding showing conformational imperfections.

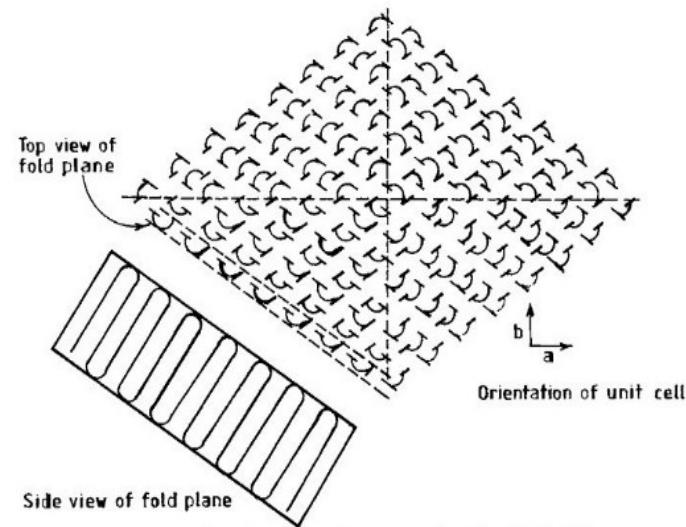
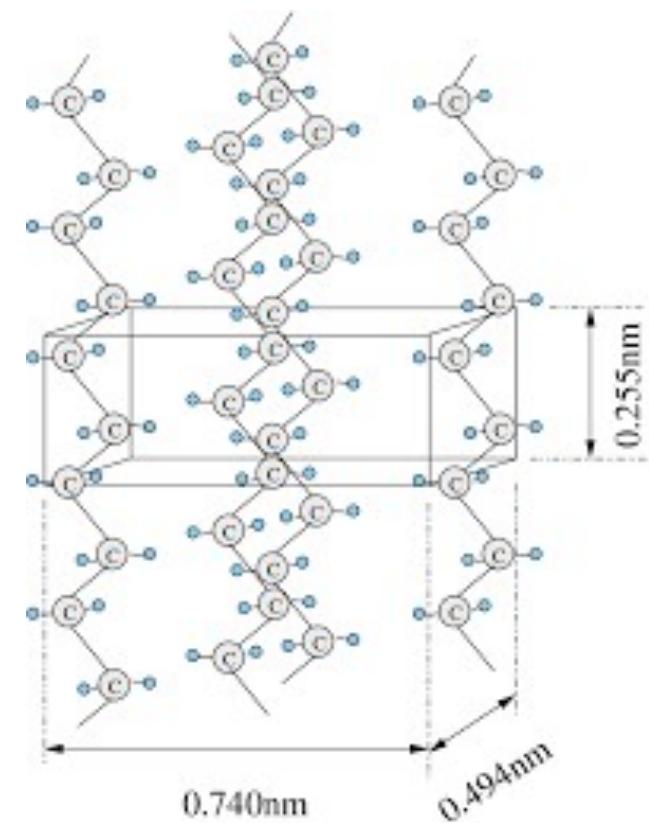


Figure 3.17 Fold packing in a polyethylene single crystal. (From Reneker, D.H. and Geil, P.H., *J. Appl. Phys.*, 31, 1916, 1960. With permission.)



Unit Cell Dimensions of Crystalline Polyethylene

Polyethylene Single Crystals have Three Dimensional Structure

Polyethylene single crystals

(A fantastic electron micrograph by D.C. Bassett)



PE crystallised from solution can form beautiful crystals. Here is an electron micrograph of a stack of PE Chain Folded crystals that have grown on top of each other. The symmetry is incredible when you think that these crystals are formed from one of the most flexible polymer chains in the world.

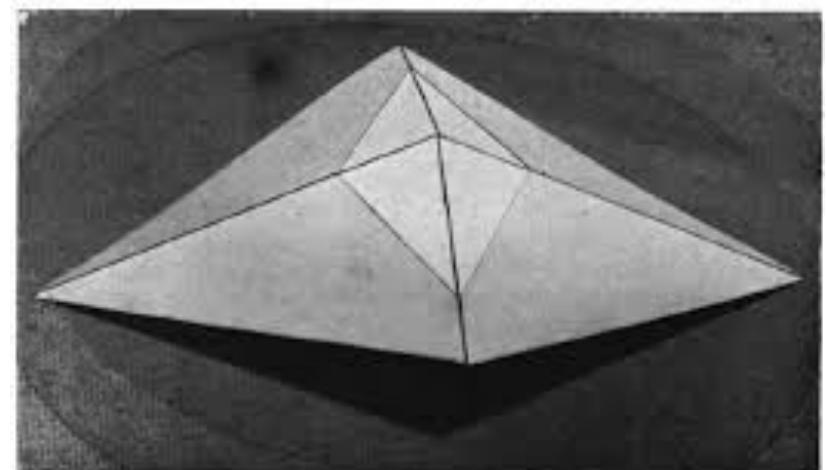
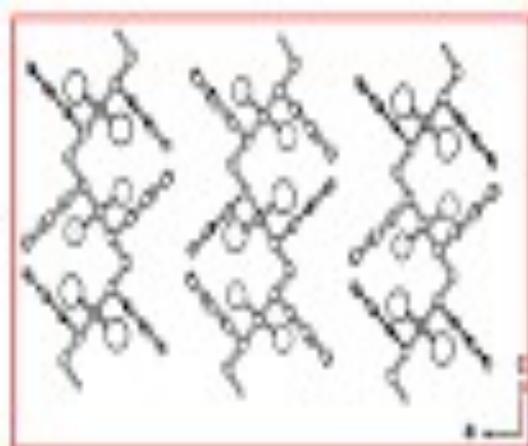
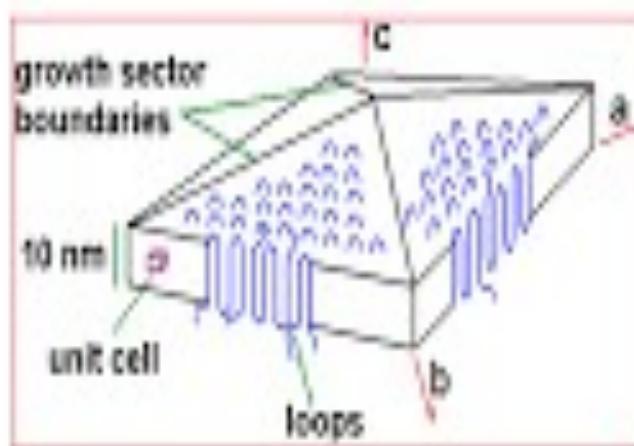


Figure 9—Model of a non flat-based hollow pyramid. This is the true three-dimensional configuration of some of the simplest monolayer polyethylene crystals. The transparent disc illustrates the relation of the pyramid to a flat base (plane perpendicular to the pyramid axis).

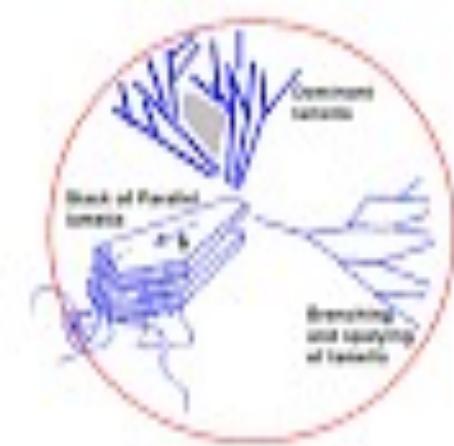
Spherulitic Growth from Propagating Polyethylene Lamella



crystal
structure



folded chains packed
in a lamellae



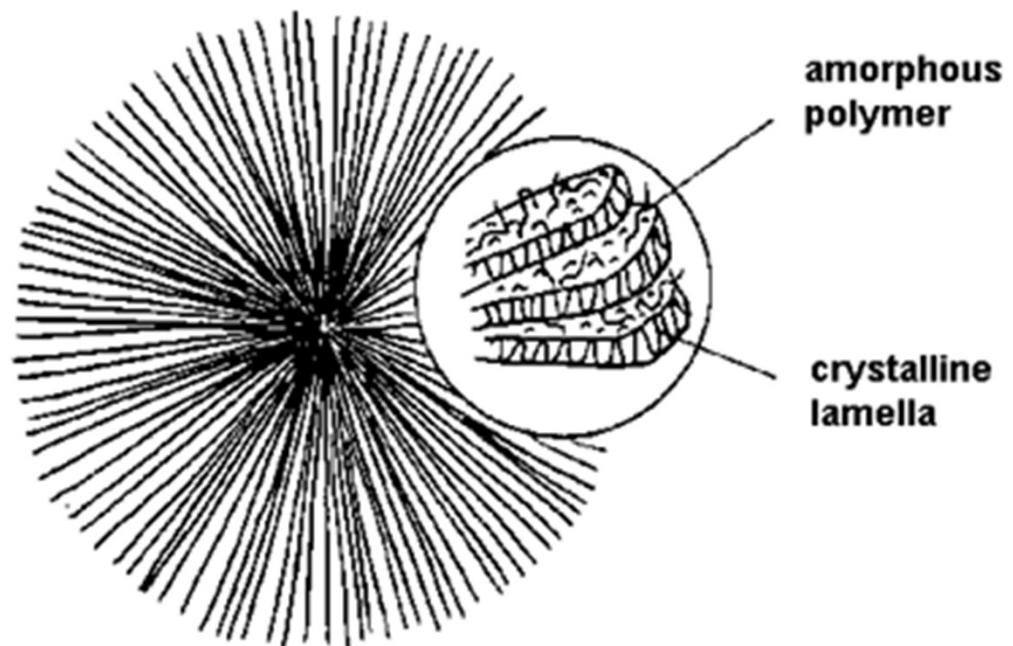
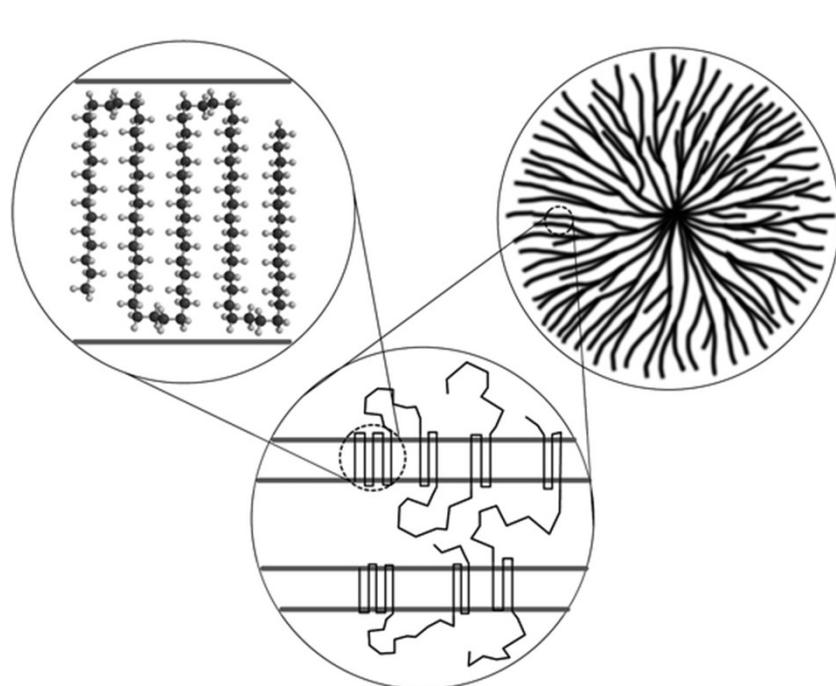
stacked lamellar
structures in a spherulite

Å

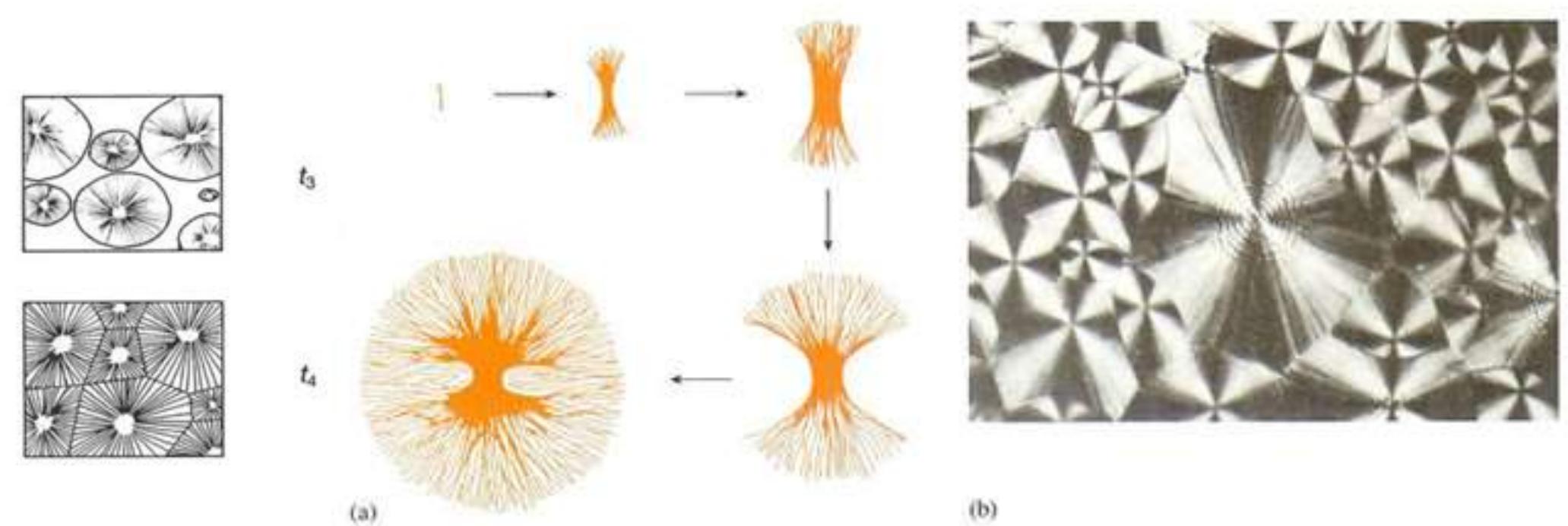
nm

μm

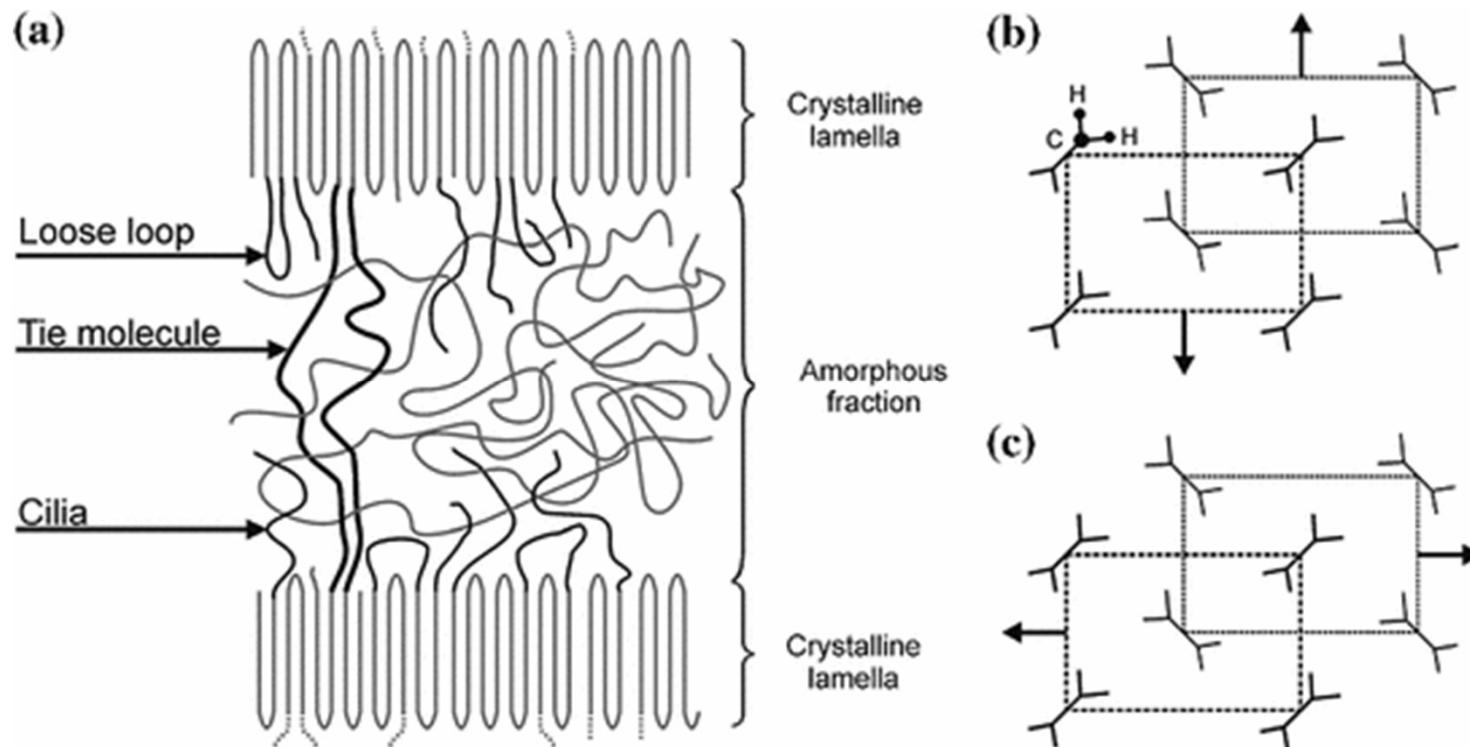
Spherulitic Growth from Propagating Polyethylene Lamella



Formation of Bulk Polyethylene by Spherulitic Growth



The Interlamellar and Interspherulitic Regions are the Amorphous Regions of Polyethylene



Boyer proposed that there exists two glass transition temperatures for polyethylene.

Glass Temperatures of Polyethylene

Raymond F. Boyer

The Dow Chemical Company, Midland, Michigan 48640. Received July 3, 1972

Macromolecules, 6, 288 – 299 (1973)

J. Poly., Sci., Symposium No. 50, 189 – 242 (1975)

"Linear and branched polyethylenes, especially in the Range of 50 – 75% crystallinity,, exhibit three amorphous Phase transitions or relaxation phenomena at the following temperature regions: 145 ± 10 K (-128 ± 10 C), 195 ± 10 K (-78 ± 10 C) and 240 ± 20 K (-33 ± 20 C)."

"Each of these regions has one or more characteristics of a true glass transition, i.e., an abrupt increase in the Coefficient of thermal expansion, and an abrupt increase in the specific heat; a dynamic mechanical loss peak Whose magnitude increases with amorphous content; . . ."

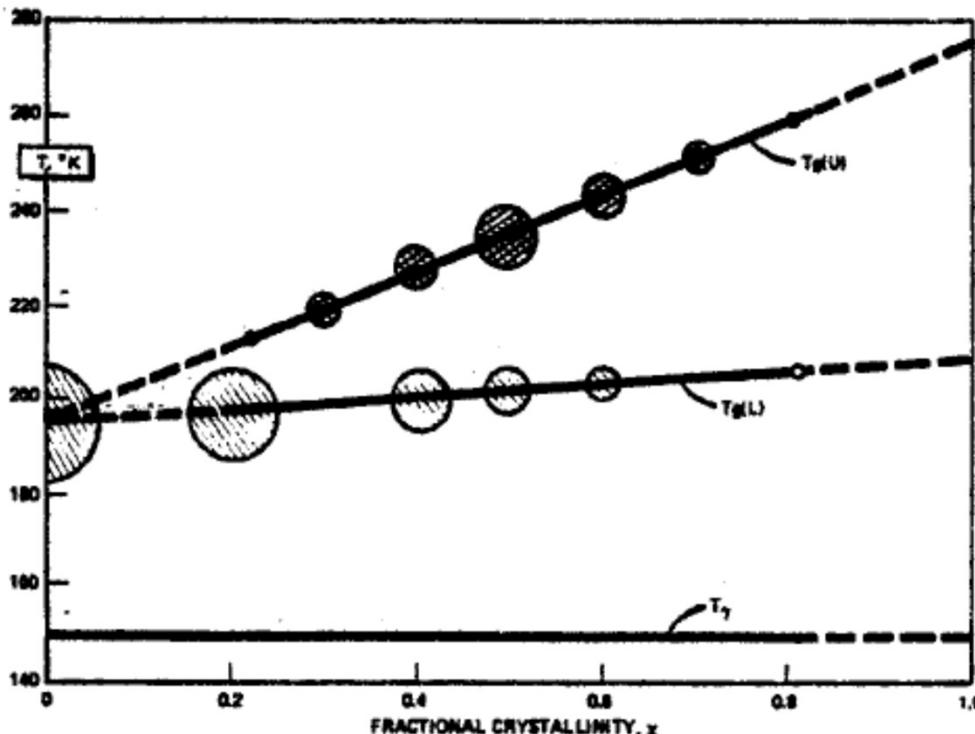


Figure 1. The double glass transition, $T_g(L)$ and $T_g(U)$, and the T_y amorphous relaxation in linear polyethylene. The size of the circles indicate the intensity of the two glass transitions. Intensity of the T_y transition increases continuously to the left. We associate $T_g(L)$ with cilia and polymer chains rejected by crystallites; and $T_g(U)$ with loose loops and/or tie molecules. This plot has been estimated by us from the thermal expansion data of Stehling and Mandelkern.²

Proposed Origin of $T_g(L)$ and $T_g(U)$

(4) Partially crystalline polyethylenes exhibit two glass transitions: a $T_g(L)$ around 195 K (-78 C) and a $T_g(U)$ around 240 K (-33 C) but both increase linearly with crystallinity. (5) These are ascribed to the existence of two types of amorphous material. For example, $T_g(L)$ may be associated with cilia and $T_g(U)$ may arise from loose loops and or tie molecules.

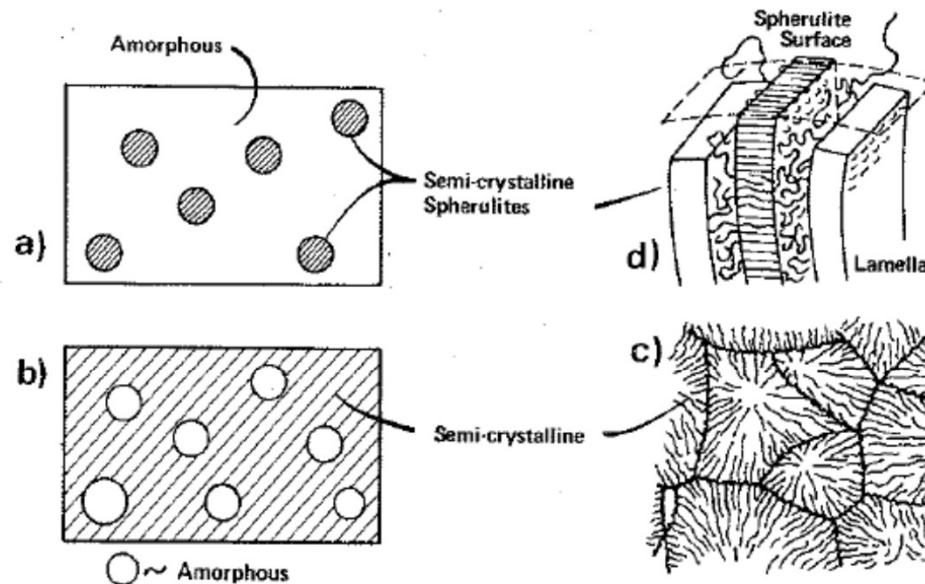
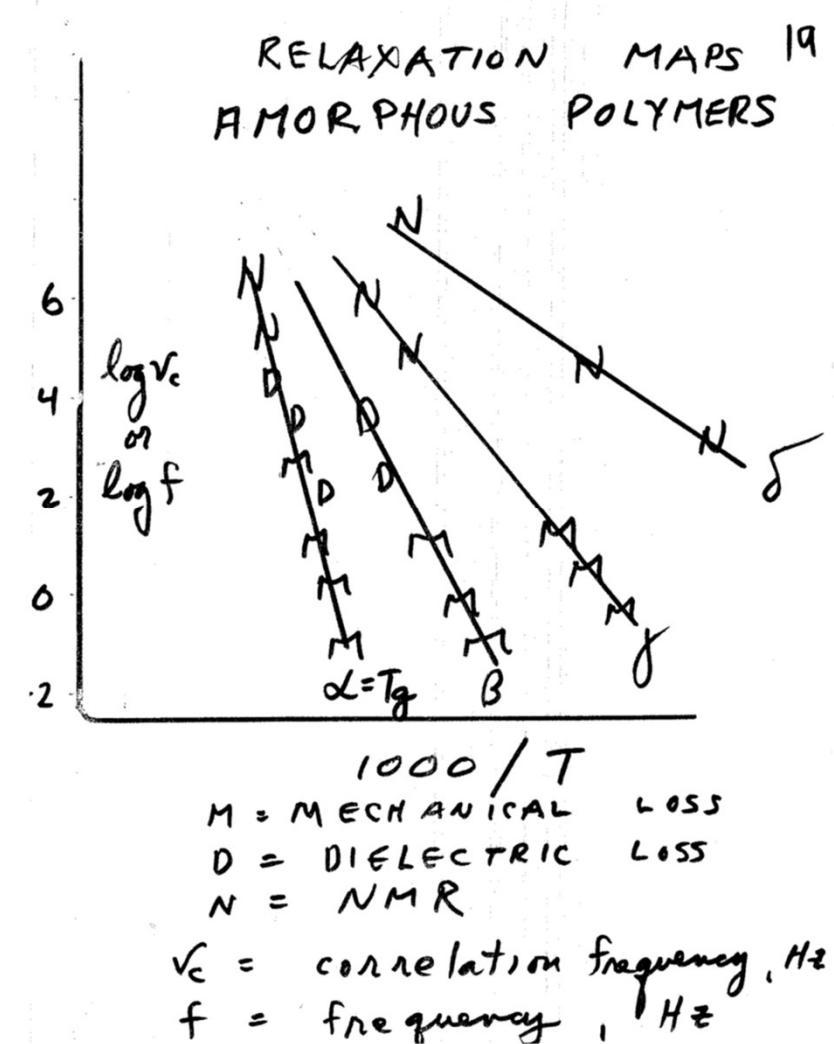


FIG. 9. Schematic morphology for the existence of a double glass transition. (a) isolated spherulites in continuous amorphous phase of $T_g = T_g(L)$; (b) rejected amorphous material of $T_g(L)$ at high x_c , actually appearing in grain boundaries as at (c); (d) Takayanagi model [34] showing interlamellar disorganized, or amorphous, material which may give rise to $T_g(U)$.

Image of Ray Boyer and Ray Boyer's class notes.



Plastics Hall of Fame Inductee



Critical Properties for the Differentiation of the Polyethylene Types

Density

Crystalline Region

Perfect 1.00 g/cm³

Unit Cell Calculation (orthorhombic) 0.996

Single Crystal Determination 0.972

Amorphous Region 0.850 – 0.855

Transition Temperatures

Glass Transition Temperature -78 C

Melt Transition Temperature (density dependent) 130-140 C

The Most Common Classification of Polyethylene is by Density

Table 1. Classification of polyethylenes by density

<i>Resin family</i>	<i>Lower density limit g/cc</i>	<i>Higher density limit g/cc</i>
High Density Polyethylene (HDPE)	0.941	0.975
Medium Density Polyethylene (MDP)	0.928	0.941
Linear Low Density Polyethylene(LLDPE/LDPE)	0.915	0.928
Very Low Density Polyethylene (VLDPE)	0.900	0.915
Elastomers/Plastomers	0.865	0.900

Lesson 9: Polyolefins – PE 1

Questions?



Dr. Andy Olah, amo5@case.edu, O: 216-368-0606, C: 216-272-0505

“You always had the power my dear, you just had to learn it for yourself.”

*Glenda, (the good witch)
The Wizard of Oz (1939)*

EMAC 276

Lecture 12 : The Polyolefin Family

Polyethylene – PE: Part 4: PE ULMWPE, UHMWPE, Multimodal

Polypropylene - PP

Poly(1-butene) – Polybutylene – PB

Andy Olah, Ph.D.

February 17, 2025

There will be a quiz on Monday, February 24th



* From the Hitchhikers Guide to the Galaxy – Douglas Adams

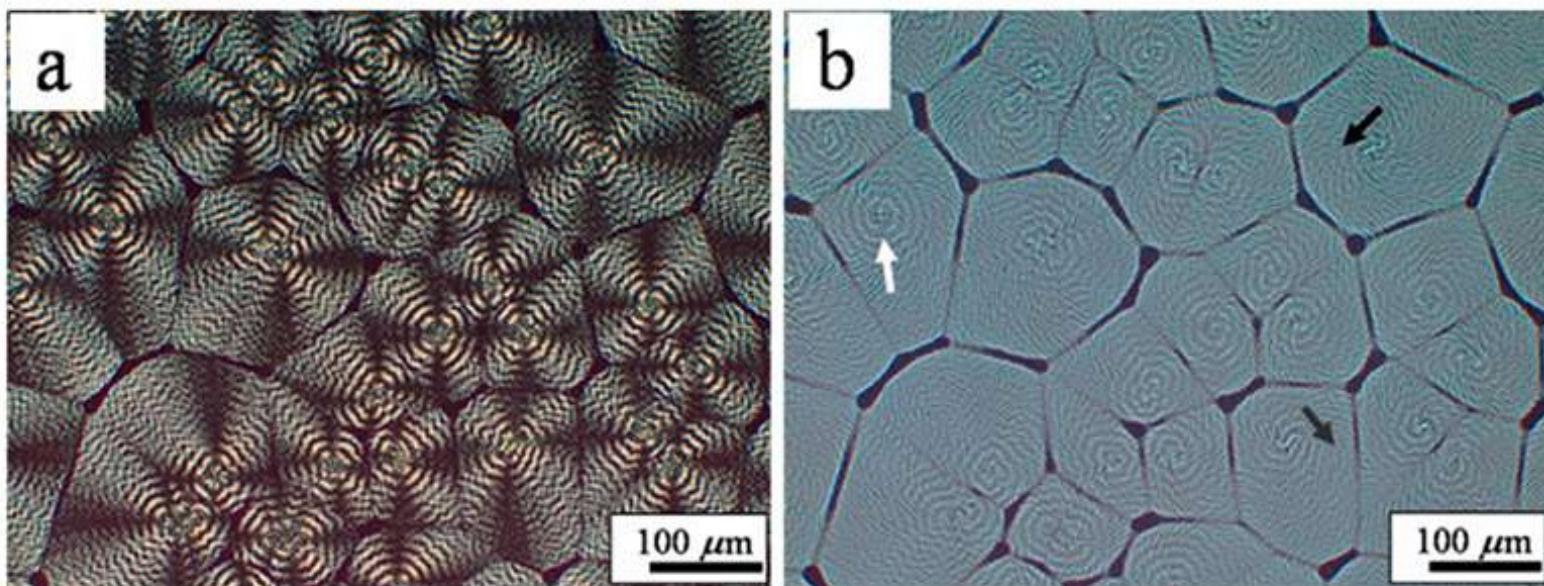


Figure 8. POM (**a**) and OM (**b**) micrographs of $\text{PCL}_{84.4\text{k}}$ CEBS formed from a $50 \text{ mg}\cdot\text{mL}^{-1}$ solution-cast film. Reproduced from [49] with permission from the Royal Society of Chemistry.

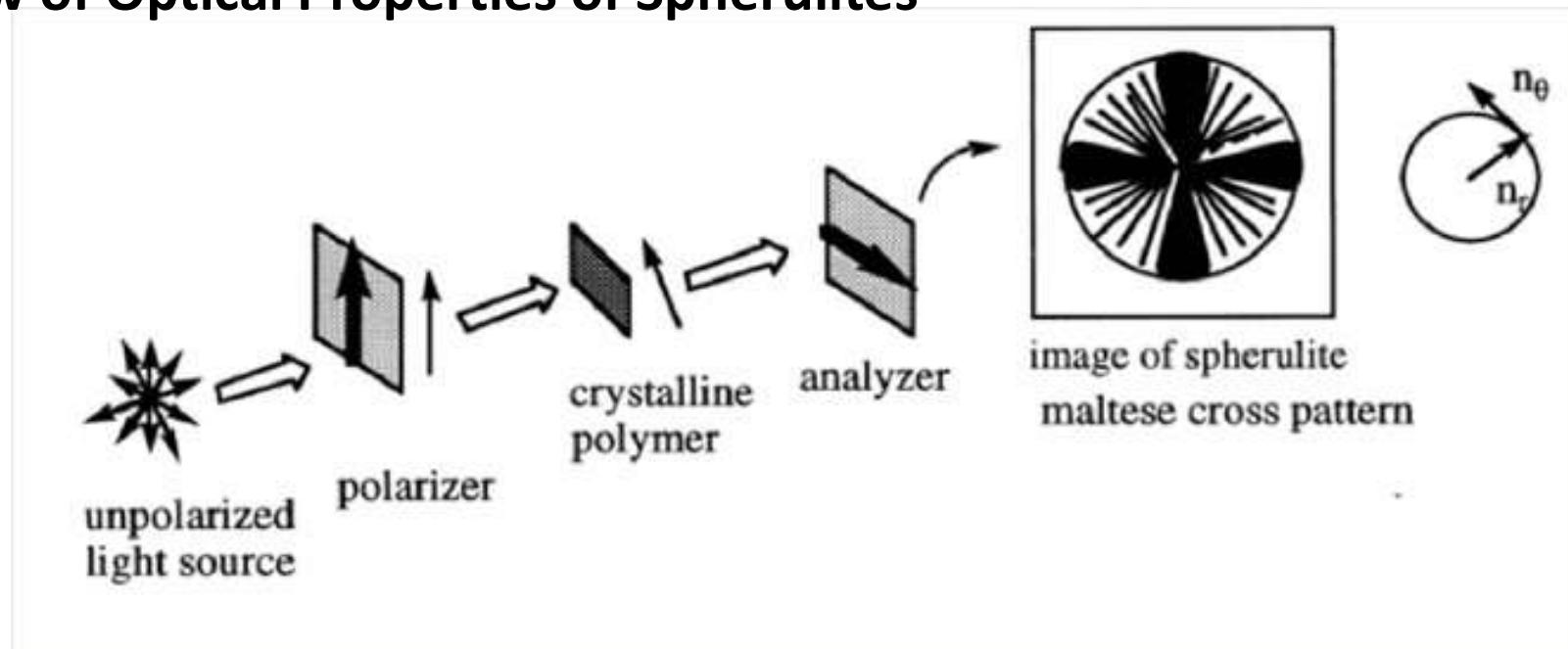
Review

Morphological Control of Polymer Spherulites via Manipulating Radial Lamellar Organization upon Evaporative Crystallization: A Mini Review

Yiguo Li ^{1,*}, Zongbao Wang ^{2,*} and Tianbai He ³

Review of Optical Properties of Spherulites

Review of Optical Properties of Spherulites



The Maltese cross is seen because polymers are birefringent. Polarised light cannot travel through a crystalline polymer if the direction of the polarisation of the light is perpendicular to the direction of carbon chain in the polymer. As a result, when a sample is studied under crossed polars, only those polymer chains perpendicular to neither polariser nor the analyser are visible - these are at approximately 45° to each polaroid.

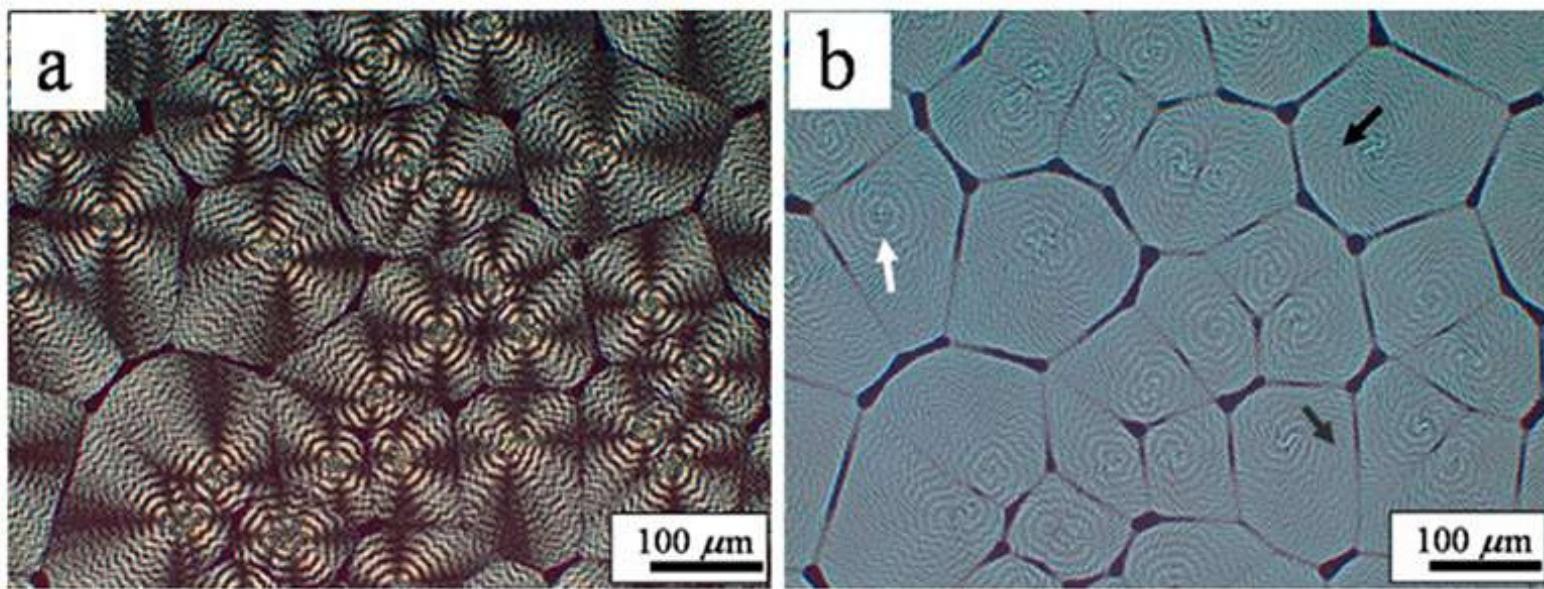


Figure 8. POM (**a**) and OM (**b**) micrographs of $\text{PCL}_{84.4\text{k}}$ CEBS formed from a $50 \text{ mg}\cdot\text{mL}^{-1}$ solution-cast film. Reproduced from [49] with permission from the Royal Society of Chemistry.

Review

Morphological Control of Polymer Spherulites via Manipulating Radial Lamellar Organization upon Evaporative Crystallization: A Mini Review

Yiguo Li ^{1,*}, Zongbao Wang ^{2,*} and Tianbai He ³

Crystals **2017**, *7*, 115; doi:10.3390/crust7040115

Review of Optical Properties of Spherulites

Review of Optical Properties of Spherulites

Banded spherulites and twisting lamellae in poly- ϵ -caprolactone

Wilhelm Kossack¹ · Friedrich Kremer¹

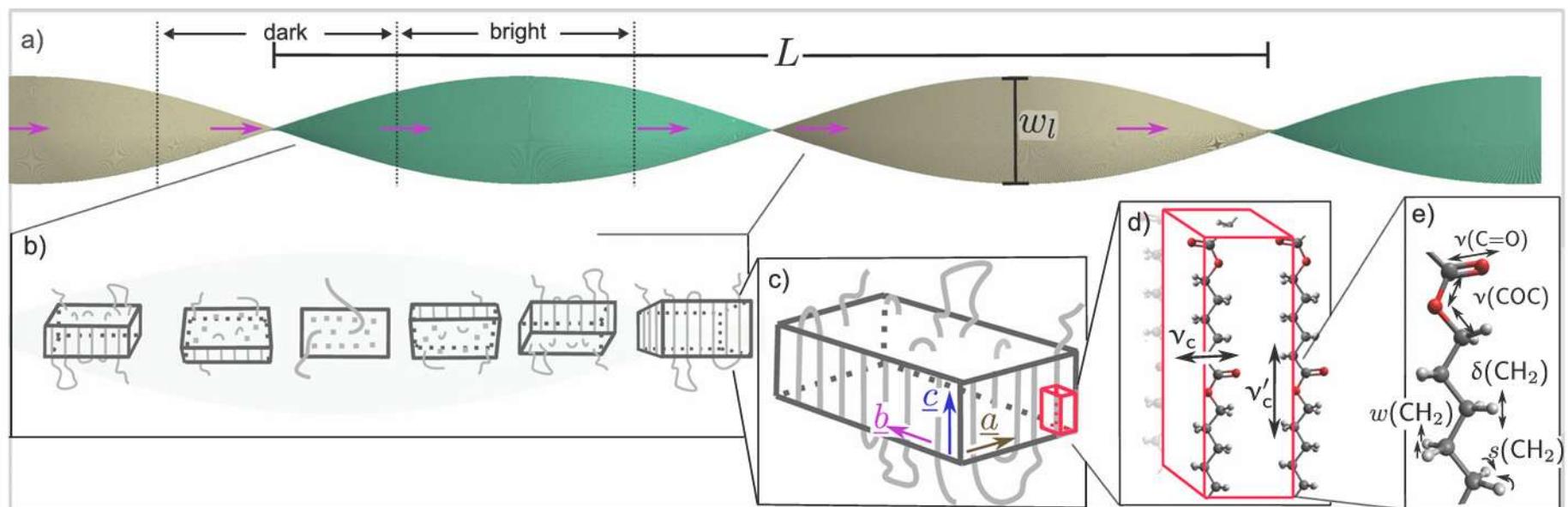


Fig. 7 Proposed model of a helicoidally growing lamellae (a twisted ribbon) within a spherulite of PCL. Green and beige coloring is a guide for the eye and marks the two sides of the lamellae. Lamellar growth direction (*b*) is indicated by magenta arrows. Orientation of parts of the growing lamellae are indicated by gray outlines on the twisted ribbon

in b. In panel (c), the orientation of the polymer strands and the crystalline unit cell (red) are indicated together with the crystal axes of the lamella. Panels (d) and (e) show the molecular structure and IR active transition dipole moments of the crystalline unit cell (d) and the monomer (e)

These Variations of Polyethylene Lead to a Diversity of Products

Linear Versions:

High density polyethylene (HDPE)

Ultra-high molecular weight polyethylene (UHMWPE)

Branched Versions:

Low-density polyethylene (LDPE)

Linear low density polyethylene (LLDE)

Medium-density polyethylene (MDPE)

Very-low-density polyethylene (VLDPE)

High-molecular-weight polyethylene (HMWPE)

Ultra-low-molecular-weight polyethylene (ULMWPE)

Chlorinated polyethylene (CPE)

Bimodal and Multimodal Polyethylene

Cross-linked polyethylene (PEX): four forms (PEX-a, PEX-b . . etc)

Simplest of Molecular Structures Can Lead to a Large Diversity of Structures.

Three fundamental features of polyethylene leading to the diversity of structures and in turn performance are:

- a. Short chain and long chain branching.
- b. Co-monomer content and distribution.
- c. **Molecular weight and molecular weight distribution.**

Molecular weight Dependence on Polyethylene Properties

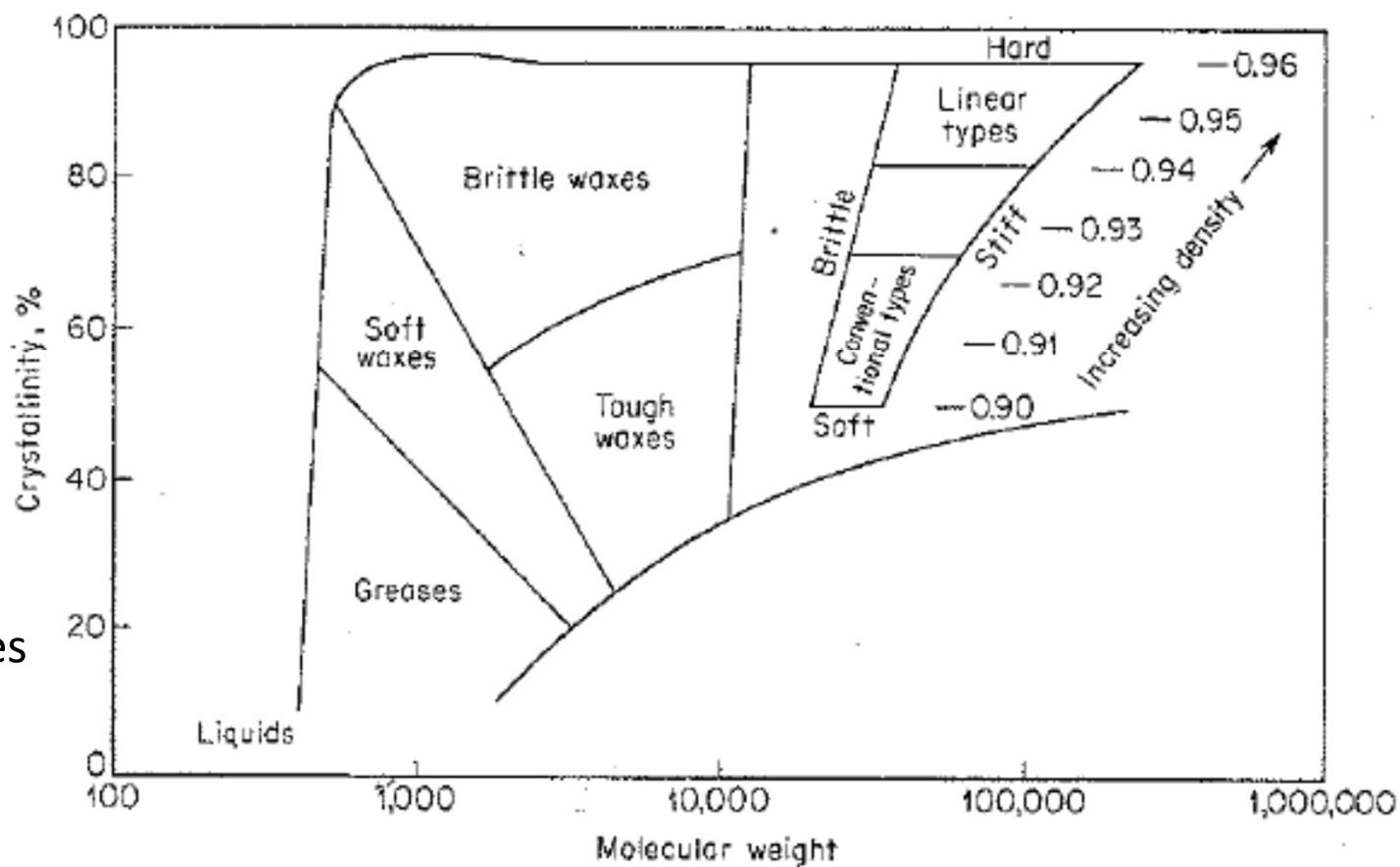


FIGURE 13-1

Relationships between crystallinity, molecular weight, and mechanical properties of polyethylene [3]. (After Kratz and Lyle, *Encyclopedia of Chemical Technology*, First Suppl., Interscience, 1957.)

Ultralow Molecular Weight Polyethylene

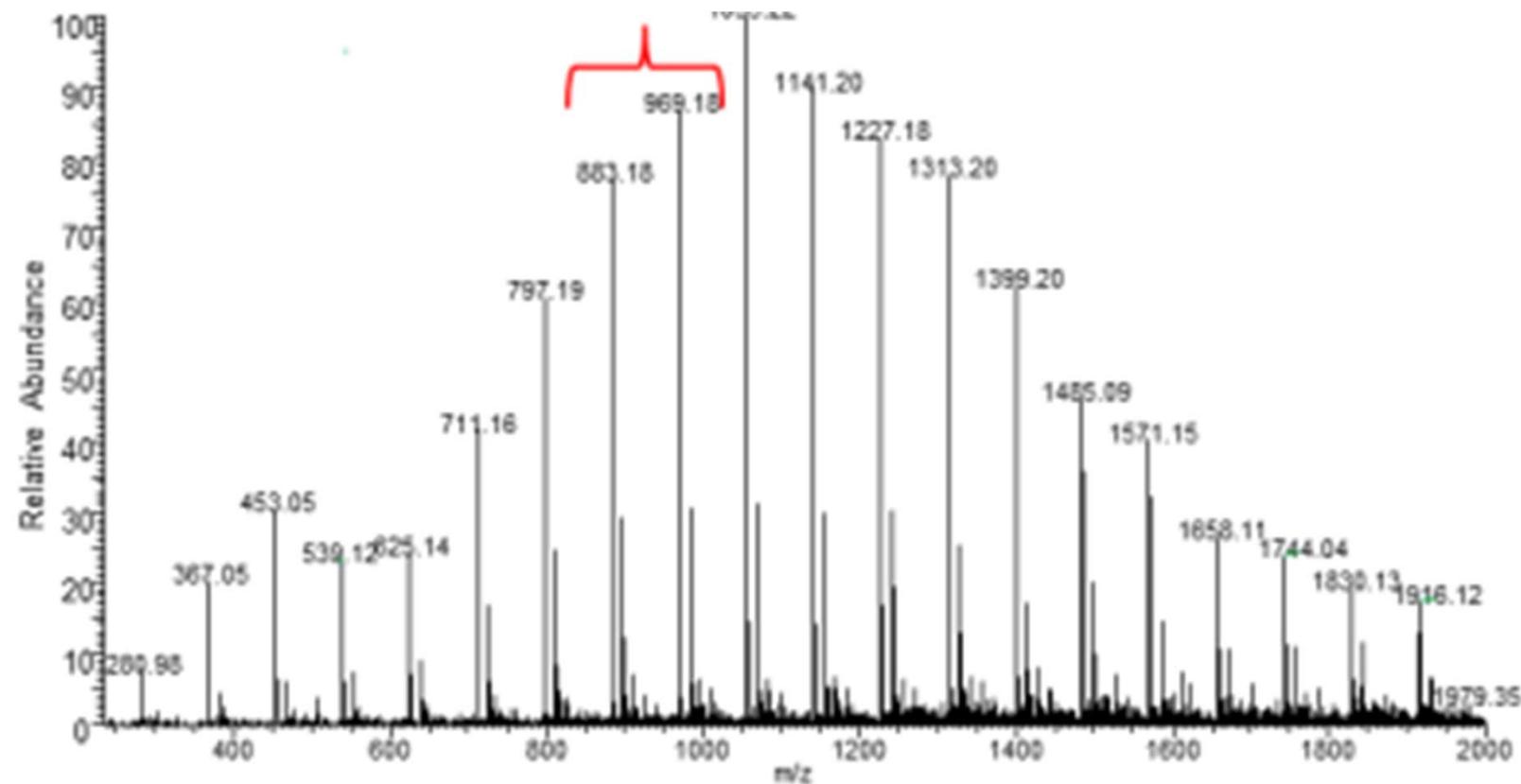
Polyethylene Wax, also known as PE Wax, is an ultra low molecular weight polyethylene consisting of ethylene monomer chains.

PE wax has a large variety of uses and applications.

PE Wax is available from on-purpose production and as a byproduct of polyethylene production. This material is available in both HDPE and LDPE forms.

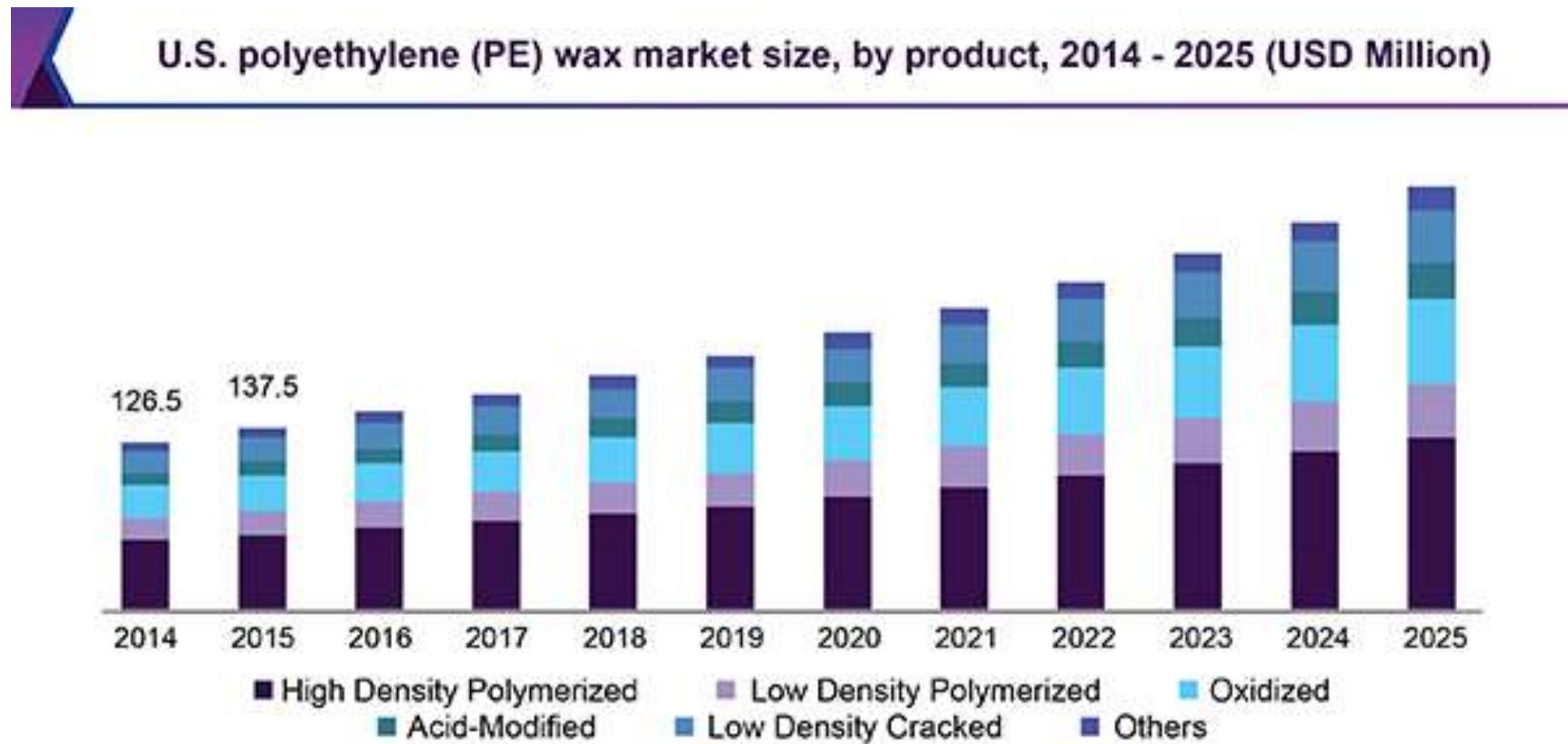


MW Distribution of OPE Wax



Polyethylene Waxes	Melting Point (°F)	Melting Point (°C)	Viscosity at 300°F, cPs	Penetration, at 77 °F , dmm
Indrapol 31	230-240	110-116	10-50	3 typ
Indrapol 70	235-245	113-118	60-100	2 typ
Indrapol 100-C	212-248	100-120	30-70	9 max
Indrapol 235	225-245	107-118	55 max	9 max
Indrapol 400-C	239-250	115-121	350-450	1 typ
Indrapol 400-H	223 typ	106 typ	375 typ	4 typ
Indrapol 34-OX (oxidized)	229-239	109-115	20-40	4 max

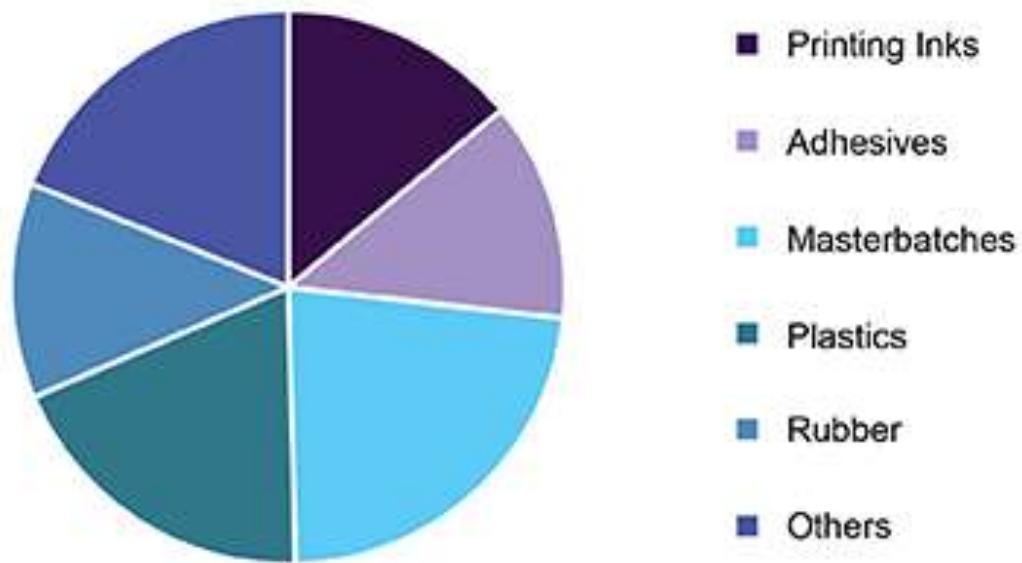
Market Size of ULDPE (Wax)



Source: www.grandviewresearch.com

Applications of ULMWPE

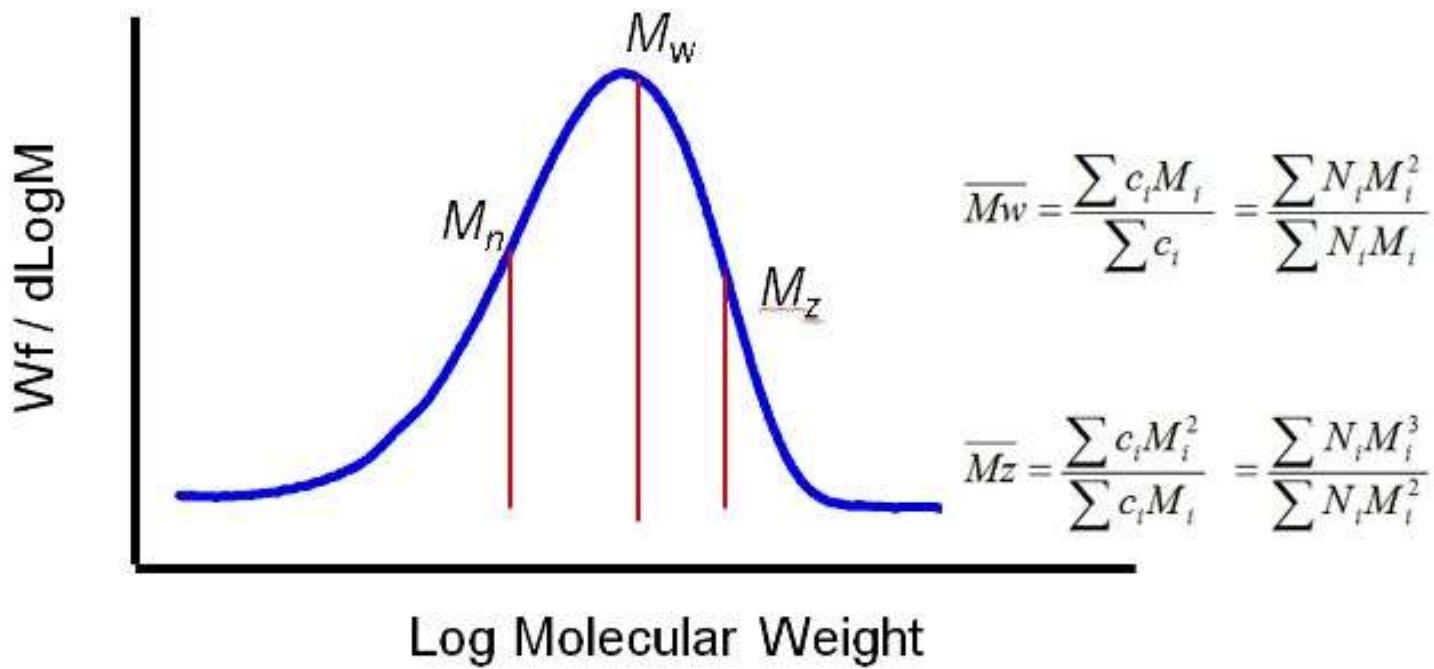
Polyethylene (PE) wax market share, by application, 2018 (%)



Source: www.grandviewresearch.com

Review of Molecular Weight and Molecular Weight Distribution

$$\overline{M_n} = \frac{\sum c_i}{\sum c_i / M_i} = \frac{\sum N_i M_i}{\sum N_i}$$



Viscosity Average Molecular Weight (M_v)



VISCOSITY MEASUREMENT

Ubbelohde Viscometer, for measuring viscosity of dilute solution

upper and lower level

(measure the flow time t , of solution, drop from upper level to lower level)

$$\eta = kpt$$

k = viscometer constant

ρ = density of solution

t = flow time

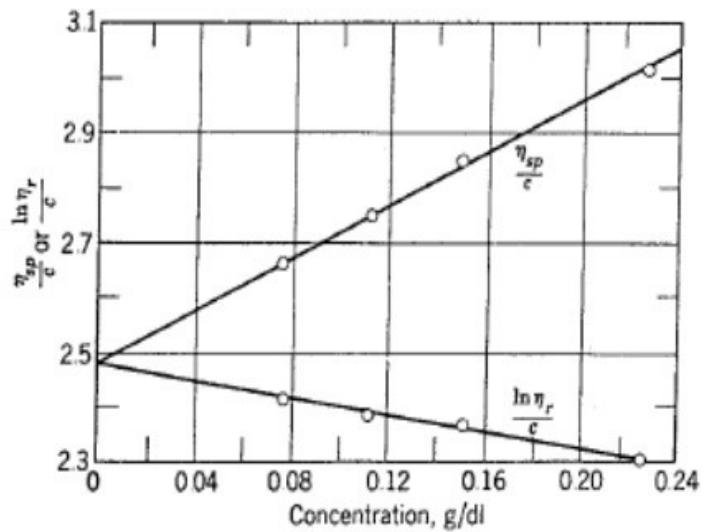
If, t = time for solution

t_0 = time for solvent

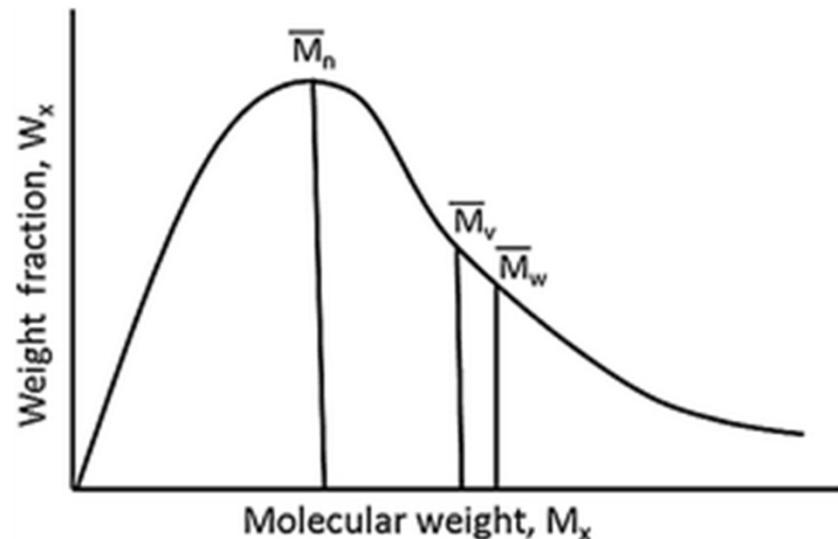
$\rho = \rho_0 \therefore$ dilute solution

ρ_0 = solvent density

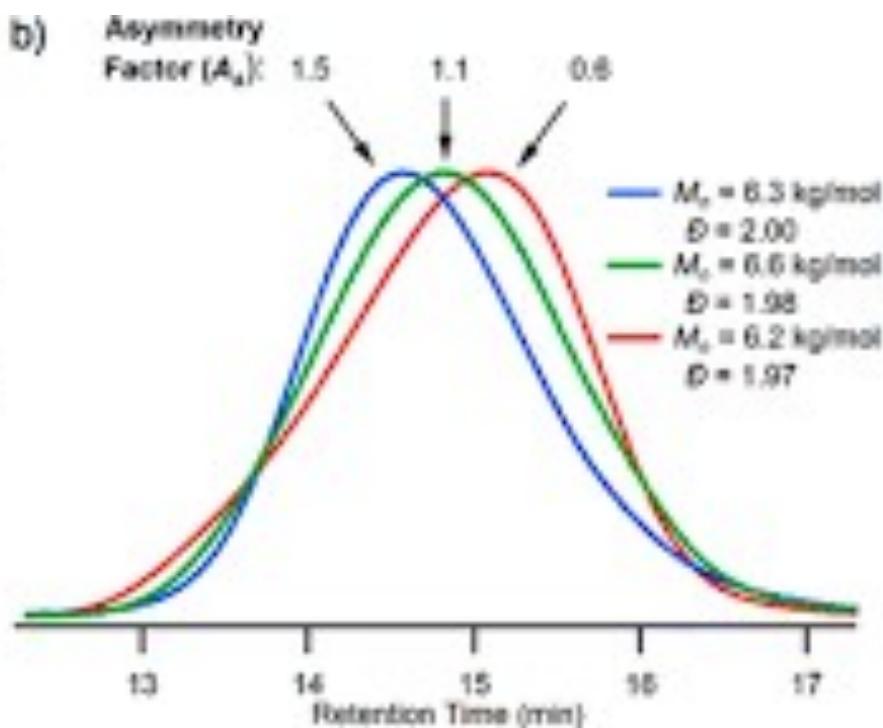
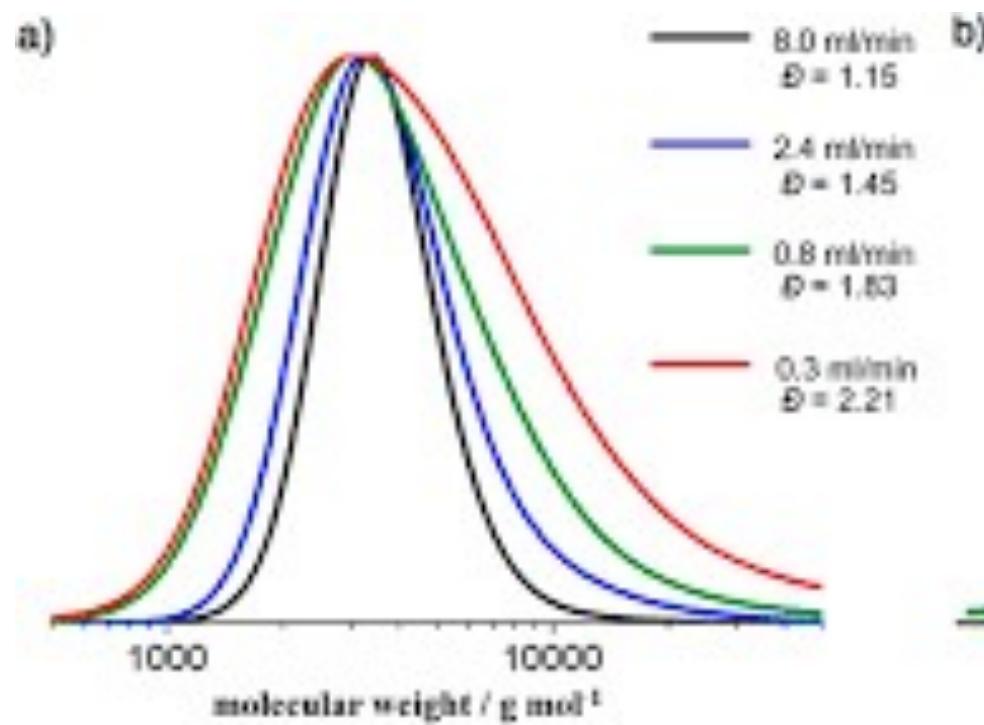
Viscosity Average Molecular Weight (M_v)



Reduced and inherent viscosity-concentration curves for a polystyrene in benzene (Ewart 1946).



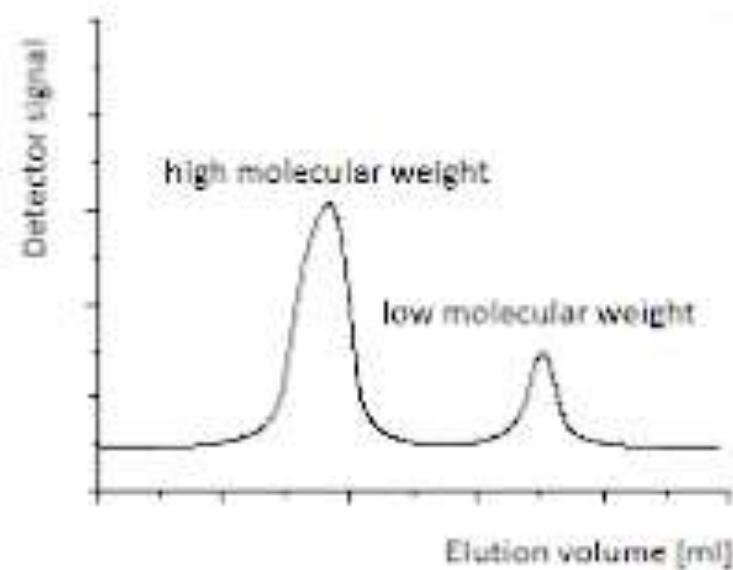
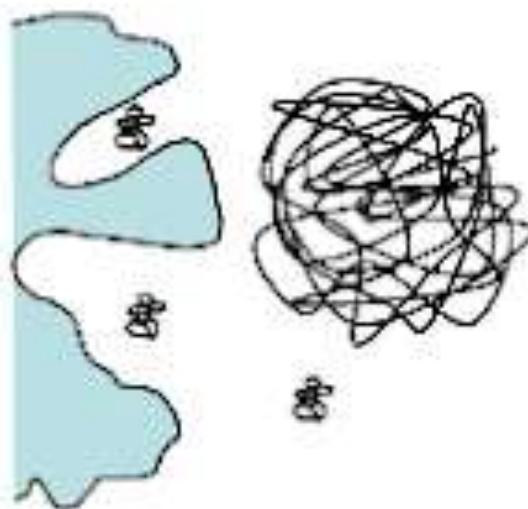
Gel Permeation Chromatography of Polymers



Jordi Gel



Gel Permeation Chromatography or Size Exclusion Chromatography



Certain Polymerization Reactions have a Unique Control Over the Polydispersity

Table 1: Typical values for PDI

Polymerization technique	Typical PDI
Free radical polymerization	1.5–2
Controlled or living polymerization	1.01–1.3
Step growth polymerization	2
Polymerization with several active species	>>2

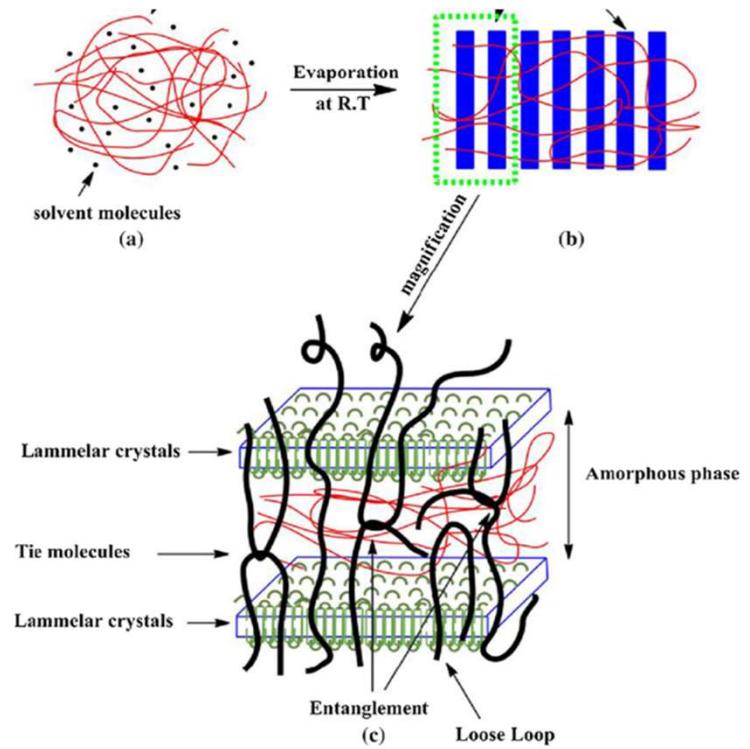
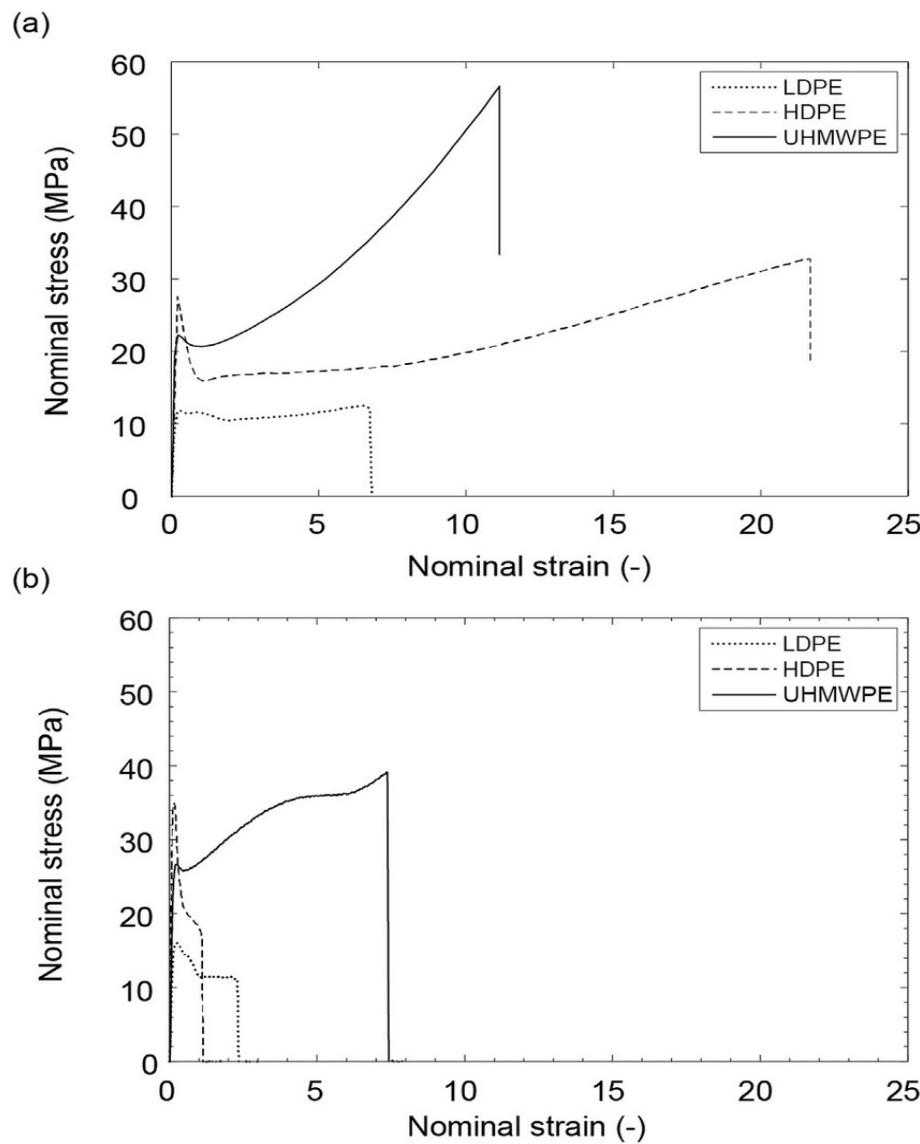
Ultrahigh Molecular Weight Polyethylene

Synthesis

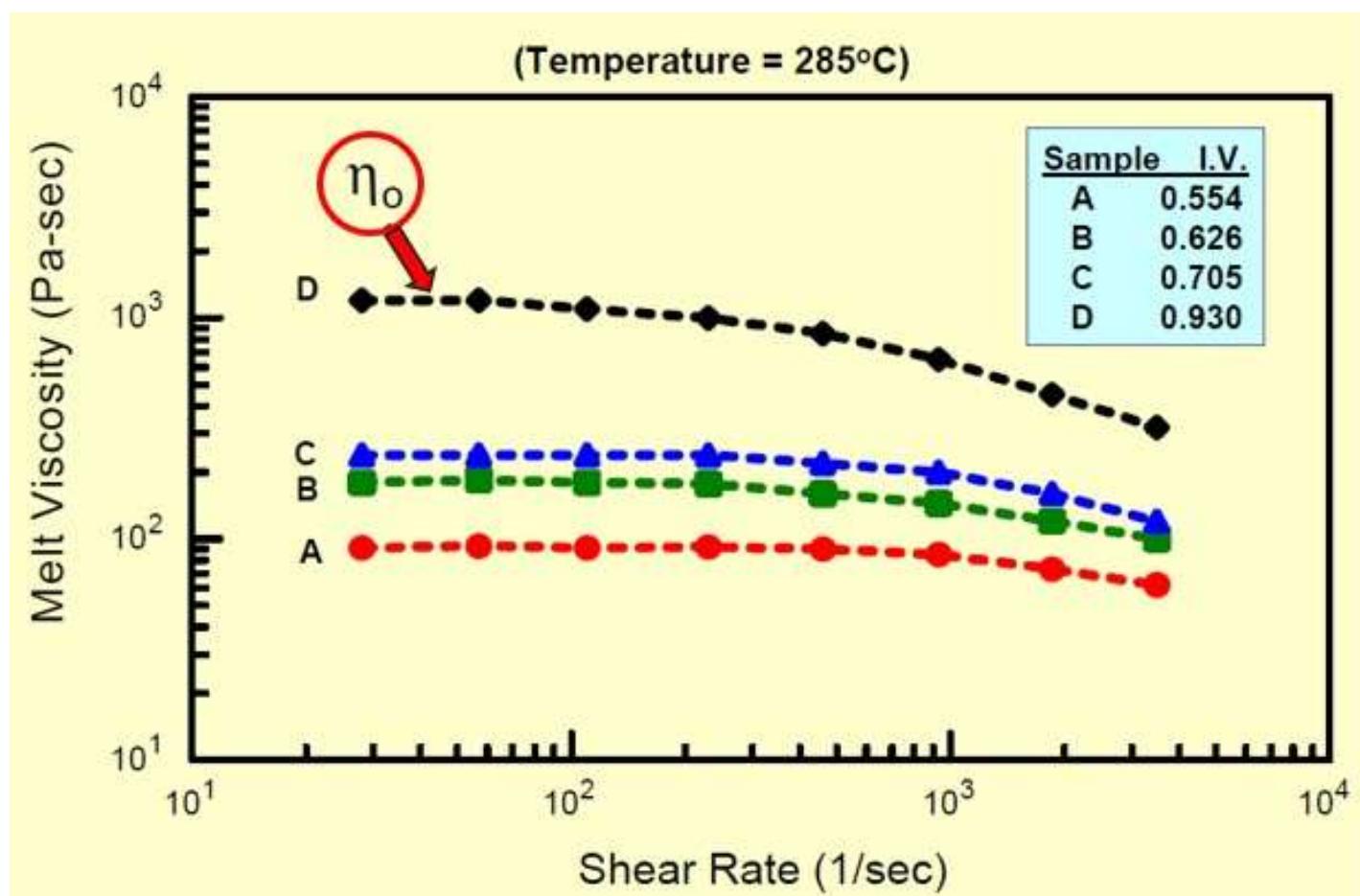
- By use of Ziegler Natta coordination catalyst under low pressure(TiCl-Al.Alk)
- Heterogeneous system(hexane solvent , ethylene gas , catalyst)
- Press. 0.4-0.6 Mpa
- Temp. 66-90 oC
- Results white granular powder
- Calcium sterate is added for isolation

Property	HDPE	UHMWPE
Molecular weight (10^6 g/mole)	0.05 - 0.25	2 - 6
Melting temperature (°C)	130 - 137	125 - 138
Poisson's Ratio	0.40	0.46
Specific gravity	0.952 - 0.965	0.932 - 0.945
Tensile modulus of elasticity* (GPa)	0.4 - 4.0	0.8 – 1.6
Tensile yield strength* (MPa)	26-33	21 – 28
Tensile ultimate strength* (MPa)	22 – 31	39 – 48
Tensile ultimate elongation* (%)	10 – 1200	350 – 525
Impact strength, Izod*		>1070
(J/m of notch: 3.175 mm thick specimen)	21 – 214	(No Break)
Degree of crystallinity (%)	60 – 80	39 - 75

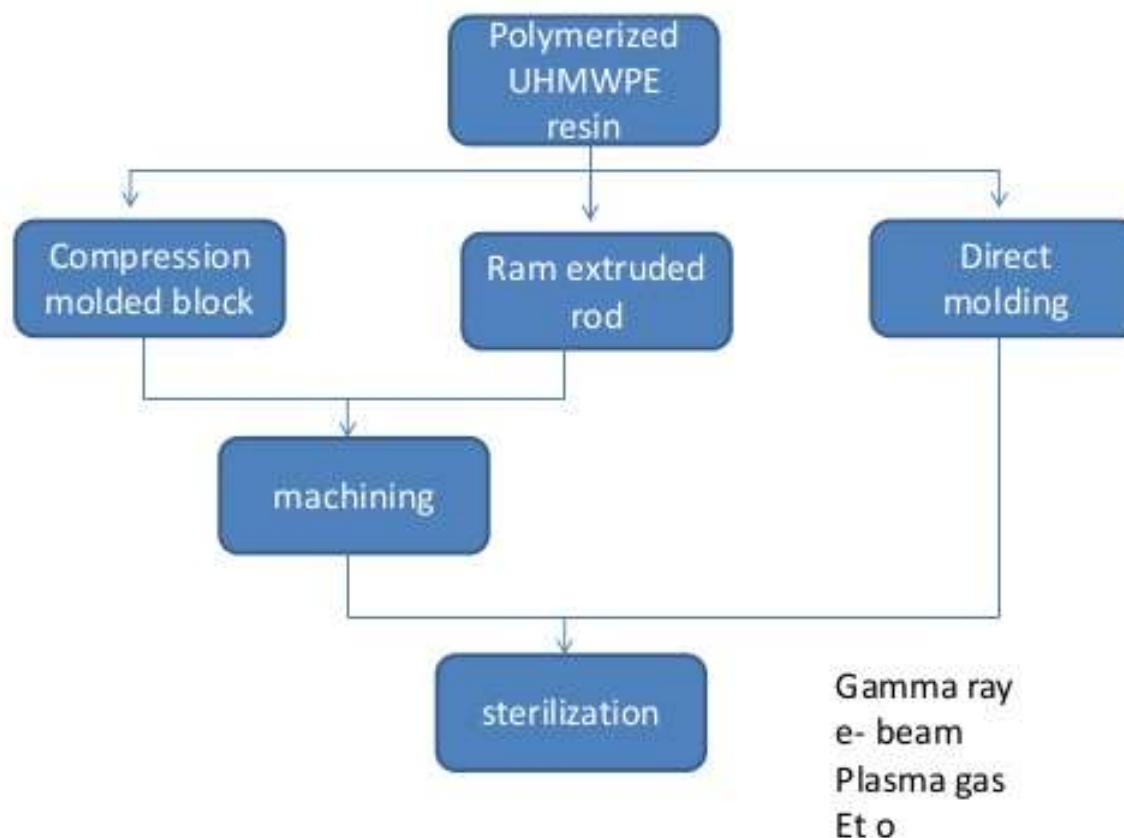
Mechanical Performance Enhancement with UHMWPE



Downside to HMWPE is the Increase in Melt Viscosity and Difficulty to Process on Conventional Equipment

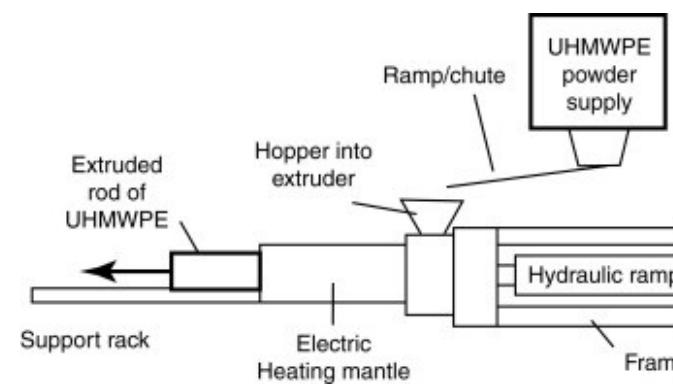
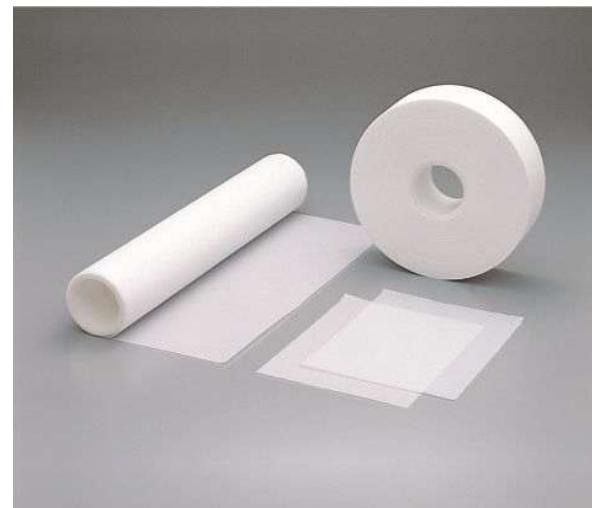


Processing



Commercial Forms of UHMWPE

UHMWPE has very good abrasion resistance.



ASTM F1473 or the PENT Test



Designation: F1473 – 18

Standard Test Method for Notch Tensile Test to Measure the Resistance to Slow Crack Growth of Polyethylene Pipes and Resins¹

This standard is issued under the fixed designation F1473; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

ASTM F1473 or the PENT Test

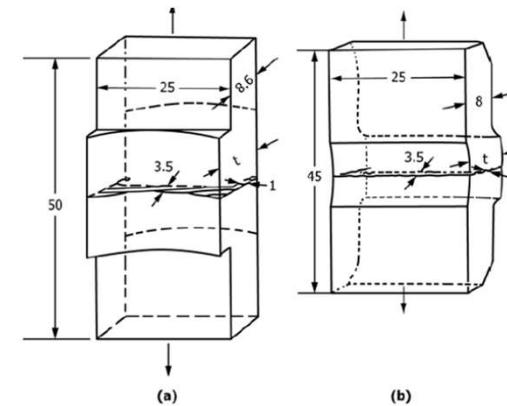
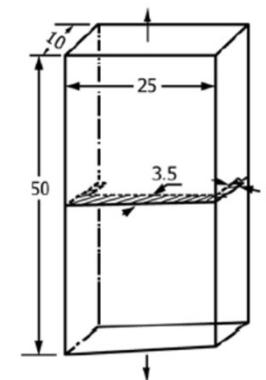
Measures the amount of time for a pre-notched crack to propagate through a polyethylene specimen of a specific dimension.

4. Summary of Test Method

4.1 Specimens are prepared from compression molded plaques, precisely notched and then exposed to a constant tensile stress at elevated temperatures in air. Time on test is recorded for tests conducted against a minimum time before failure requirement or the time to complete failure is recorded.

NOTE 2—Minimum time before failure requirements are found in material or product specifications, codes, etc.

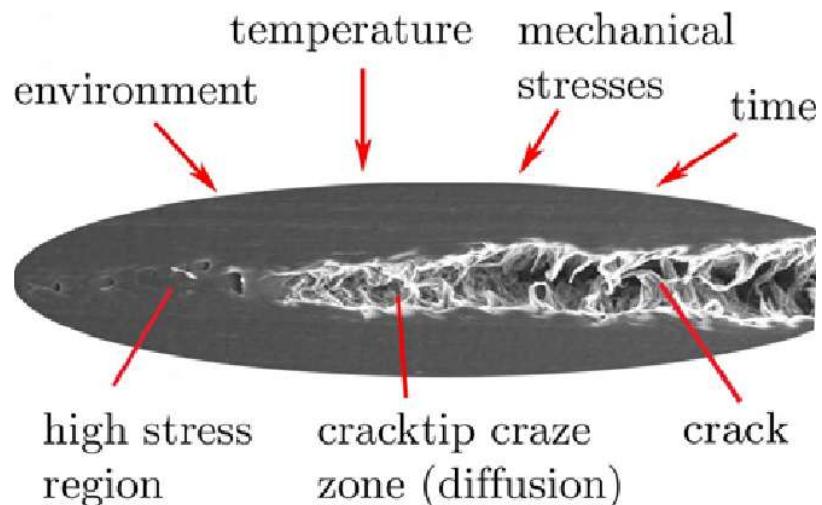
Polyethylene Pipe Materials are Tested at 80C
at a Tensile Stress of 2.4 MPa until Failure.



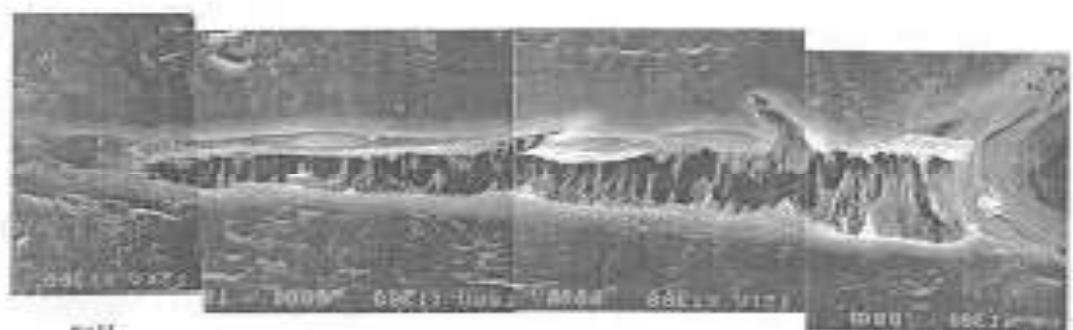
(a) Longitudinal Specimen from 110-mm SDR 11 Pipe with Tensile Axis Parallel to Extrusion Direction

(b) Same as (a) With Tensile Axis Perpendicular to Extrusion Direction

Review of Craze-Crack Propagation



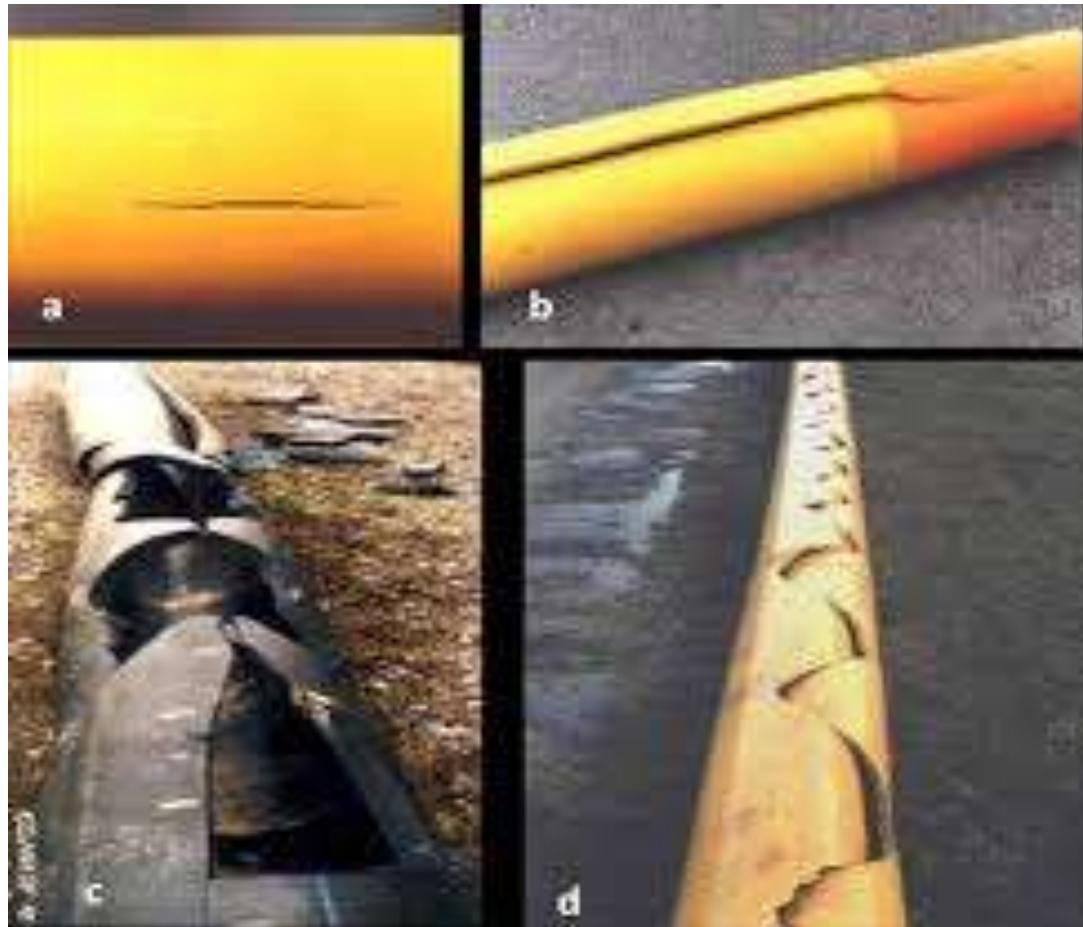
KU21000, T.R. Kratochvila



Traditional HDPE and MDPE Polyethylene Pipe Exhibits a Ductile to Brittle Transition at a Specific Stress and Temperature Condition

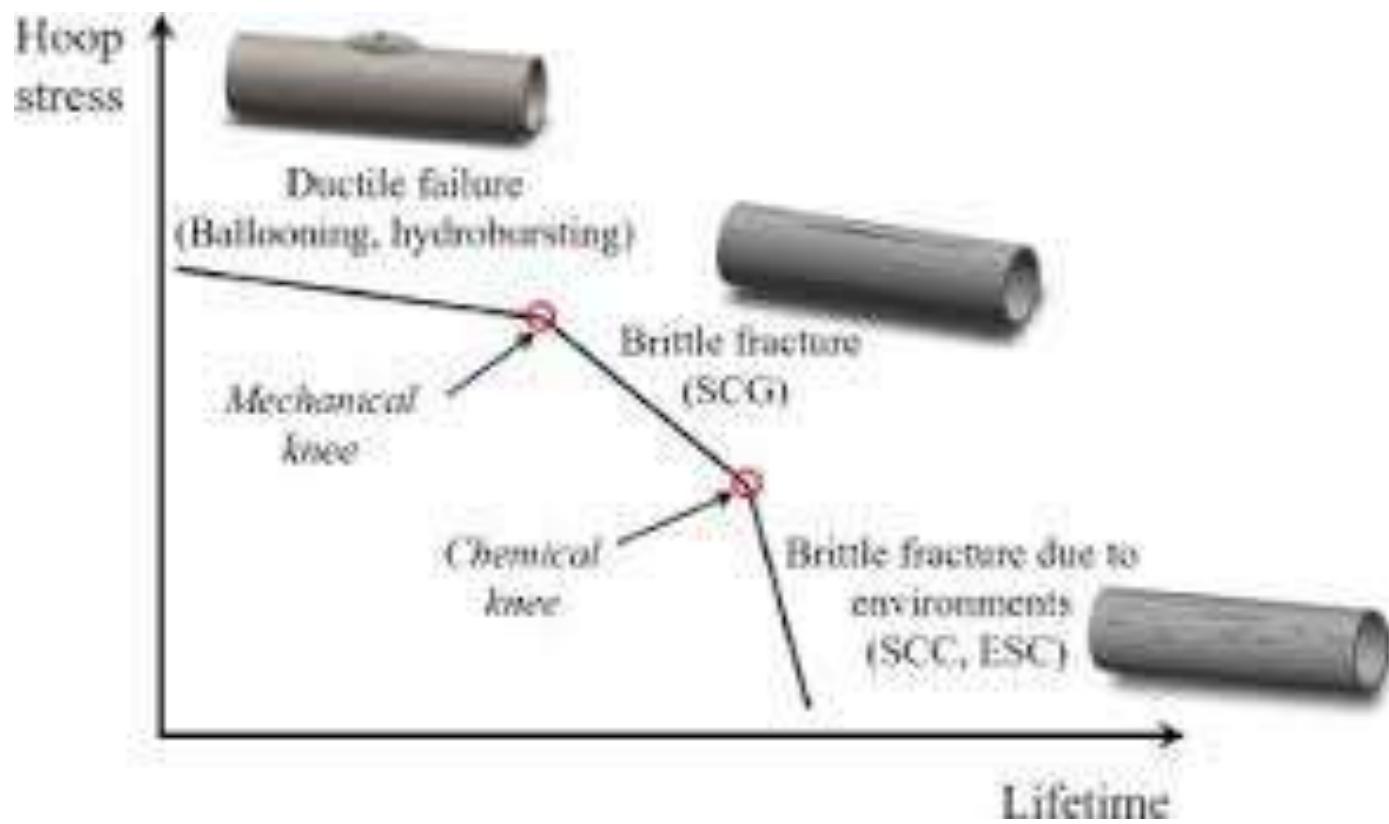


Ductile Polyethylene Pipe Failure

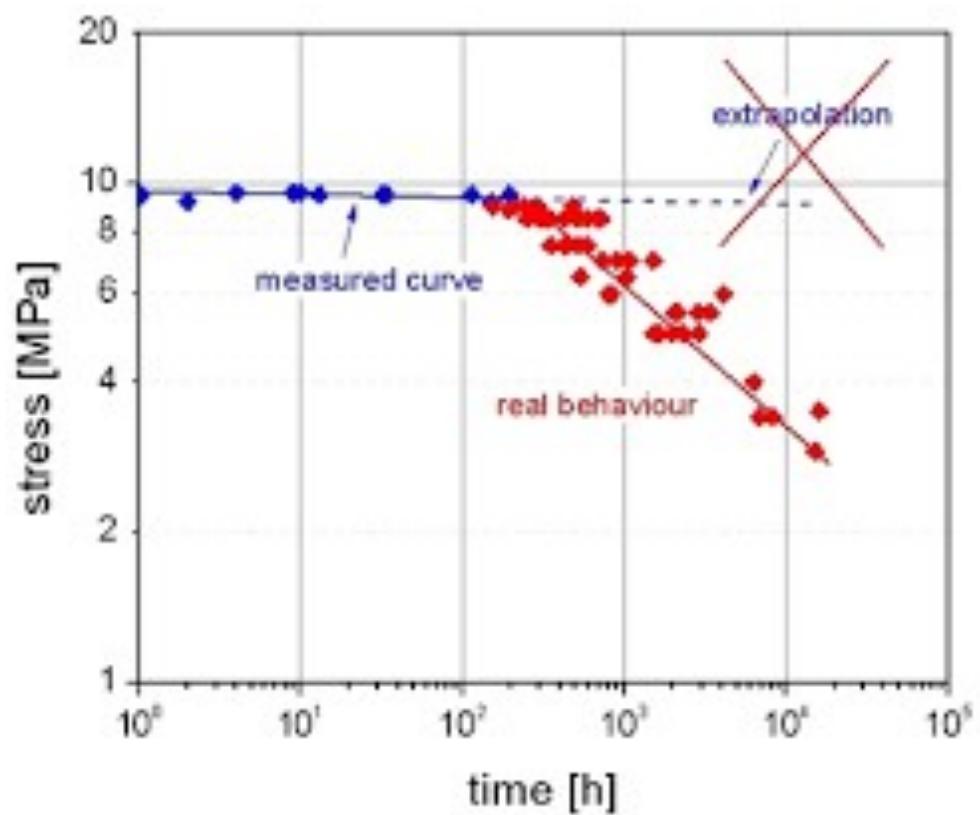
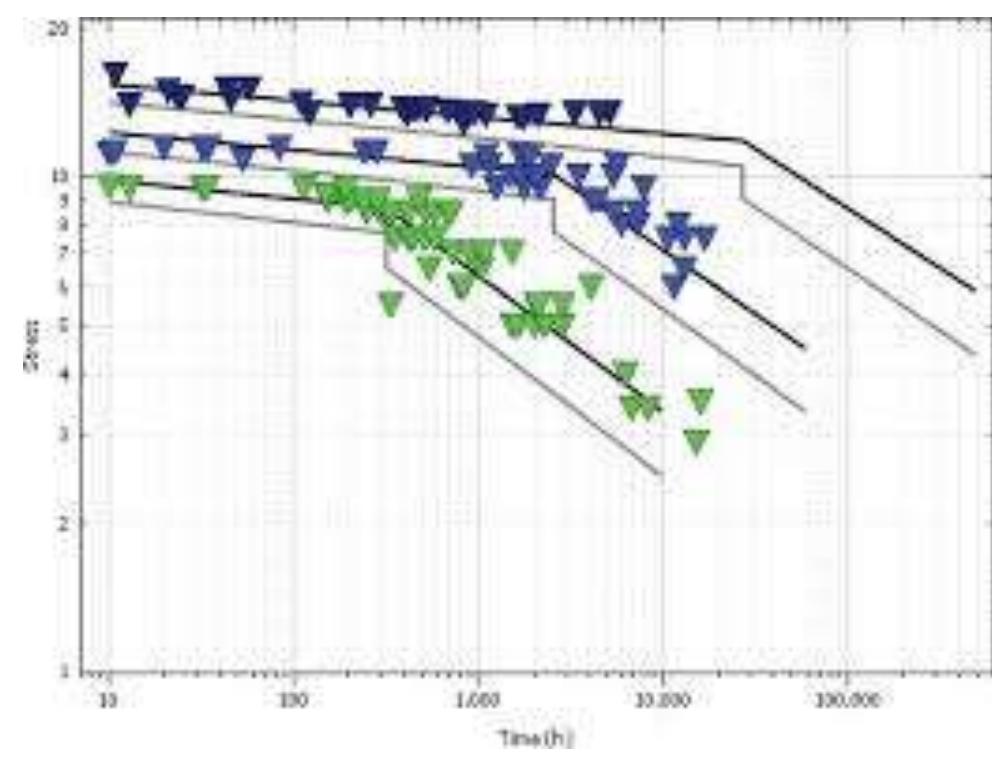


Brittle Polyethylene Pipe Failure

Illustration of the Ductile-Brittle Failure on a Hoop Stress vs Failure Time Plot



Actual Ductile-Brittle Transition for HDPE



(12) **United States Patent**
VanDun et al.

(10) Patent No.: US 6,787,608 B2
(45) Date of Patent: Sep. 7, 2004

**BIMODAL POLYETHYLENE COMPOSITION
AND ARTICLES MADE THEREFROM**

Inventors: **Jozef J. VanDun**, Freeport, TX (US);
Patrick J. Schouterden, Terneuzen (BE); **Peter F. M. van den Berghe**, Graauw (NL); **Ruddy Nicasy**, Tessenderlo (BE); **Johan Vanveorden**, Diepenbeek (BE); **Frederick E. L. Gemoets**, Terneuzen (BE); **Kalyan Sehanobish**, Lake Jackson, TX (US); **Noorallah Jivraj**, Lake Jackson, TX (US); **Ravi S. Dixit**, Lake Jackson, TX (US)

Assignee: **Dow Global Technologies, Inc.**, Midland, MI (US)

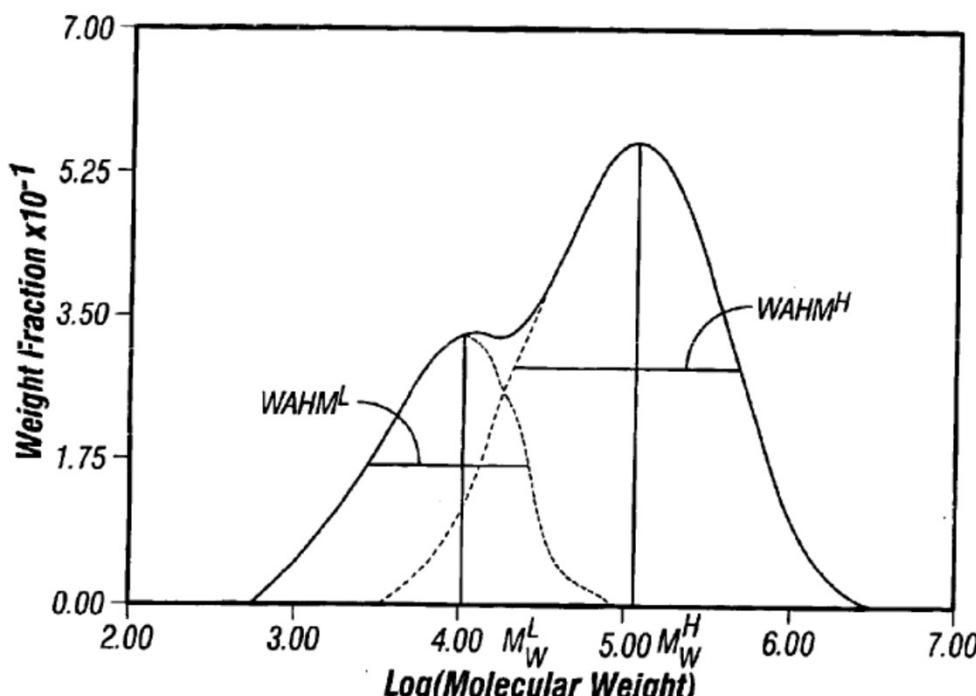
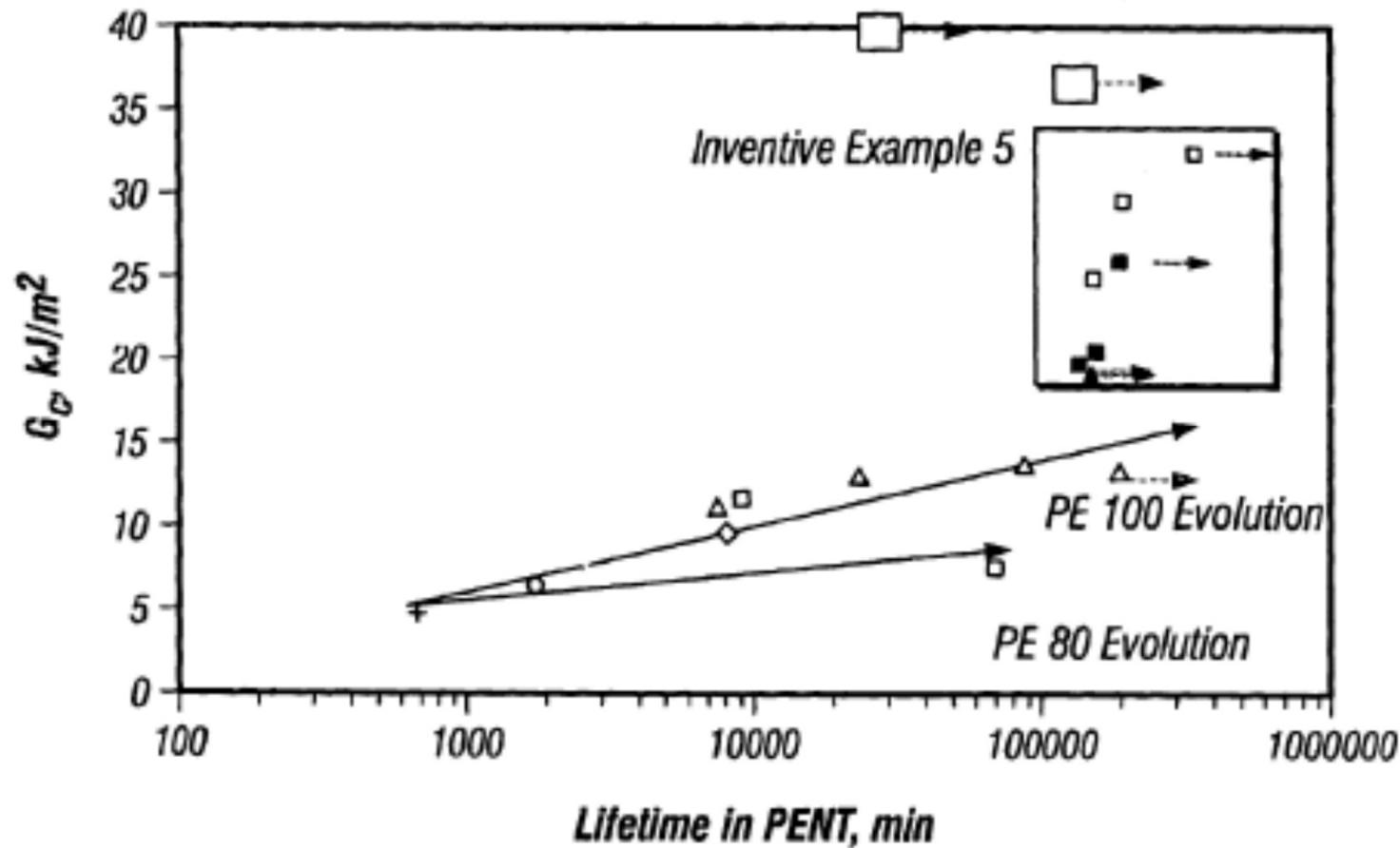


TABLE 11

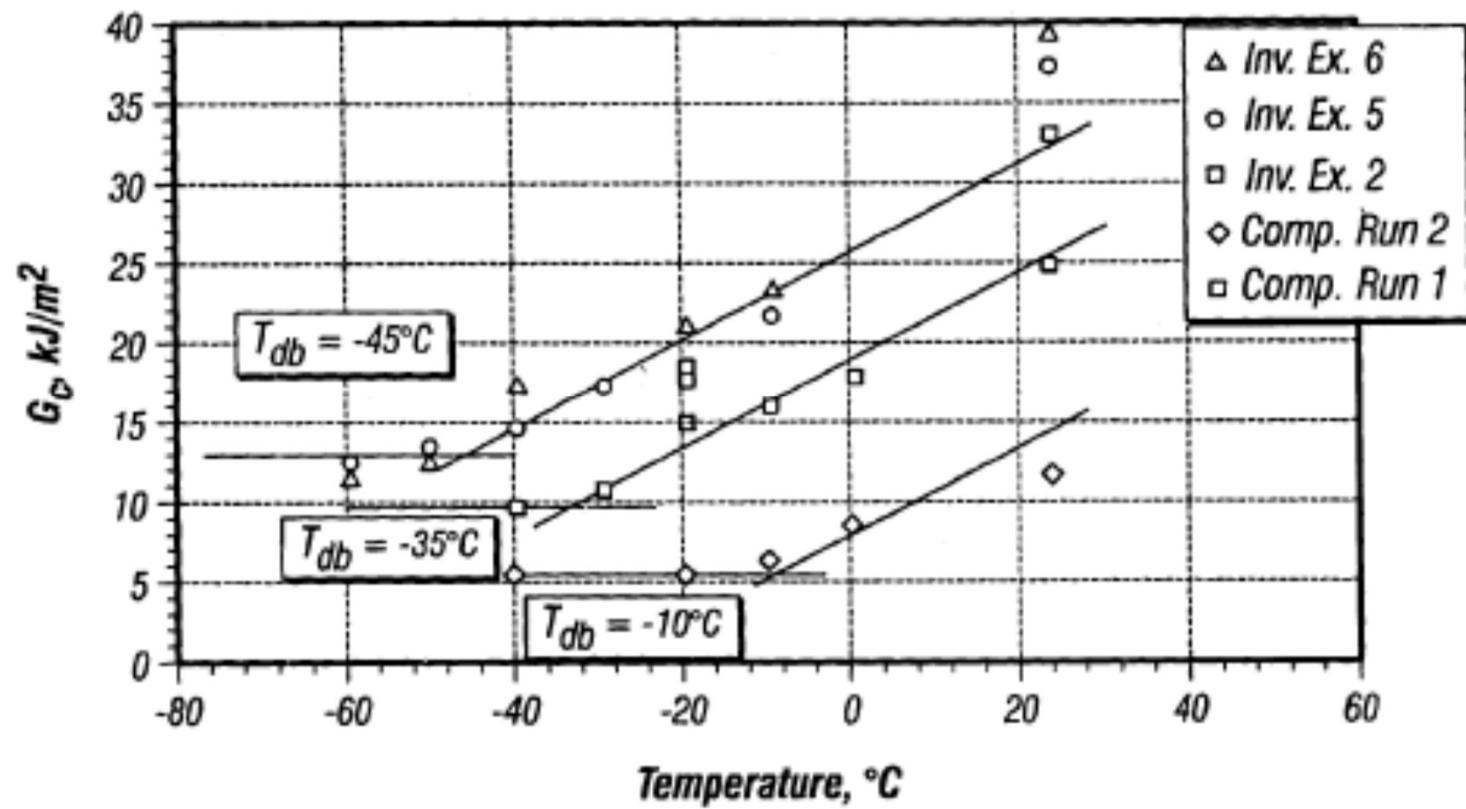
Product and Performance Properties of Inventive Examples		2	5	6
Inventive Example				
Density	g/cm ³	0.9511	0.9508	0.9508
<u>GPC</u>				
M _w		229900	223100	201400
M _n		13213	15200	15700
M _w /M _n		17.4	14.68	12.83
M _z			832600	727200
RCD (Fractionation)		Yes	Yes	Yes
Calcium Stearate	ppm		680	
Irganox™ 1010	ppm	2080	845	329
Irgafos™ 168 total	ppm	2691		1900
Irgafos™ 168 remaining	ppm	2784	2000	1723
<u>DSC</u>				
T _g	° C.	122.2	122.1	121.2
T _m	° C.	133.2	134.4	133.1
Crystallinity	%	72.77	68.11	69.0
OIT ° C.	min.	66	46	50
PENT	min.	>464484	>179796	>150000
<u>Tensile properties</u>				
Yield stress	MPa	23.1	23.7	24.8
Yield strain	%	11.7	10.6	11.0
Break stress	MPa	36.6	42.4	42.2
Ultimate tensile stress	MPa	36.6	42.4	42.2
Elongation	%	673	683	697
Secant modulus	MPa	556	622	614
Young's modulus	MPa	954	1044	957

Properties of Dow's Early Investigation into Bimodal PE Materials

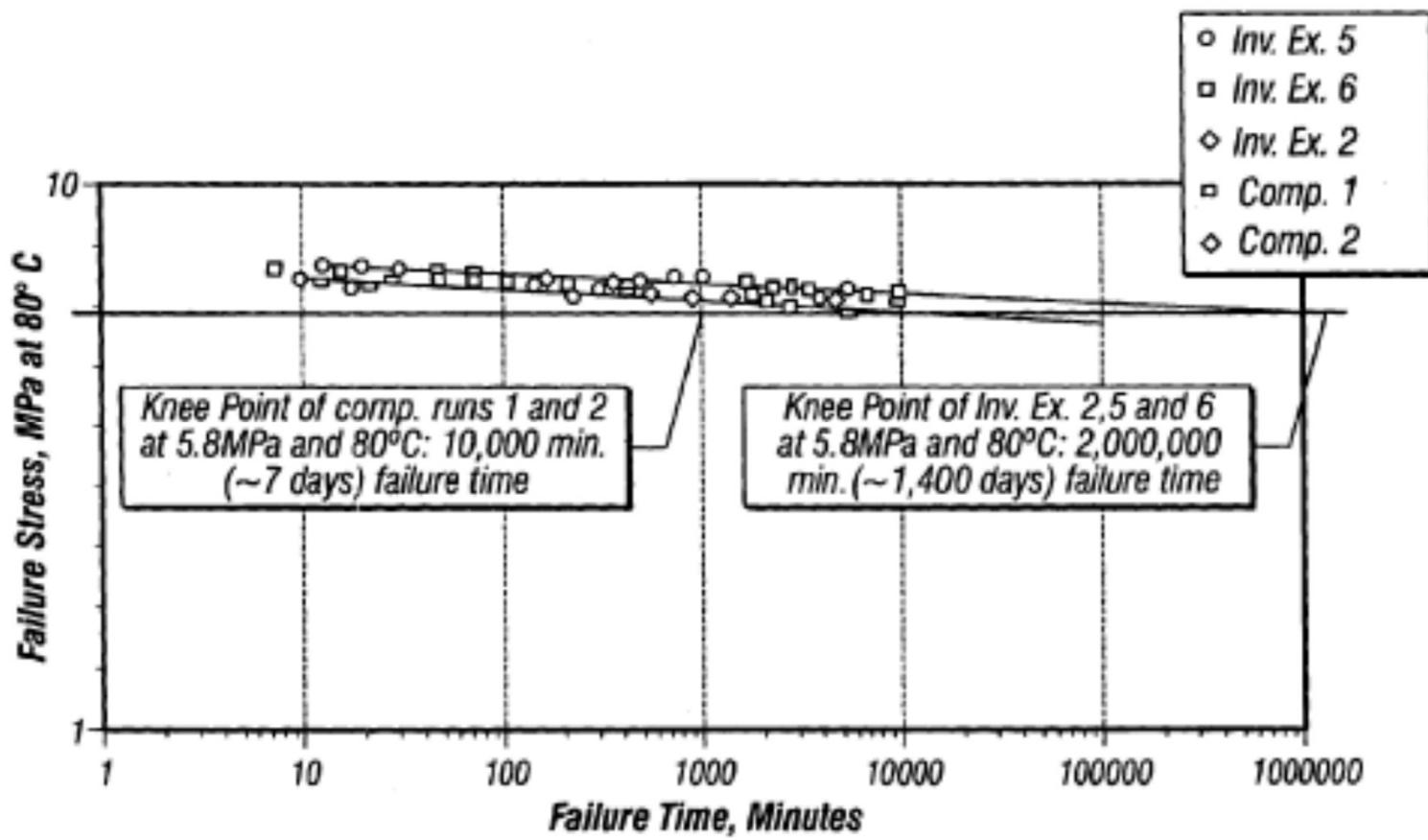
Bimodal PE Enhances the PENT Test Lifetime



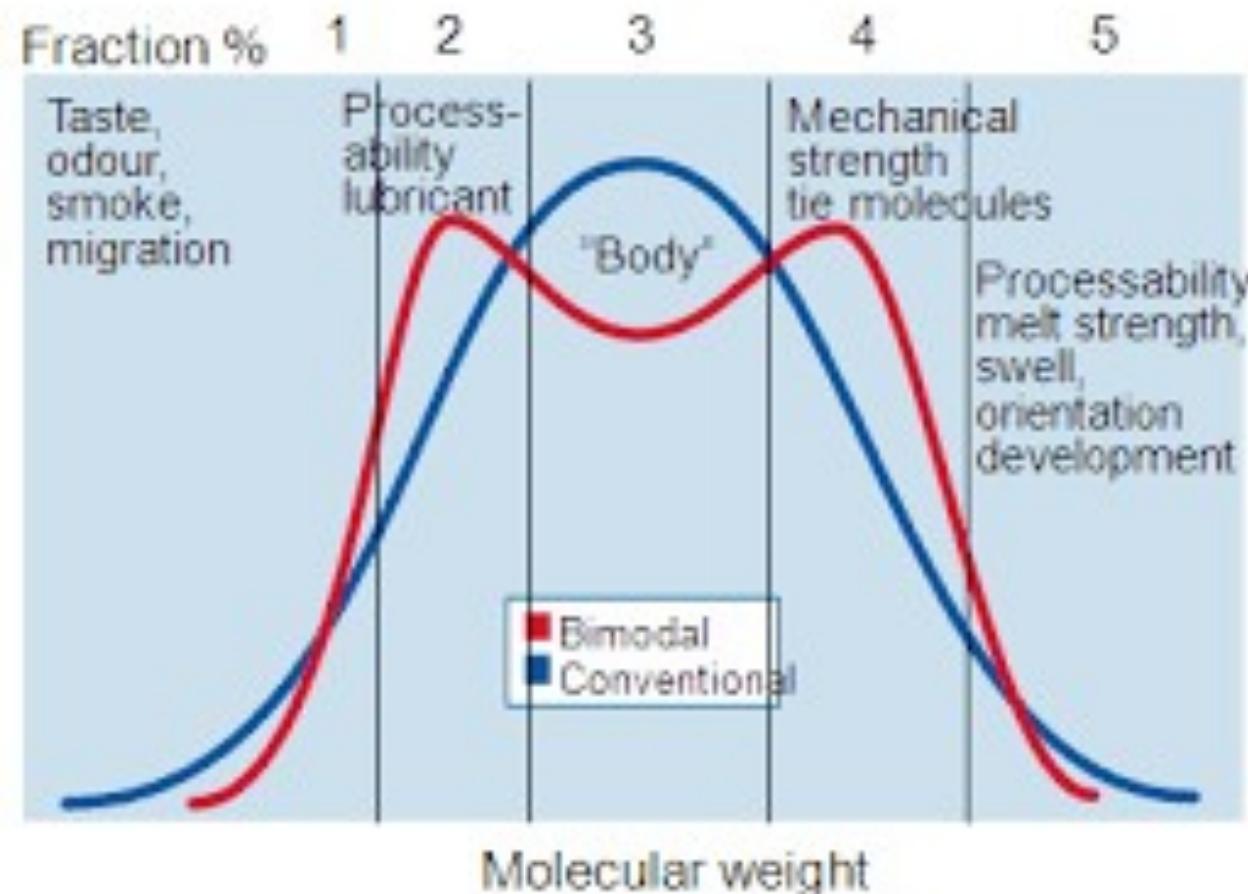
Bimodal PE Extends in Time the Ductile-Brittle Transition



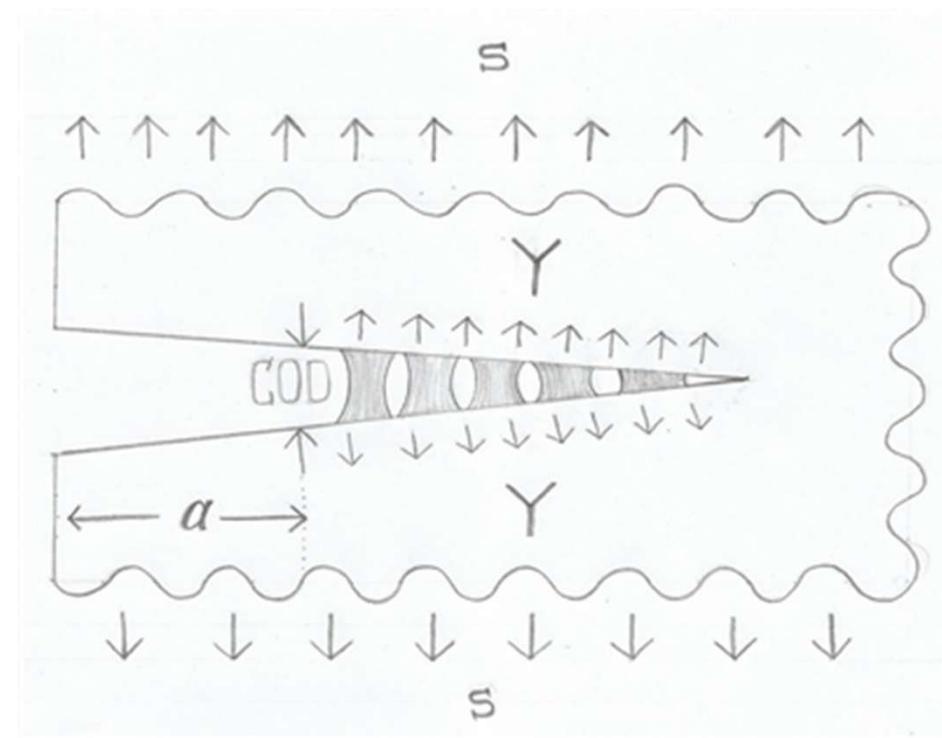
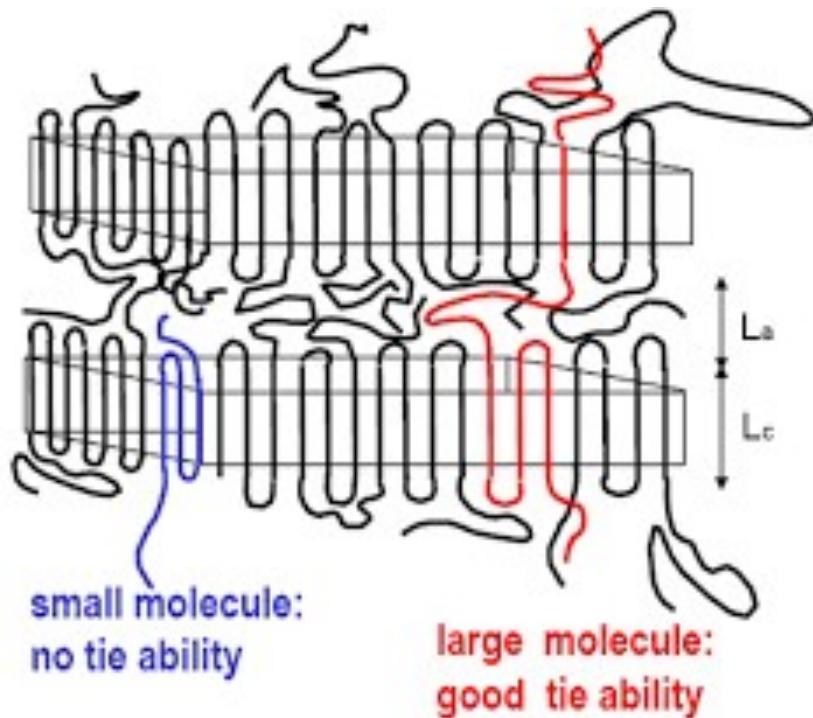
Bimodal PE Extends Improves in the Long-Term Stress Rupture Performance



Proposed Performance Mechanism for Bimodal PE Materials



Tie Molecule Influence in Slow Crack Growth

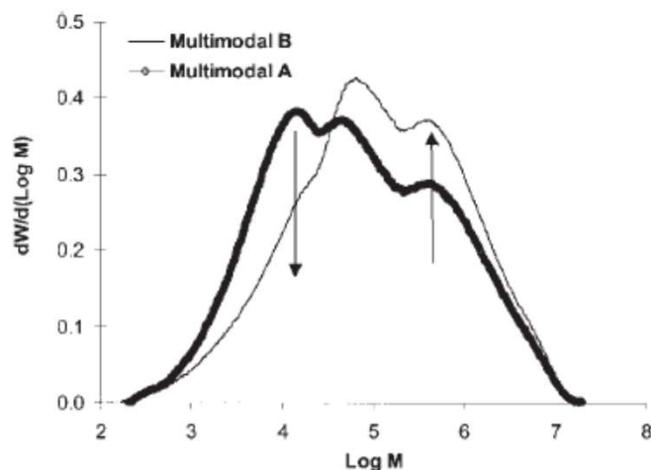


A Comparative Study of Multimodal vs. Bimodal Polyethylene Pipe Resins for PE-100 Applications

Paul J. DesLauriers, Max P. McDaniel, David C. Rohlffing, Rajendra K. Krishnaswamy, Steven J. Secora, Elizabeth A. Benham, Pamela L. Maeger, A.R. Wolfe, Ashish M. Sukhadia, Bill B. Beaulieu
Chevron Phillips Chemical Company LP, Bartlesville, Oklahoma 74004

Portions of this paper were presented at the Society of Plastics Engineers International Conference on Polyolefins, Houston, TX, February, 2004.

Polymer Engineering and Science, 2005, DOI 10.1002/pen.20390



Molecular weight values*					
	M_p	M_n	M_w	M_z	M_{z+1}
Multimodal A	14.3	9.7	528	3,800	6,830
Multimodal B	64.9	13.3	645	3,814	6,864

*kg/mol

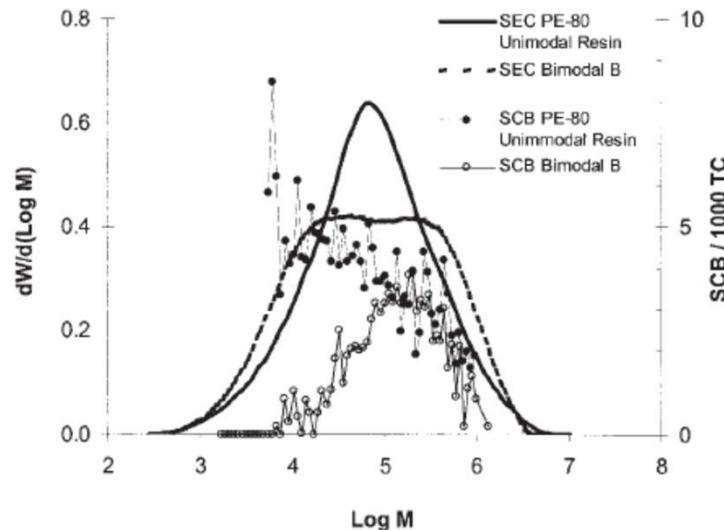


FIG. 11. Comparative SCB profiles across the MWD for a PE-80 sample made using a Cr/silica-titania catalyst and PE-100 Ziegler based bimodal resin (resin B in Table 3).

Results from Phillips Petroleum Multimodal PE

TABLE 2. Nominal physical property values of selected pipe resins.

Property	Unimodal resin	Bimodal resin A	Bimodal resin B	Bimodal resin C	Multimodal resin C	Multimodal resin D
Density (g/cm ³)	0.944	0.950	0.949	0.950	0.950	0.952
Tensile modulus (GPa)	1.4	1.55	1.5	1.52	1.53	1.63
Yield stress (MPa)	23.2	25	25.6	25.3	25.2	25.9
Mw (g/mol)	210,000	217,000	238,000	255,000	481,000	579,000
Mw/Mn	10.8	12.6	14.7	22.8	68.6	83.1
Rheology data						
HLMI, g/10 min.	10.0	7.1	7.0	17.0	2.3	2.8
η_0 (Pa s)	1.01E+06	3.00E+05	2.45E+05	5.26E+05	3.04E+08	8.27E+07
η at 0.1/sec (Pa s)	5.68E+04	7.80E+04	9.28E+04	9.21E+04	3.38E+05	3.81E+05
η at 100/sec (Pa s)	1.86E+03	2.42E+03	2.71E+03	1.87E+03	2.46E+03	2.77E+03
τ_η (s)	4	2	2	6	252	89
PENT [ASTM F1473; h]	150	~2,000	~3,000	~2,500	> 18,000 ^a	> 10,000 ^a
Abrasion resistance [grams lost per 1000 rev] ^b	0.014		0.012	0.012	0.006	
Charpy T _{db} [°C]	~−15	~−35	~−40	~−35	~−23	~−30
S4 ^c	+11	−24	—	—	—	−8

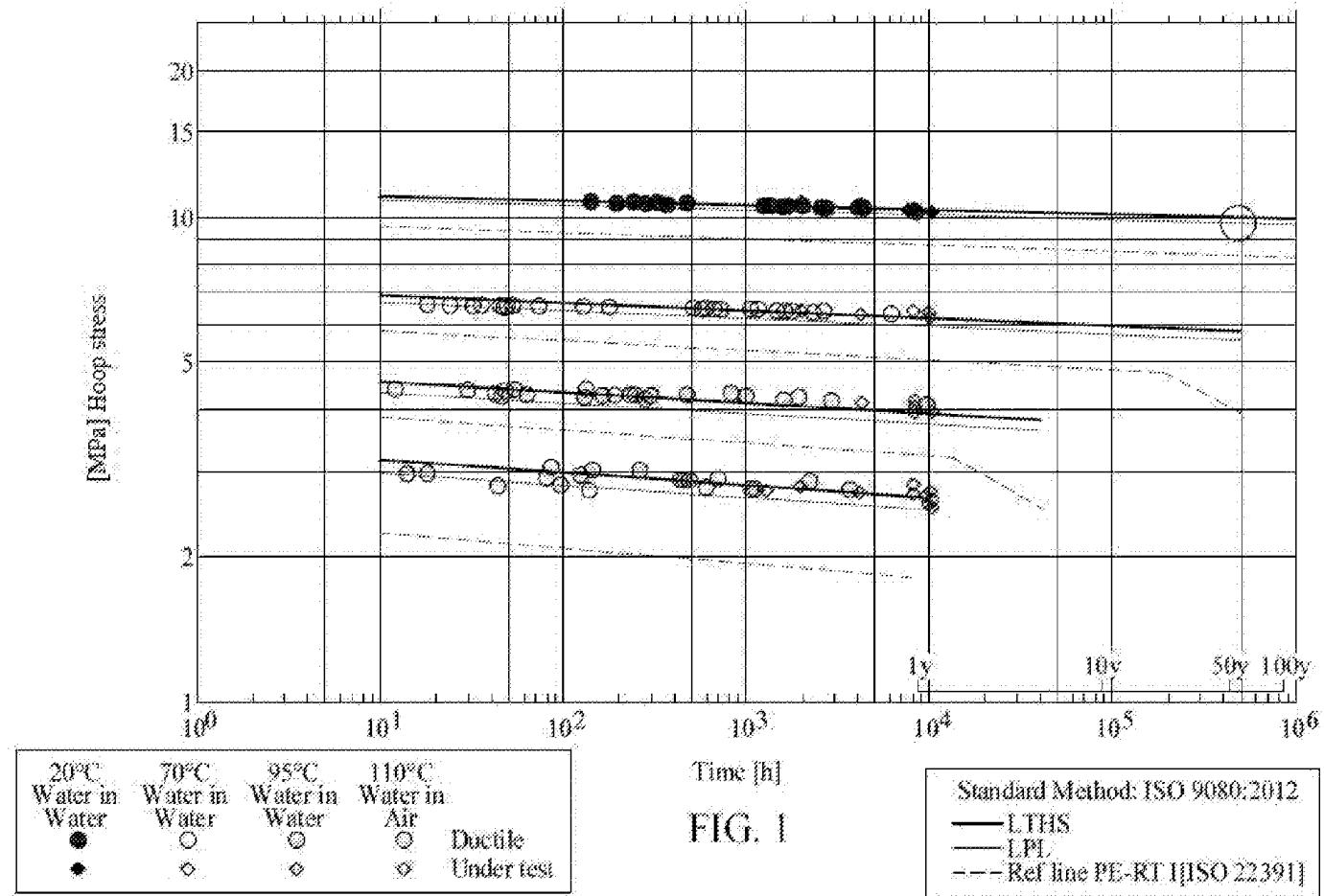
^aSamples still on test.

^bUltra-high MW-PE resins (Ticona) GUR4120 and GUR4150 gave values of 0.006 and 0.0045, respectively.

^cValues for 203-mm black pipe.

Basis for the PE100 Designation

Likewise, today we seem to be on the verge of another mass upgrading of pipe quality, this time to “PE-100” status (i.e., pipe must withstand hoop stress of 10 MPa for up to 50 years at 20°C). Again, this movement is driven by advancements in catalyst and polymerization technology, namely by the introduction of so-called “bimodal” resins.



Performance Enhancement for Bimodal PE

	MDPE	HDPE	PE-RT Bimodal
Designation	PE 2406/2708	PE 4710	PE-RT
Density	0.943 g/cm³	0.950 g/cm³	0.950 g/cm³
PENT @ 80C; 2.4 MPa	>1000 h	>2000 h	>12,000 h
HDB @ 23C	1250 psi	1600 psi	1600 psi
HDB @ 60C	1000 psi	1000 PSI	N/A
HDB @ 82C	N/A	N/A	800 psi

Lesson 12: Polyolefin – PE 4: ULMWPE, UHMWPE, Multimodal

Questions?



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“I’m getting so old that all my friends in heaven will think I didn’t make it.”

EMAC 276

Lecture 13: The Polyolefin Family

Polyethylene – PE: Part 5: Chlorinated Polyethylene (CPE),
and Cross-linked Polyethylene (PEX)

Polypropylene - PP

Poly(1-butene) – Polybutylene – PB

Andy Olah, Ph.D.
February 19, 2025

These Variations of Polyethylene Lead to a Diversity of Products

Linear Versions:

- High density polyethylene (HDPE)
- Ultra-high molecular weight polyethylene (UHMWPE)

Branched Versions:

- Low-density polyethylene (LDPE)
- Linear low density polyethylene (LLDE)
- Medium-density polyethylene (MDPE)
- Very-low-density polyethylene (VLDPE)
- High-molecular-weight polyethylene (HMWPE)
- Ultra-low-molecular-weight polyethylene (ULMWPE)
- Chlorinated polyethylene (CPE)**

Bimodal and Trimodal Polyethylene

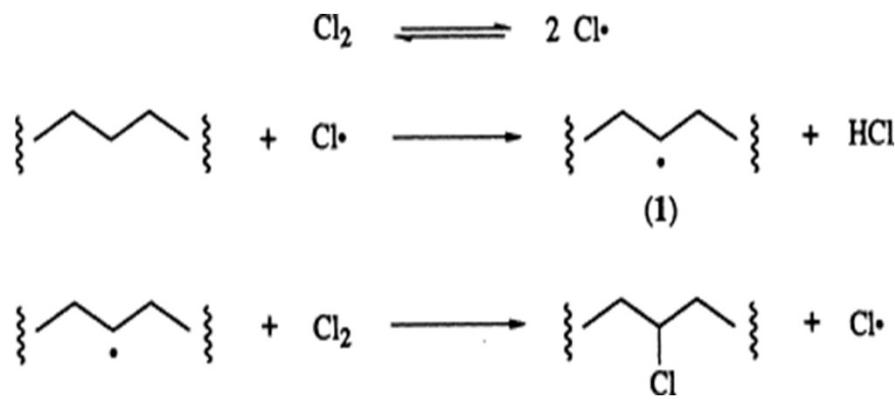
Cross-linked polyethylene (PEX): four forms (PEX-a, PEX-b . . etc)

Simplest of Molecular Structures Can Lead to a Large Diversity of Structures.

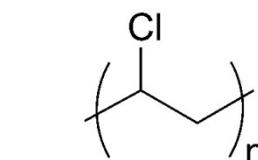
Three fundamental features of polyethylene leading to the diversity of structures and in turn performance are:

- a. Short chain and long chain branching.
- b. Co-monomer content and distribution.
- c. Molecular weight and molecular weight distribution.

Chlorinated Polyethylene (CPE)

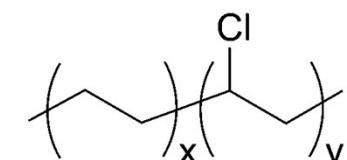


Basic PE Chlorination Reaction



polyvinyl chloride

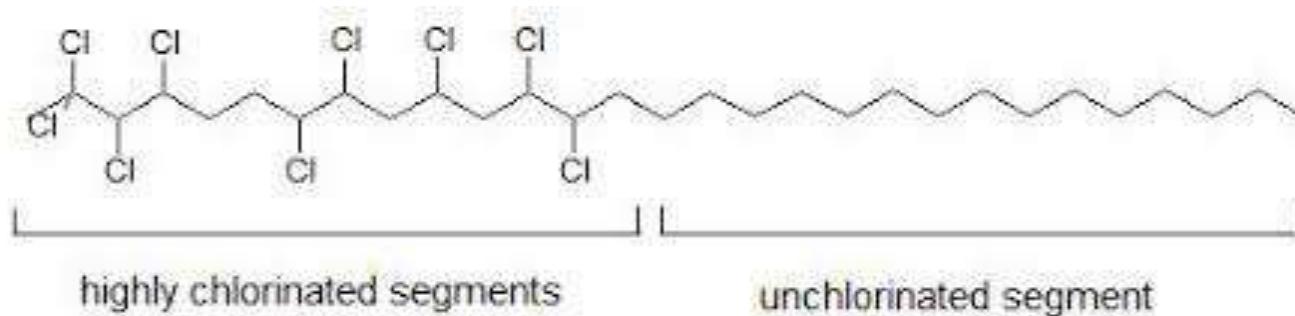
(PVC)



chlorinated polyethylene

(CPE)

Comparison to PVC (57% Chlorine)
CPE (33 – 44% Chlorine)



Chlorination can be Either Block or Homogeneous

Properties of Chlorinated Polyethylene

- 1) CPE is a saturated rubber with excellent chemical properties, such as resistance to thermal oxygen aging, ozone aging, and acid and alkali resistance.
- 2) CPE has excellent oil resistance. Its oil resistance is comparable to that of NBR.
- 3) CPE has excellent flame retardant properties and is uniquely combustion-drip proof.
- 4) CPE is non-toxic and contains non-heavy metals fully meeting environmental requirements.
- 5) CPE has a high filling performance and can be made in accordance with various performance requirements. CPE has good processing performance. Thus, various CPE grades are available.

Applications of CPE

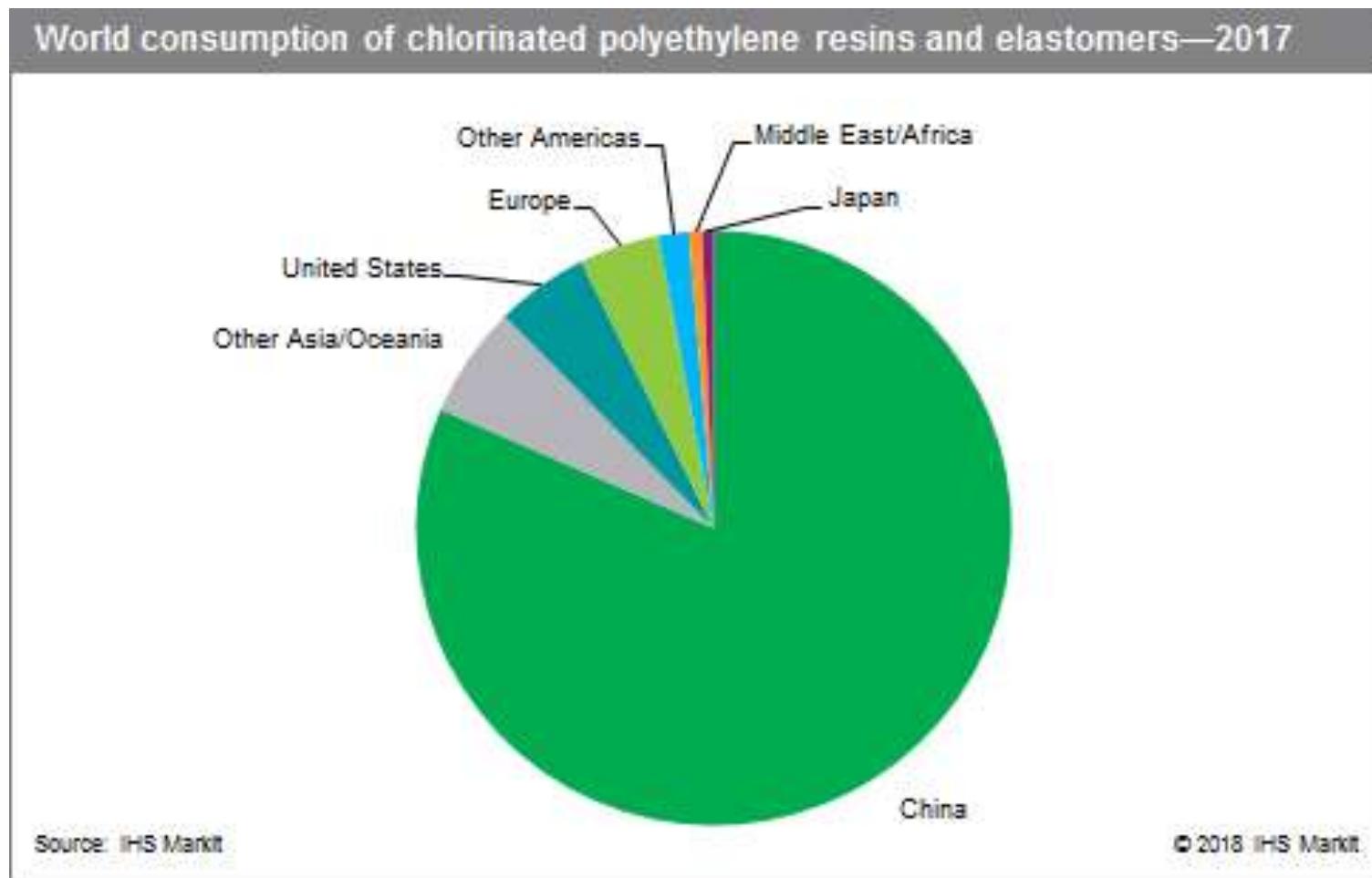
CPE can be divided into two categories: (1) resin-type CPE and (2) elastomer-type CPE.

CPE can be used alone or mixed with PVC, polyethylene, polypropylene, polystyrene, ABS, and even polyurethane.

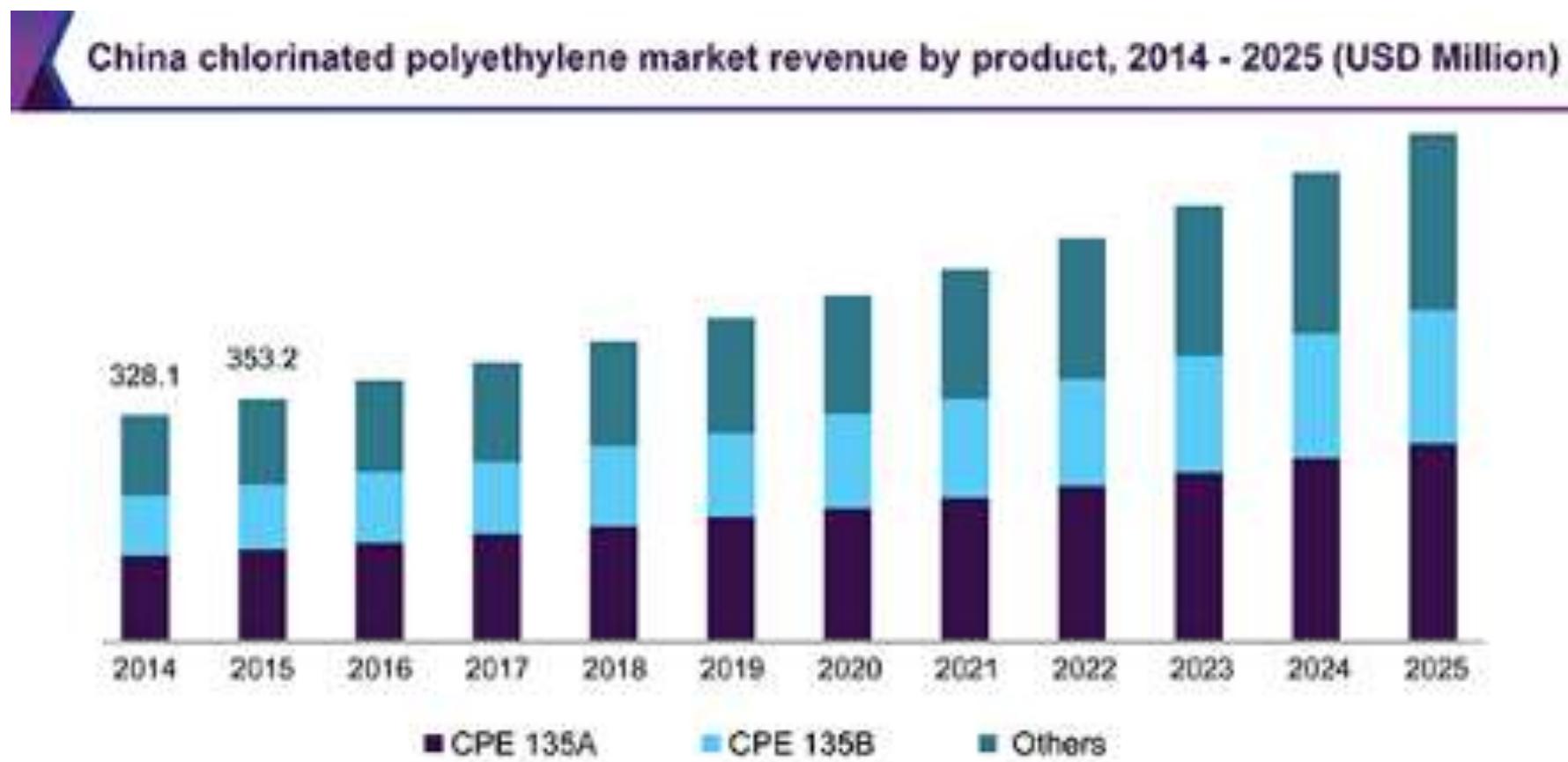
CPE can be used as a high-performance, high-quality rubber and can be applied with ethylene propylene rubber, butyl rubber, nitrile rubber, chlorosulfonated polyethylene.

CPE modified with other rubber materials is mainly used in the production of wires and cables, standard use wire, UL, and VDE, and in the production of hydraulic hose, automotive hose, tape, and plastic sheets.

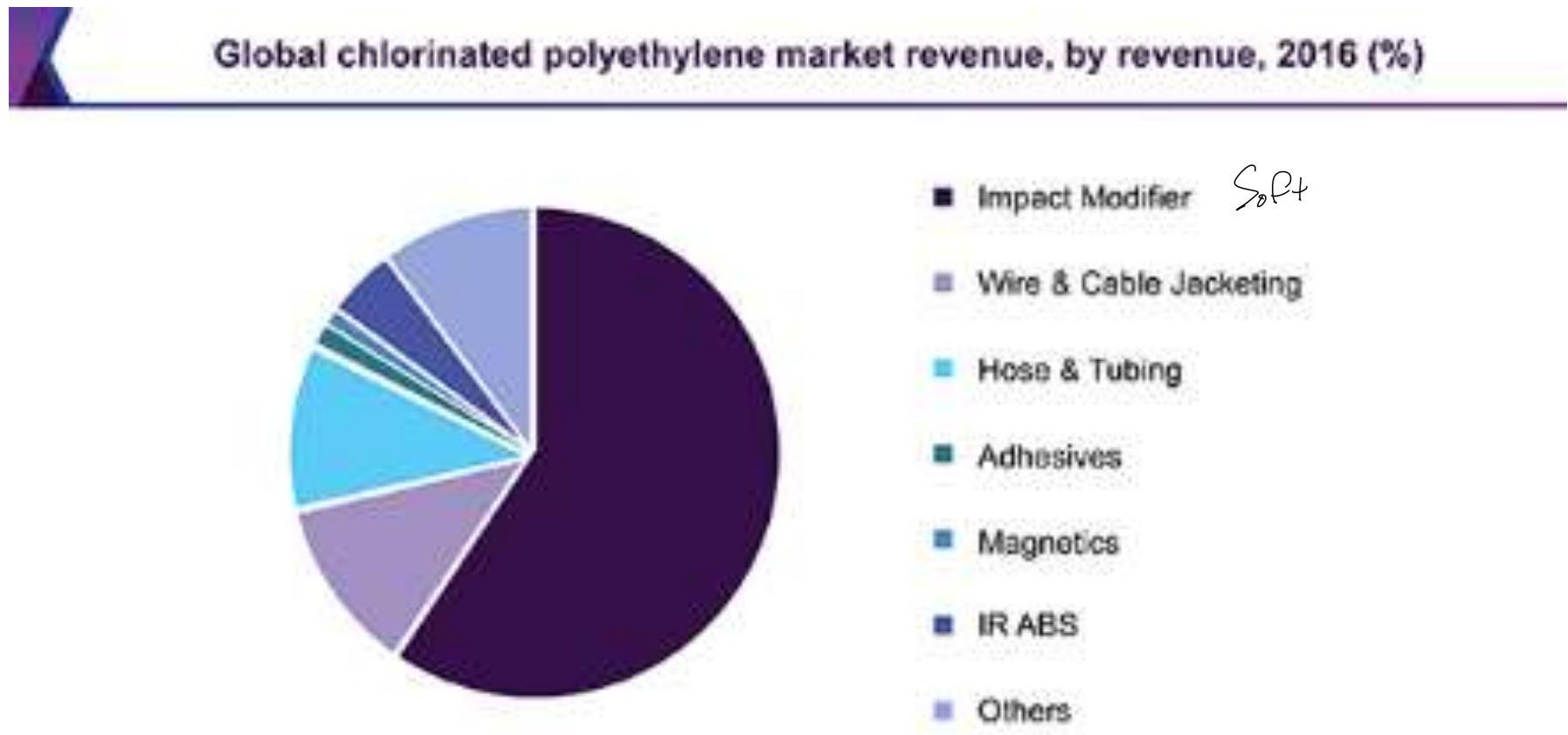
China is the Major Producer of CPE



China is the Major Producer of CPE



Modification of Other Polymers is the Major Use of CPE



There are Several Methods for the Cross-linking of Polyethylene:

PEX-a – Peroxide

PEX-b – Silane

PEX-c – Radiation

PEX-d – UV w/ agent

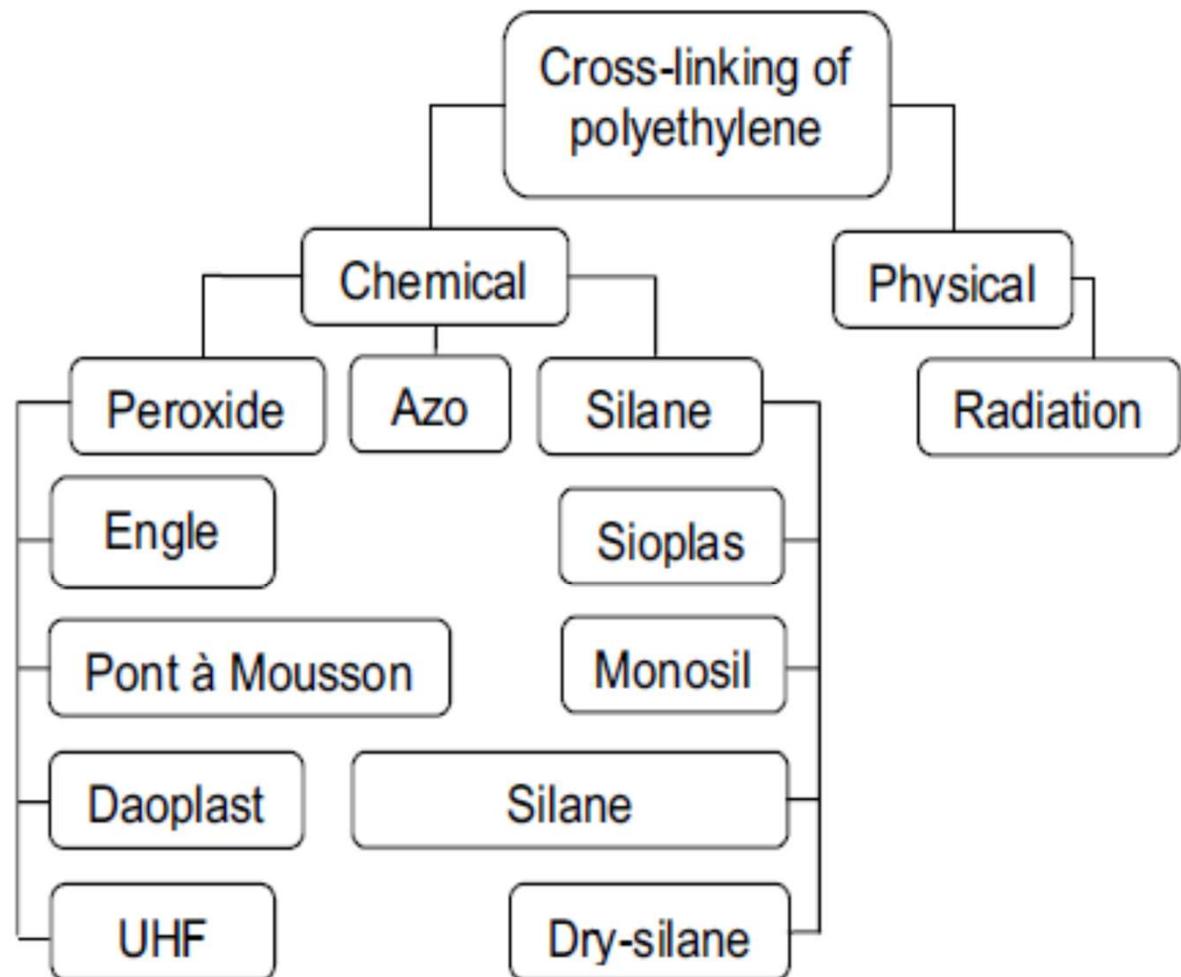


Figure 1. Polyethylene cross-linking methods.

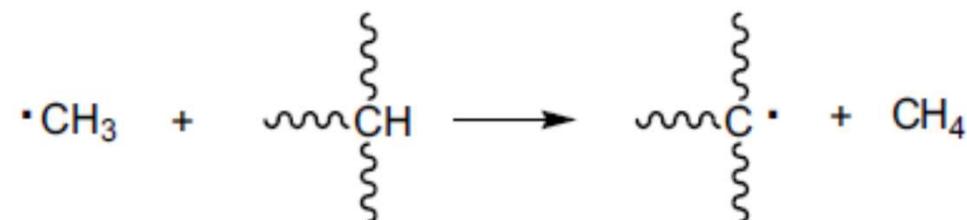
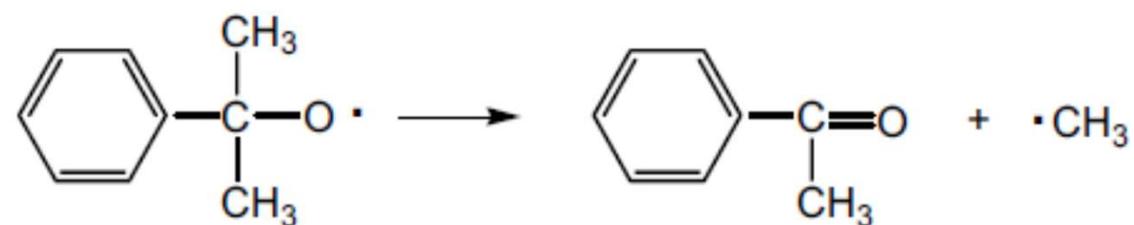
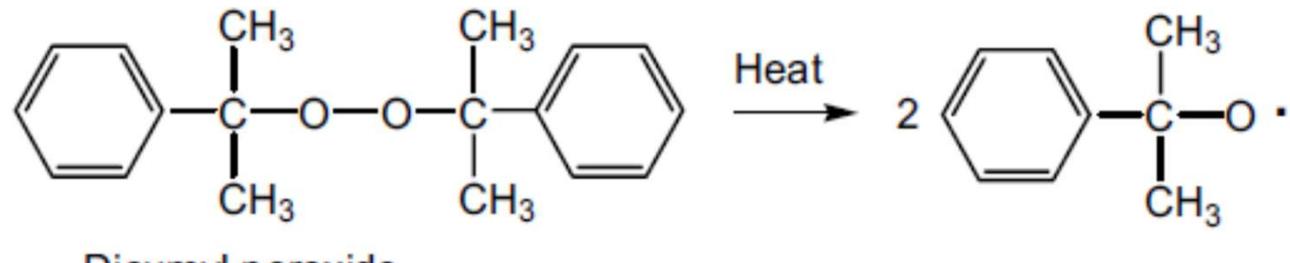
The effects of varying peroxide concentration in crosslinked linear polyethylene

T. R. MANLEY and M. M. QAYYUM

Materials

The high density polyethylene used was Lupolen 5261Z (BASF). This has a density between 0.950 and 0.953 with a melt flow index of 1.7–2.3. Trigonox B (Di-tertiary butyl peroxide) was supplied by Novadel Limited in 95% purity. Special Boiling Point Spirit No. 4; (Aniline Point 58.5°C) (Shell-Mex and BP) and silicone Fluid MS 550 (Midland Silicones Ltd) were used as a solvent for the Trigonox B and as a lubricant respectively; 100 parts of peroxide, 100 parts of solvent and 40 parts of lubricant were used to assist dispersion.

The Peroxide Cross-link Mechanism for Polyethylene is a Free Radical Reaction



Gel Content Measurements are Dependent on the Solvent Used in the Analysis

Table 3 Gel content of crosslinked polyethylene

No.	% Peroxide	Toluene (110°C)	% Gel content		
			Xylene (137-140°C)	White Spirit	Tetraline (203-209°C)
1	Nil	93.04	26.1	Nil	Nil
2	0.140	97.84	52.08	59.18	45.84
3	0.223	94.77	71.10	31.44	67.74
4	0.263	90.86	75.60	86.96	68.06
5	0.266	*	90.2	75.82	69.25
6	0.393	*	76.5	44.62	67.84
7	0.436	94.60	94.6	65.42	70.12
8	0.543	*	*	78.04	71.05
9	0.585	94.17	83.7	83.54	73.81
10	0.693	*	*	90.11	75.69

* Not determined

Mechanical Properties are Dependent on the Peroxide Concentration

Table 6 Percentage elongation at break of crosslinked linear polyethylene at 19°C (BS 2784). Mean of 10 results

Peroxide content	Nil	0·140	0·223	0·263	0·266	0·393	0·436	0·543	0·585	0·693	
Extrusion rate ft./h*	171	180	195	171	195	157	210	157	160	150	
Sample No.	Rate of strain in./min†										
1	2	(75·7) 638	(83·7) 492	(78·7) 490	(50·2) 462	(34·5) 153	(96·5) 273	(37·4) 141	(40·5) 176	(16·5) 268	(29·2) 143
2	5	(253·6) 462	(124·8) 370	(140·1) 334	(103·2) 438	(46·8) 137	(72·0) 180	(49·6) 159	(36·5) 138	(50) 168	(31·1) 127
3	12	(12·2) 100	(148·6) 244	(139·1) 258	(98·2) 259	(34·5) 157	(39·0) 137	(60·1) 159	(39·3) 214	(33·5) 115	(50·5) 153
4	20	(26·4) 98	(38·1) 179	(70·3) 219	(84·0) 268	(44·7) 177	(37·0) 161	(56·7) 161	(72·6) 189	(43·3) 143	(33·7) 149

Standard Deviation is given in brackets

* 1 ft/h = 0·305 m/h

† 1 in/min = 0·0254 m/min

After about
0.3% Peroxide
the % Gel in the
PEX Does Not
Increase Above
70%

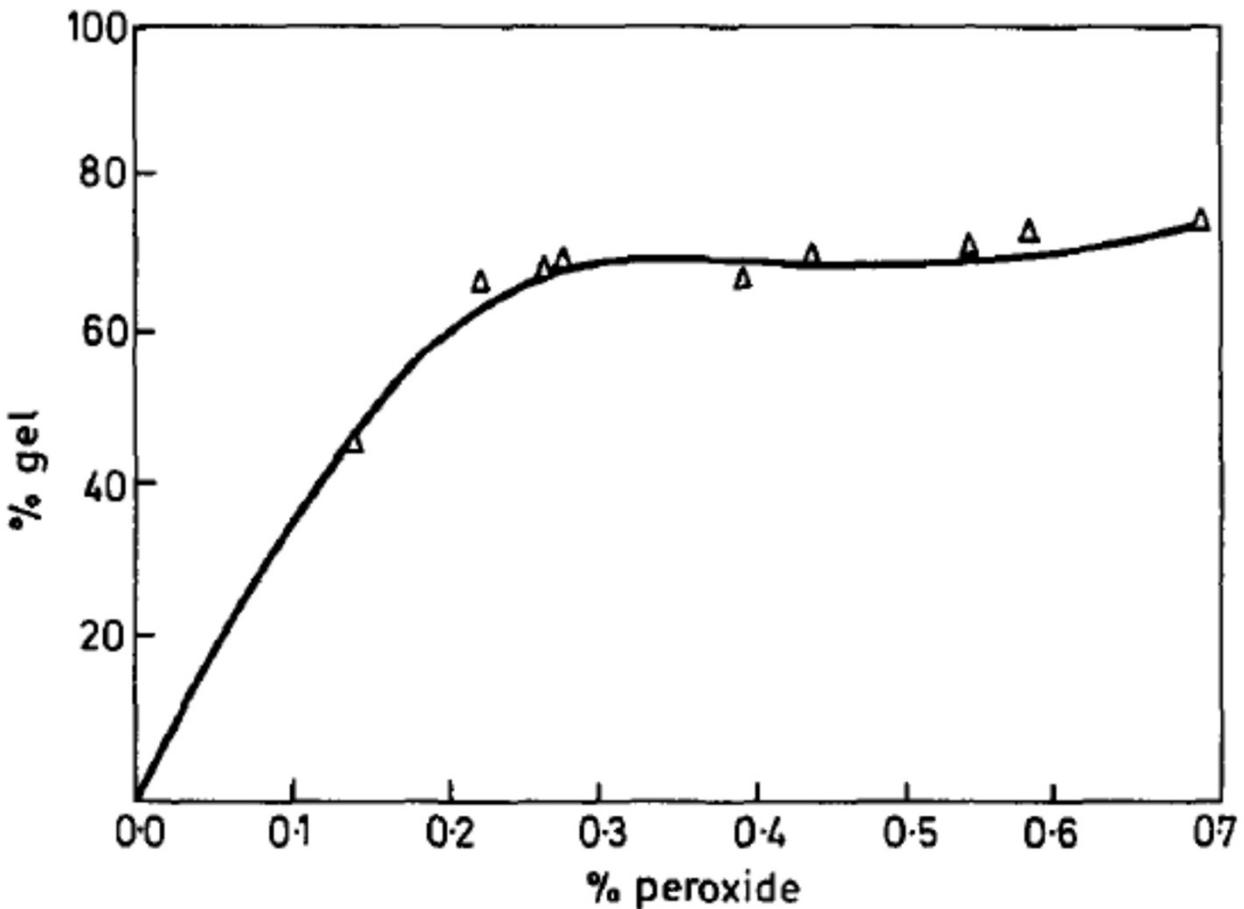


Figure 5 Gel content against peroxide content of crosslinked polyethylene

The Tensile Strength and Elongation at Break for Various Peroxide Concentrations

Table 7 Tensile strength of crosslinked polyethylene at different temperatures. Strain rate 5in./min

Temp (°C)	% of peroxide				
	0·263	0·393	0·543	0·585	0·693
19	2967	3393	2743	2549	2608
100	1645	2130	1490	1340	1845
140	1275	1260	1155	1175	1295

Results are in lbf/in². (1 lbf/in² = 6·895 kN²)

Table 8. Elongation of crosslinked polyethylene at different temperatures. Strain rate 5in./min

Temp (°C)	% peroxide				
	0·263	0·393	0·543	0·585	0·693
19	438	180	138	168	127
100	360	300	90	100	220
140	360	320	115	155	175

Results are in lbf/in². (1 lbf/in² = 6·895 KN²)

As the Cross-link Density Increases the Overall Density of the Polyethylene Decreases

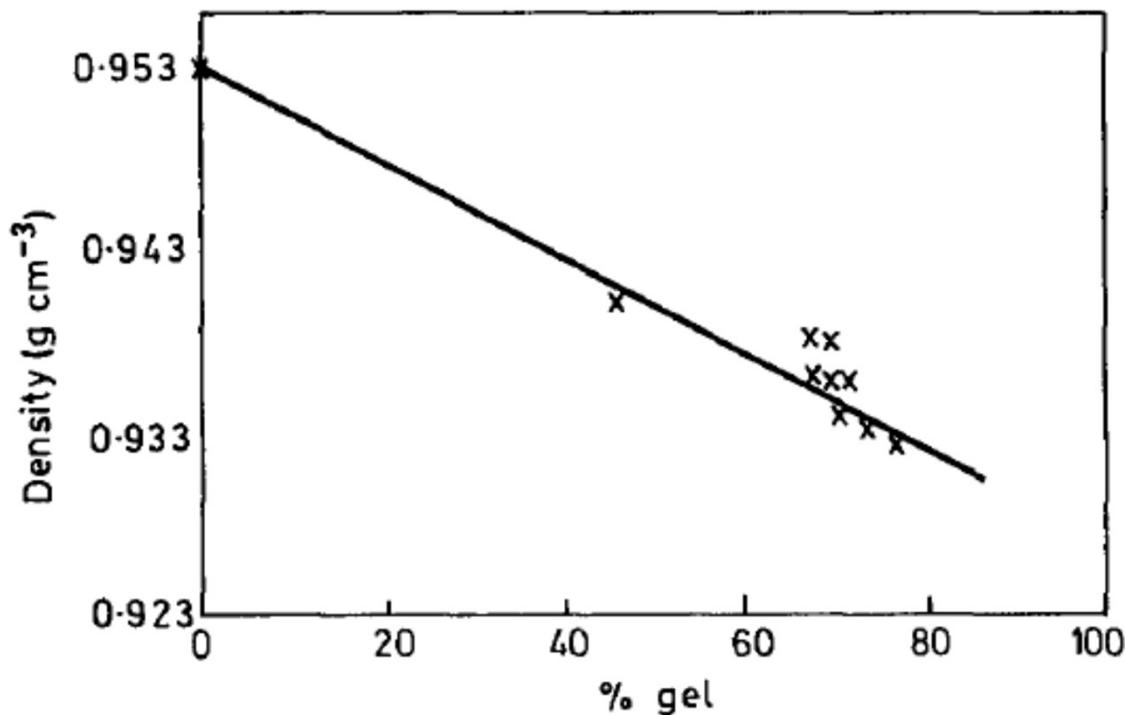
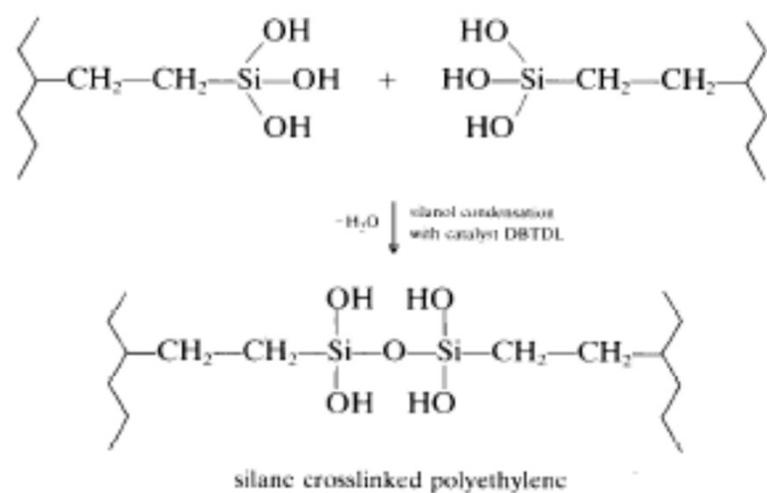
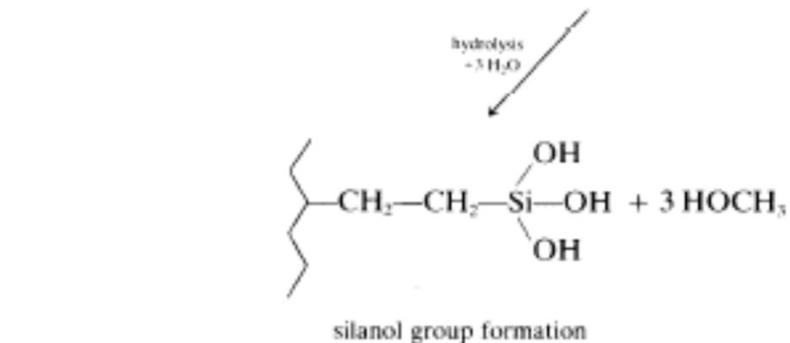
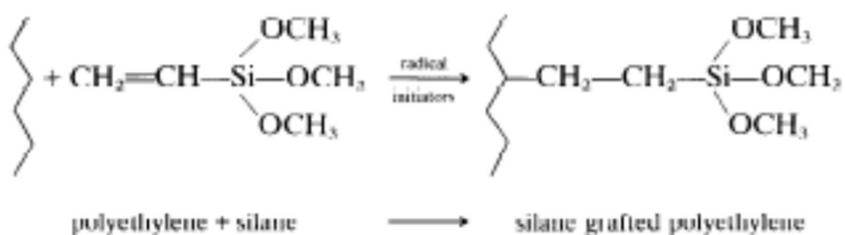


Figure 4 Densities of crosslinked polyethylene against gel content in tetralin

Polyethylene Cross-link Reaction using Silane



Silane Cross-linked
PEX Must be Cured
at a Humid - High
Temperature
Environment

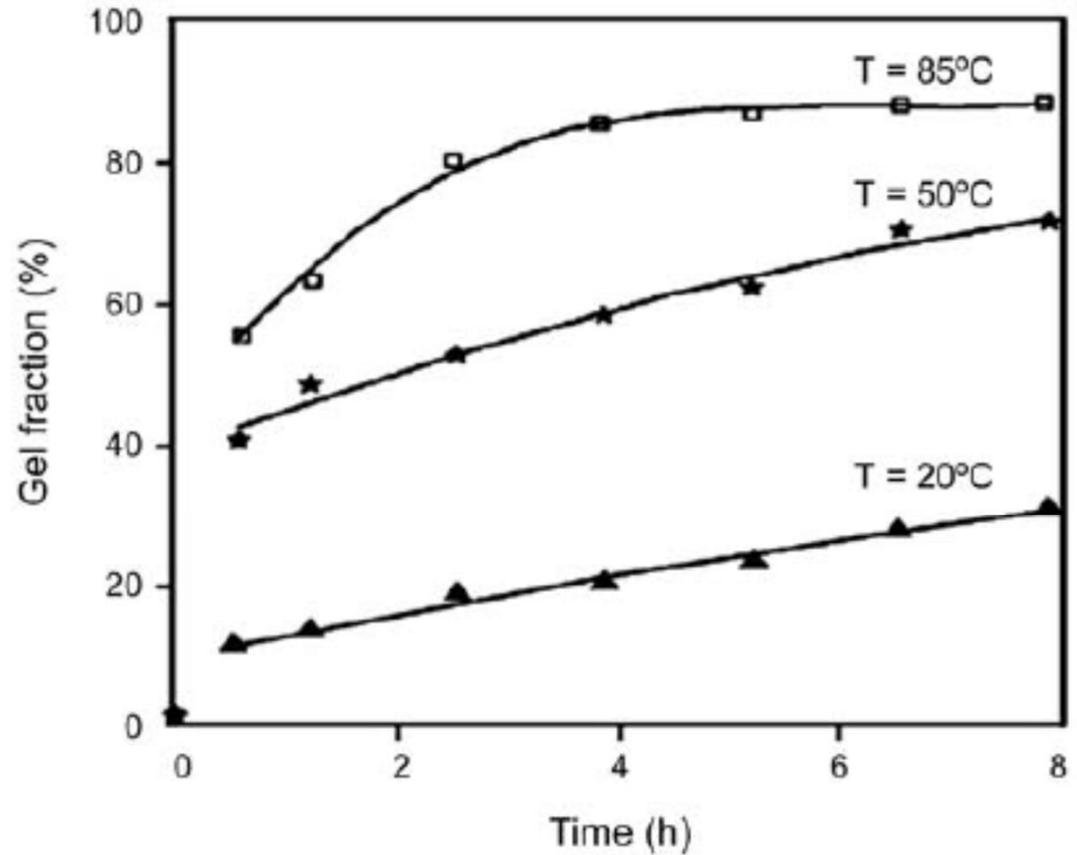


Figure 11. Effect of curing time and water temperature on silane cross-linking of LDPE [84].

Comparison of Peroxide and Silane PEX Tensile Properties

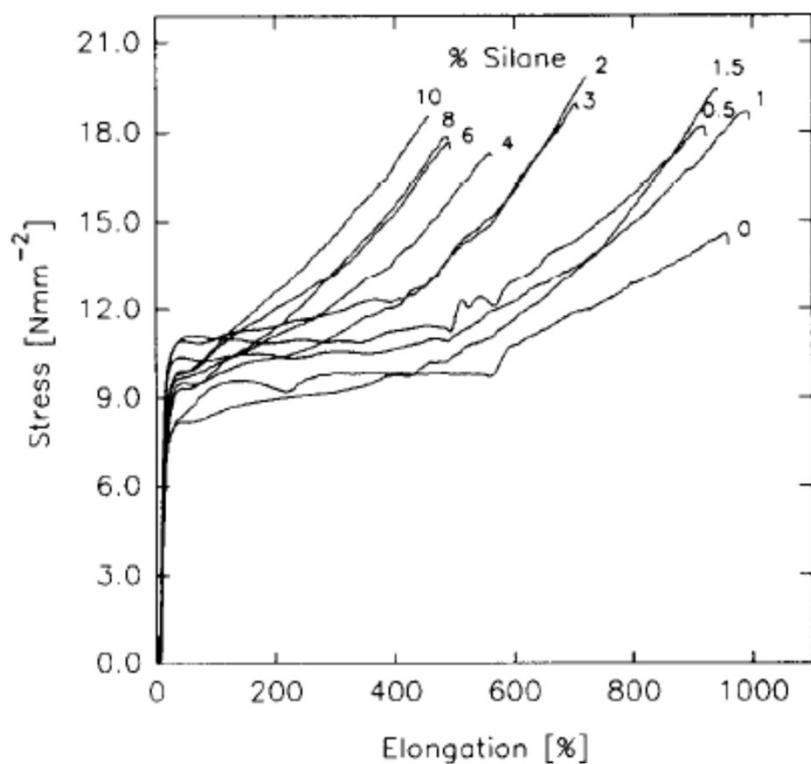


Fig. 6. Typical tensile testing results of silane XLPE samples.

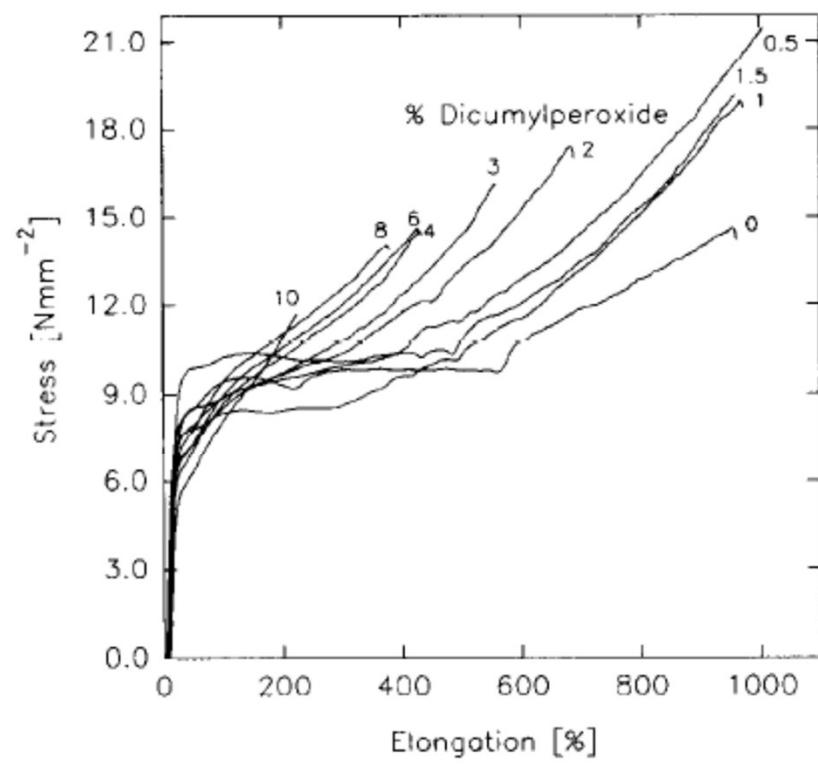


Fig. 5. Typical tensile testing results of peroxide XLPE samples.

Comparison of PEX Cross-linking Methods

Table 2. Comparison of several major cross-linking methods.

Method \ Aspect	Silane	Peroxide	Radiation
Process flexibility	Very good	Small	Very good
Operation	Easy	Difficult	Difficult
Extruder	Standard	Special	Standard
Production rate	High as for PE	Low	High as for PE
Cost of post treatment	Low	-	High
Capital investment	Low	High	High
Diameter	No limit, thickness limited by speed of cross-linking	Difficult to achieve big diameters because of output	Limited by penetration depth of electron
Scrap rates	Low	High scrap	
Raw material costs	Slightly high	Low	Low
Levels of attainable cross-link density		High	Probability of variation
Other	Wider scope for formulation through broad processing window, recyclability	Energy intensive	Clean (pipe) because of fewer additives

Both Peroxide and Silane Cross-linked Polyethylene are Influenced by UV Light Aging

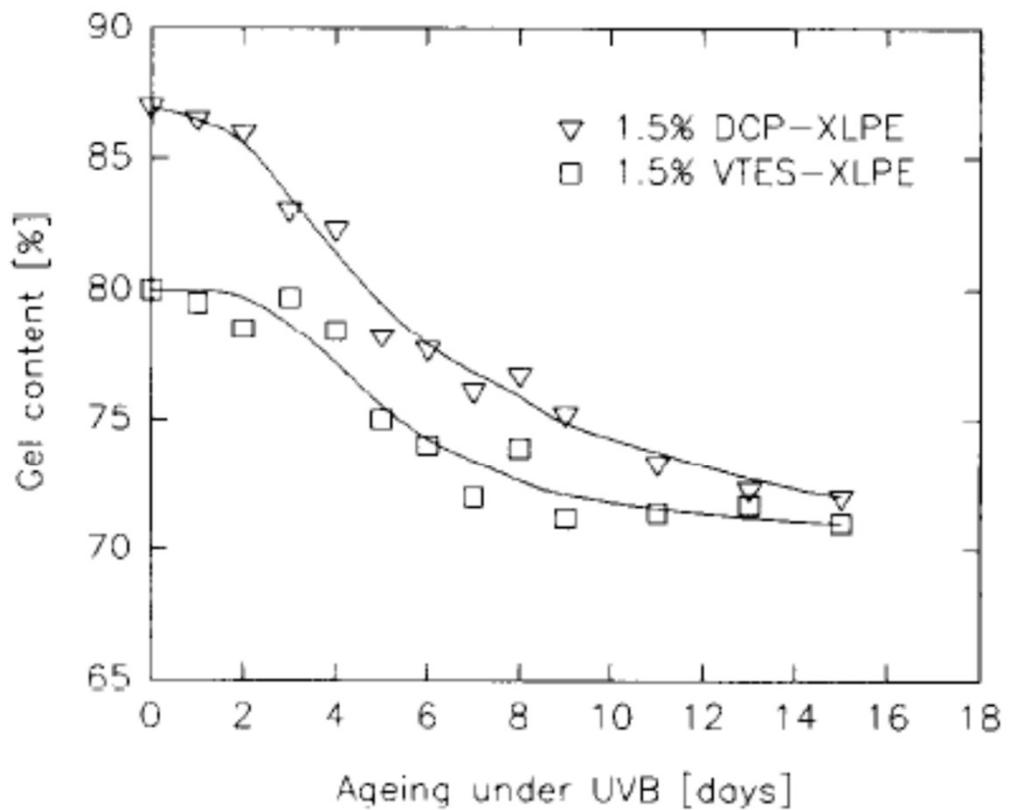


Fig. 16. Changes in the gel content of peroxide and silane XLPE during accelerated UVB exposure.

Both Peroxide and Silane Cross-linked Polyethylene are Influenced by High Temperature Aging in an Oxygen Environment

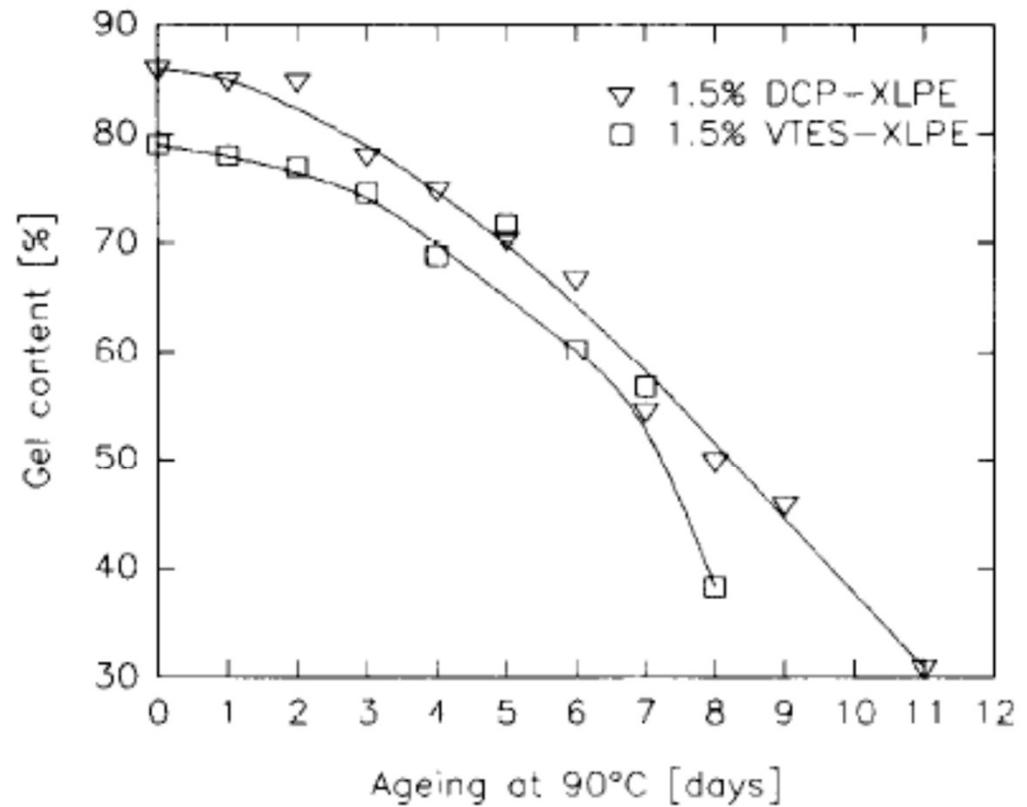


Fig. 14. Changes in the gel content of peroxide and silane XLPE during thermal ageing at 90°C under oxygen.

Both Peroxide and Silane Cross-linked Polyethylene Mechanical Properties are Influenced by High Temperature Aging in an Oxygen Environment

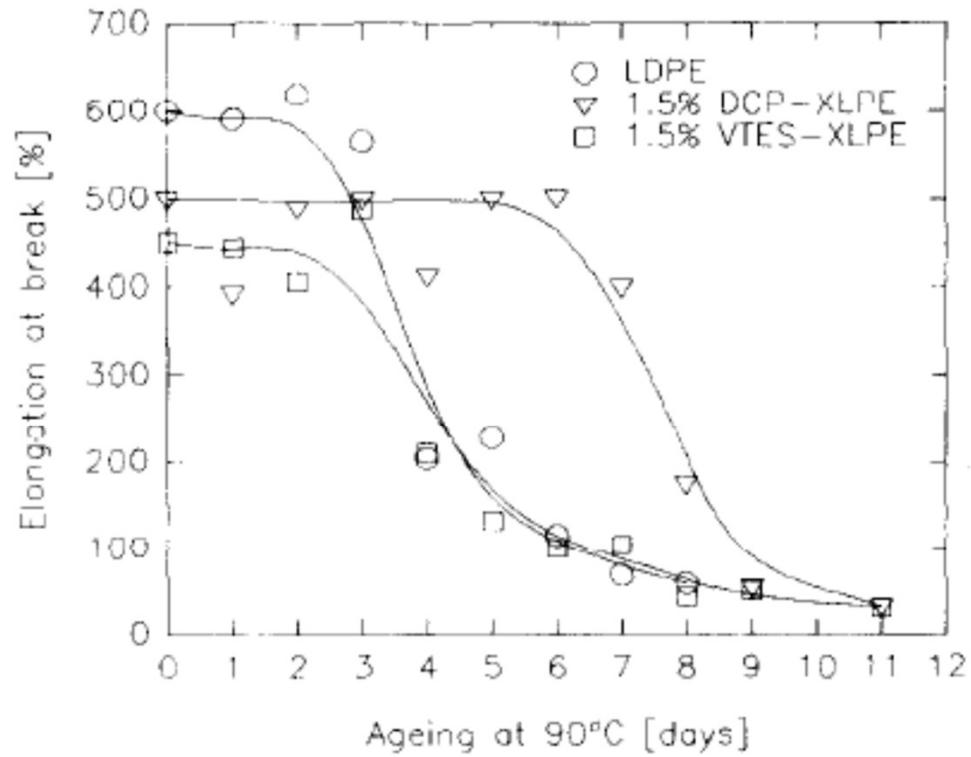
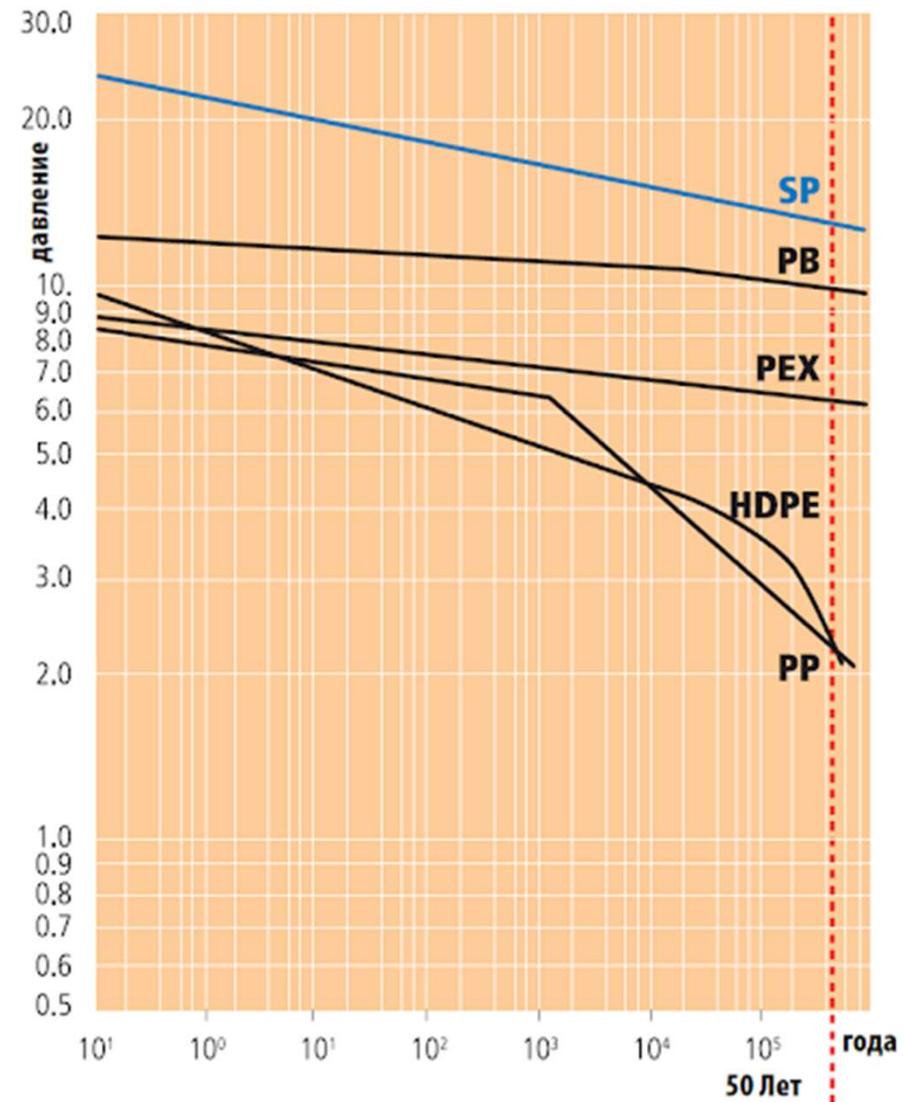


Fig. 13. Changes in the mechanical properties of LDPE and XLPE samples during thermal ageing at 90°C under oxygen.

What is the Purpose for Cross-linking PE to Produce PEX?



What is the Purpose for Cross-linking PE to Produce PEX?

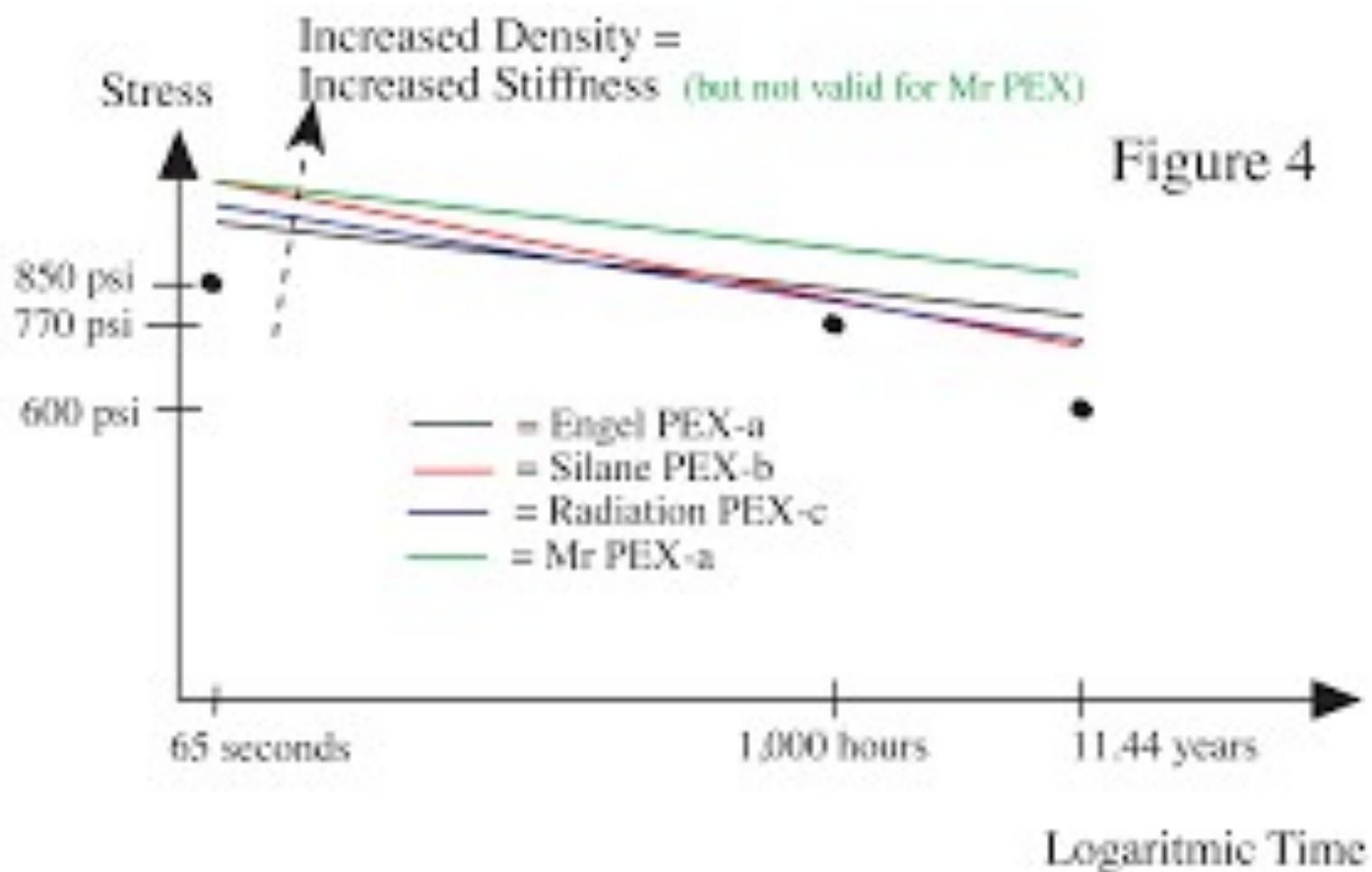
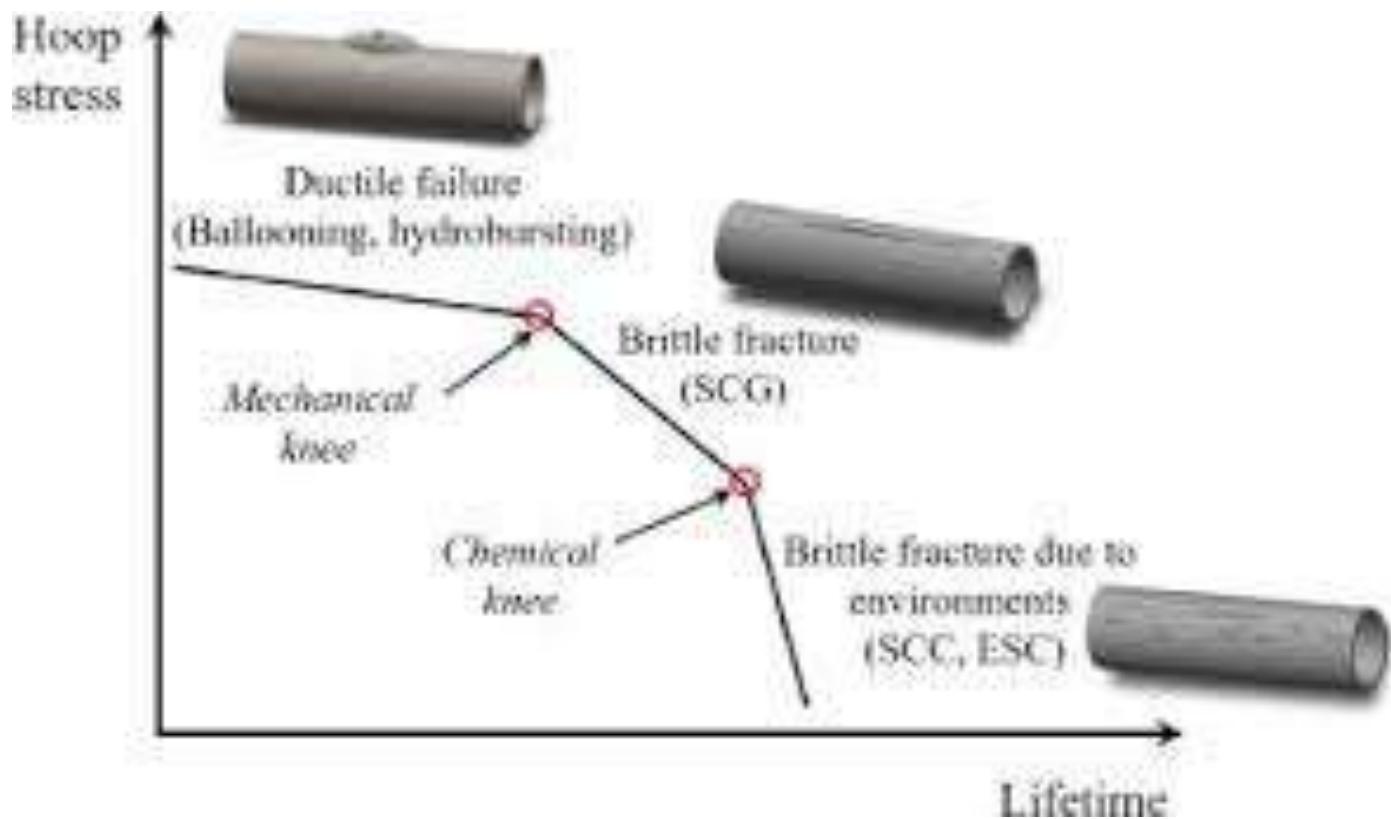


Illustration of the Environmental Degradation Failure on a Hoop Stress vs Failure Time Plot



Environmental Degradation Failure of PEX Plumbing Pipe



1.A: 10% of Pipe Lifetime



1.B: 50% of Pipe Lifetime



1.C: At Failure



2.A: 10% of Pipe Lifetime



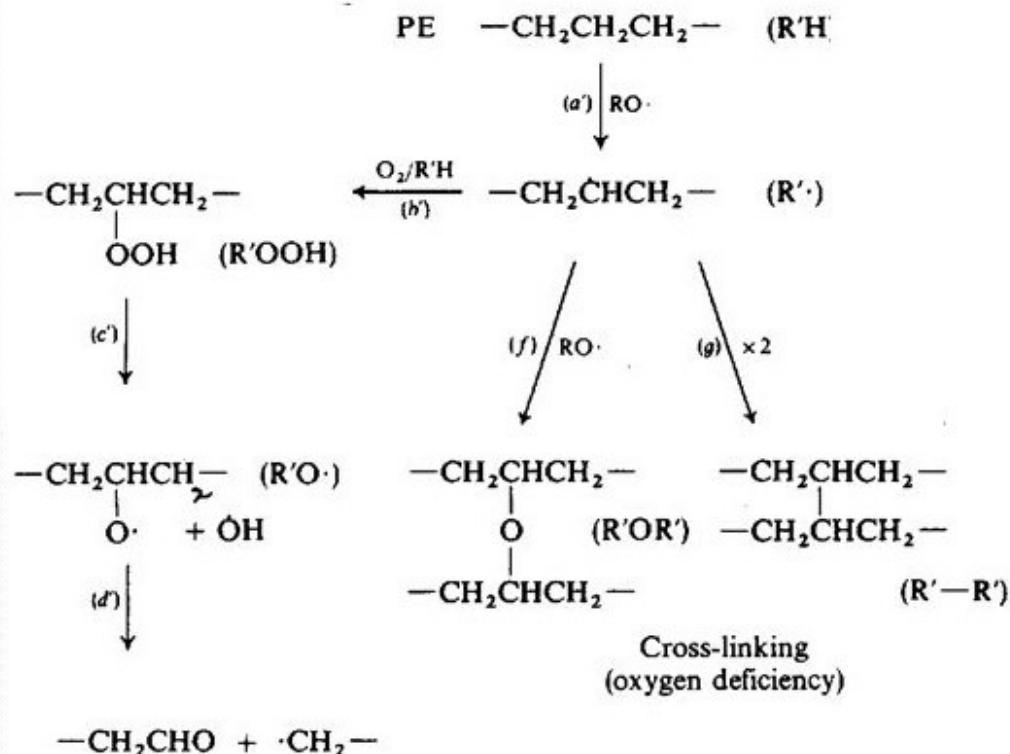
2.B: 50% of Pipe Lifetime



2.C: At Failure

Degradation Reaction

Mechanism for PEX Materials at High Temperatures and Aggressive Environment



Property	Increasing MW	Decreasing MW
Mechanical strength	increases	decreases
Toughness	increases	decreases
Stress crack resistance	increases	decreases
Melt flow	decreases	increases

Degradation of PEX in Aggressive Environments



Lesson 3: Polyolefin – PE 5: Chlorinated Polyethylene, and Cross-linked Polyethylene

Questions?



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“You know you’re getting old when the candles cost more than the cake.”

There will be a Quiz on Monday, February 24.



www/DesktopBackground.org

* From the Hitchhikers Guide to the Galaxy – Douglas Adams

EMAC 276

Lecture 14: The Polyolefin Family

Polyethylene – PE

Polypropylene - PP

Poly(1-butene) – Polybutylene – PB

Andy Olah

February 21, 2025

What is a “Olefin” Type Polymer?

Vinyl polymers are the most common type of polymers derived from “vinyl-type” monomers having the general structure:



Where,

polystyrene – R = C₆H₅

polyvinyl chloride – R = Cl

polyvinyl acetate – R = O₂CCH₃

polyacrylonitrile - R = CN

Not to be confused with poly(vinyl chloride) (PVC) materials which have traditionally been identified as “Vinyls”; i.e., vinyl siding, vinyl records, etc.

Olefin polymers are a subgroup of vinyl monomers produced from alkenes having a C_nH_{2n} monomer structure:

polyethylene – R = H => CH₂ = CH₂; (n = 2) => C₂H₄

polypropylene – R = CH₃ => CH₂ = CH-CH₃; (n = 3) => C₃H₆

polybutylene – R = CH₂-CH₃ => CH₂ = CH-CH₂-CH₃; (n=4) => C₄H₈

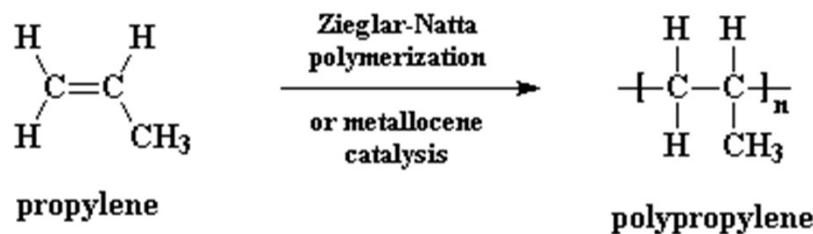
Polypropylene

Phillips Petroleum chemists J. Paul Hogan and Robert Banks first demonstrated the polymerization of propylene in 1951.

Polypropylene was subsequently polymerized by German chemist named Karl Rehn and an Italian chemist named Giulio Natta to a crystalline isotactic polymer in 1954. This discovery soon led to a large-scale production of polypropylene starting in 1957 by the Italian firm Montecatini.

Polypropylene is made from polymerization of propylene monomer (an unsaturated organic compound - chemical formula C₃H₆) by:

Ziegler-Natta polymerization or Metallocene catalysis polymerization:



The Four Generations of Polyolefin Catalysis

Catalysts:

1st Generation (<1960): Original Z-N ($\gamma\text{-TiCl}_3 + \text{AlCl}_3$).

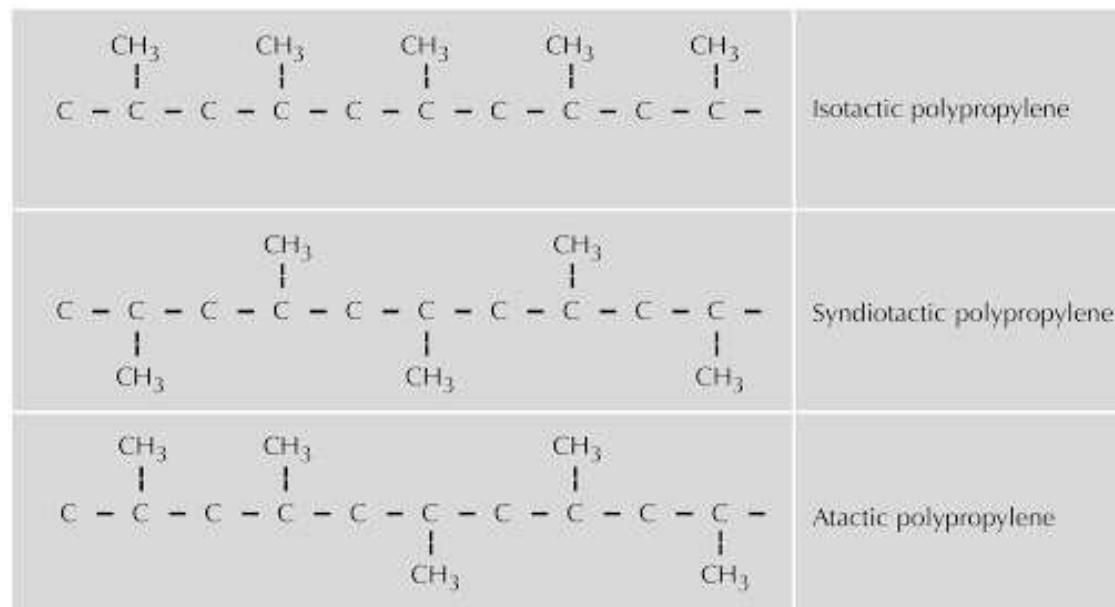
Al alkyl co-catalyst. 92% isotactic.

2nd Generation (1960's): Modified Z-N. 5x more active than original Z-N catalyst. 96% isotactic.

3rd Generation (1970's): $\text{TiCl}_3/\text{MgCl}_2$. 100x times more active than 1st generation catalyst. 94-96% isotactic.

4th Generation (1990's): Metallocenes (SSC's). 10x more active than 3rd generation catalysts. 94-96% isotactic.

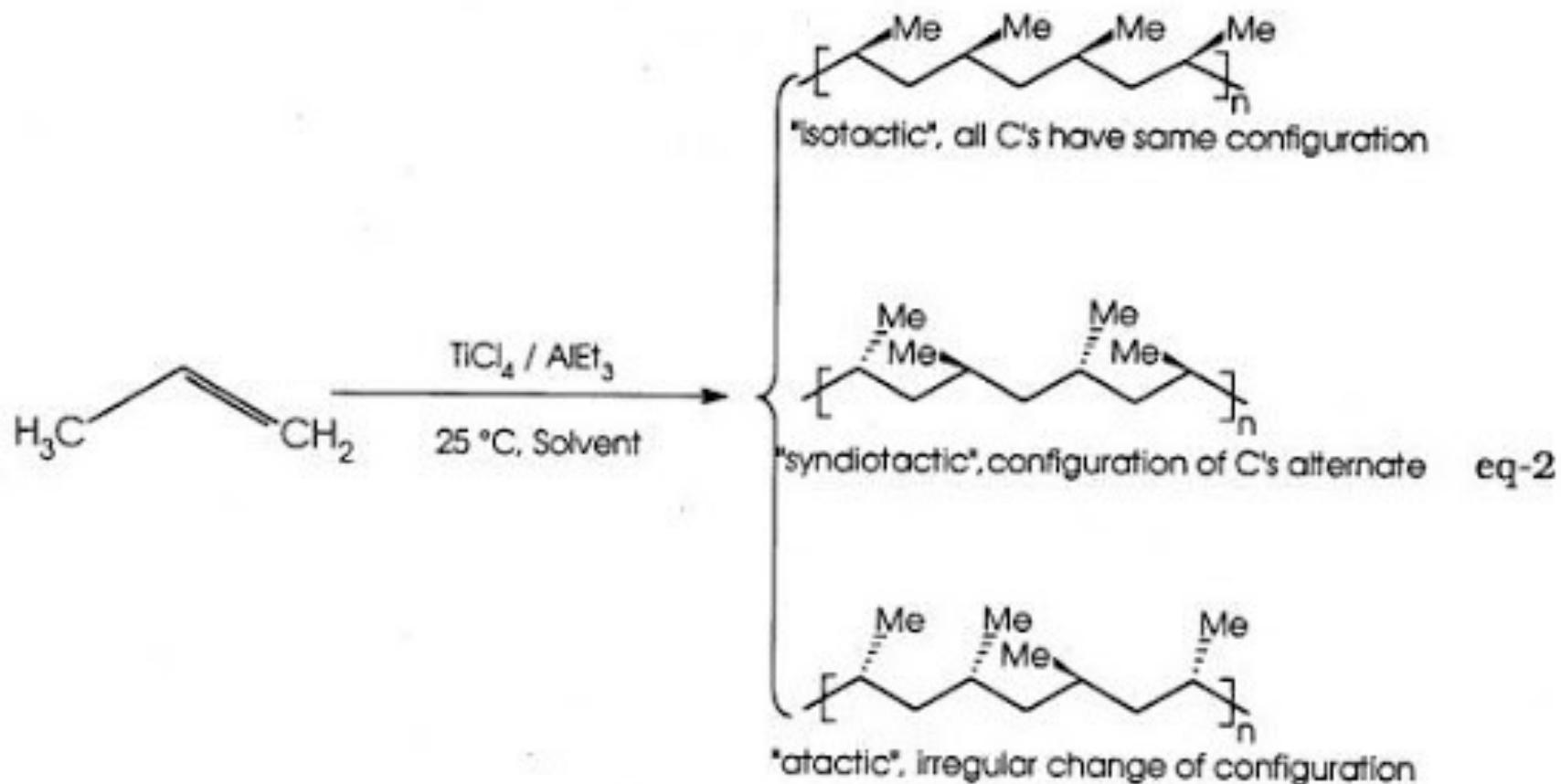
Due to the Asymmetry of the Monomer
Three Types of Tacticity for Polypropylene are Possible



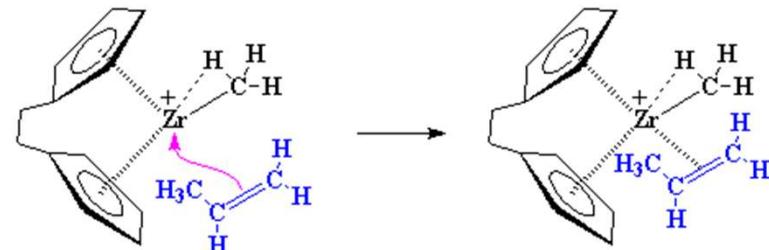
Polypropylene exists in three possible forms:

	<u>Isotactic</u>	<u>Syndiotactic</u>	<u>Atactic</u>
M.P. (°C)	170	135	---
M.W.	~500,000	~300,000	very low
Density (g/cm ³)	0.91	0.88	---
Crystallinity	crystalline	crystalline	amorphous

Ziegler – Natta Catalysts can Produce all Three Types of Polypropylene



Metallocene Synthesis can Also Produce All Three Types of Polypropylene Tacticity

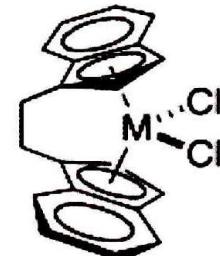


In addition, the use of chiral metallocenes that have bridged cyclopentadienyl rings has made possible highly stereoselective (or stereoregular) polymerization of α -olefins. For example, by using metallocene **1** below for polymerization of propylene, the **atactic** form of polypropylene is obtained, while **C₂** symmetric metallocene **2** and **C_s** symmetric metallocene **3** catalyst systems produce the **isotactic** and **syndiotactic** macromolecules, respectively.



1, M = Zr, Hf

atactic



2, M = Zr, Hf

isotactic

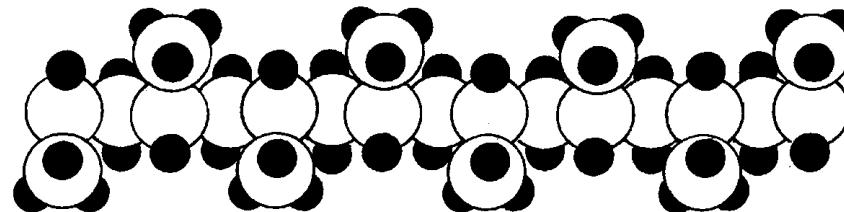


3, M = Zr, Hf

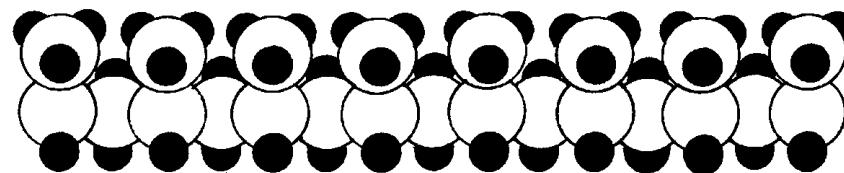
syndiotactic

“Teddy Bear” Chorus Line of Polypropylene Tacticity

Syndiotactic



Isotactic



Atactic

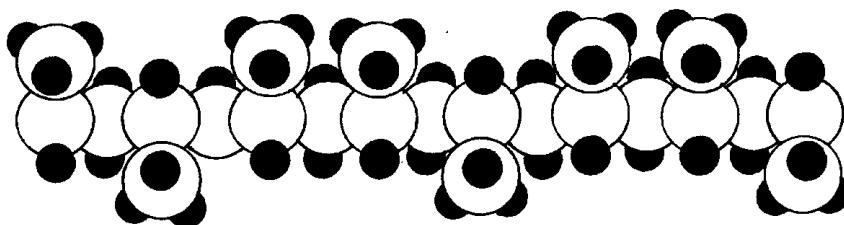
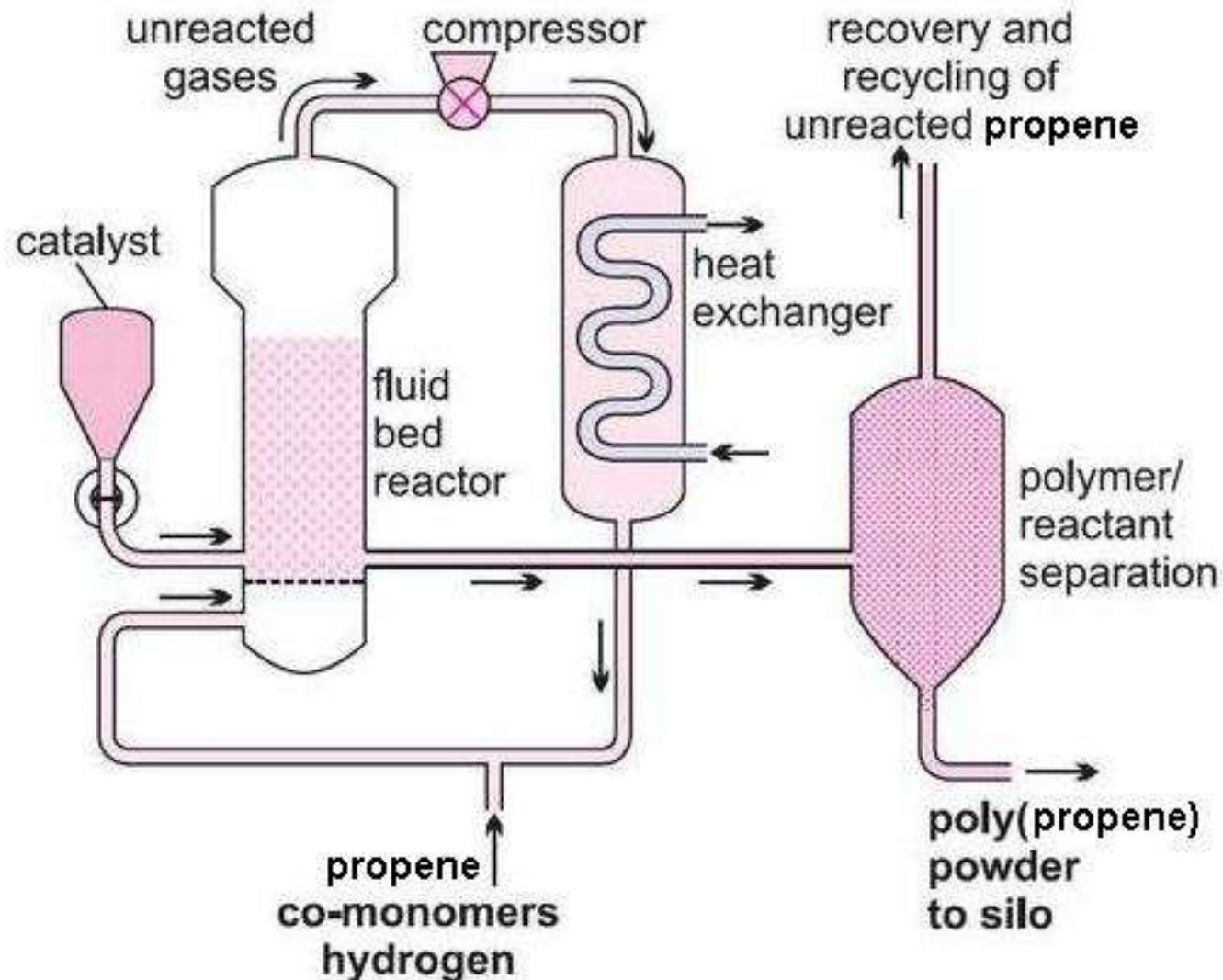
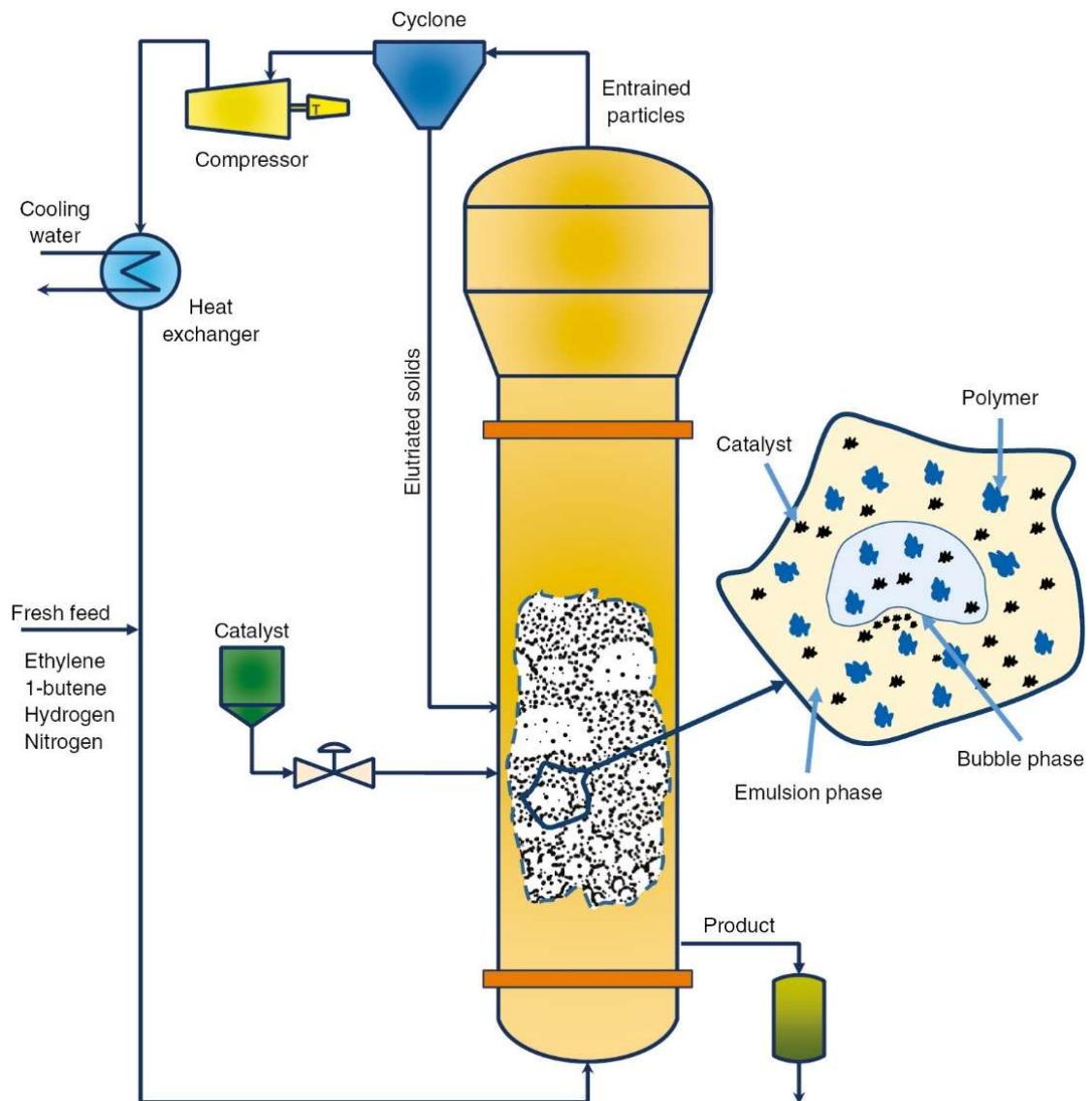
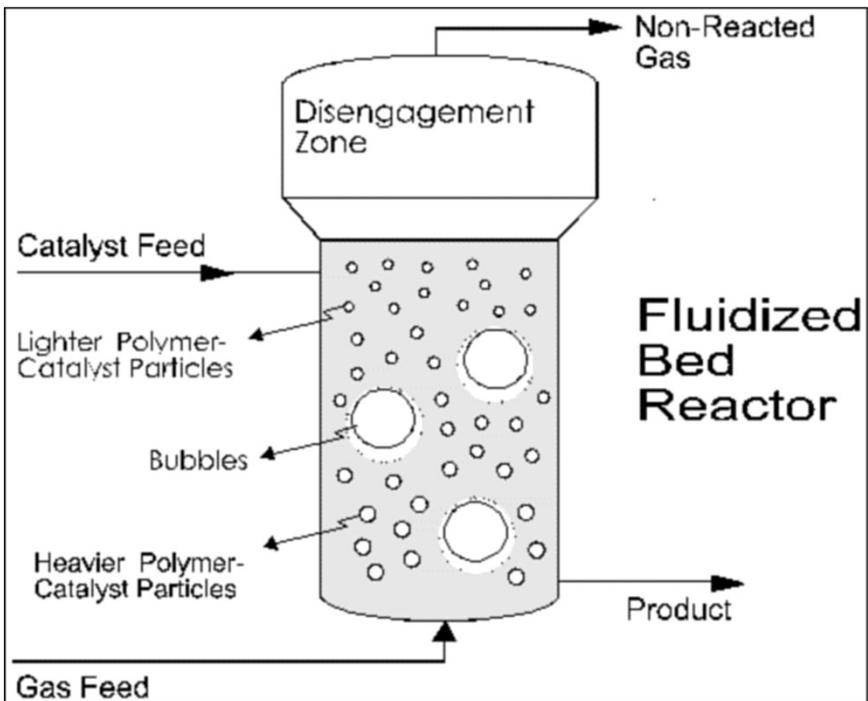


FIGURE 6.5 Space-filling models of syndiotactic (a), isotactic (b), and atactic (c) forms of polypropylene. (My children and now grandchildren believe that the isotactic polypropylene is really a chorus line of dancing teddy bears.)

Fluidized Bed
Polymerization is
a Common Type
of Olefin
Reaction Process





Details of a Fluidized Bed Polymerization Process

Both Syndiotactic and Isotactic Polypropylene can Crystallize

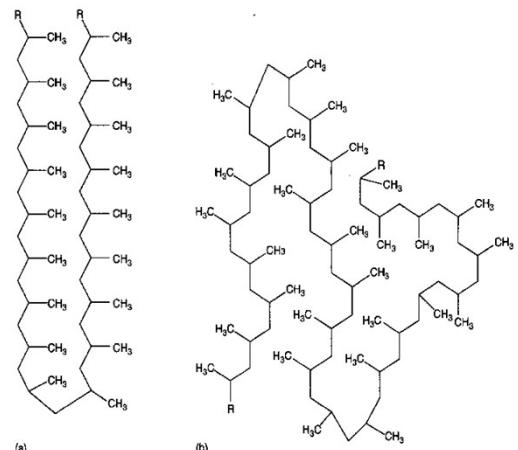
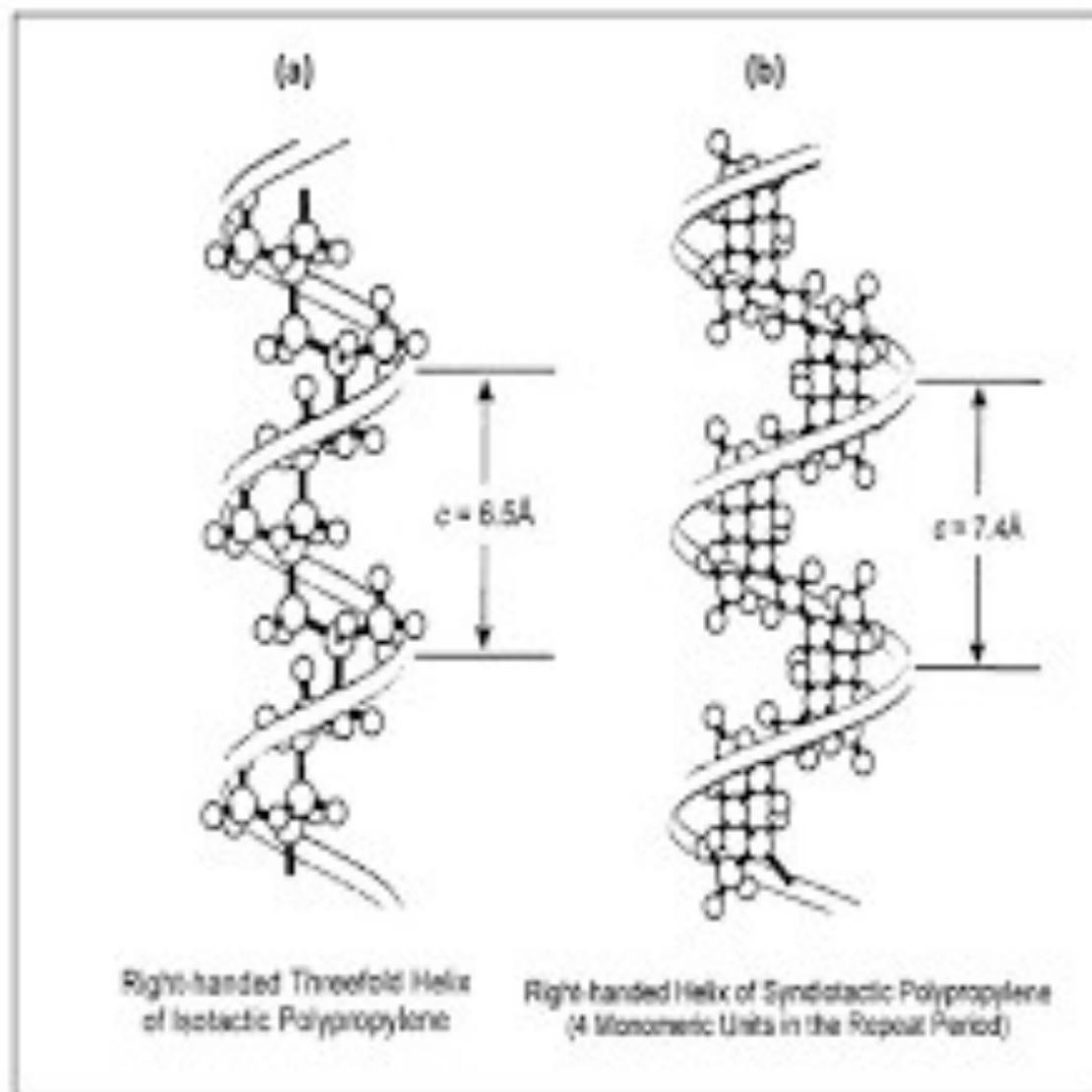


FIGURE 2.8 Representation of a crystalline portion from isotactic polypropylene (a) and an amorphous portion from atactic polypropylene (b).

Polypropylene exists in three possible forms:

	Isotactic	Syndiotactic	Atactic
M.P. (°C)	170	135	---
M.W.	~500,000	~300,000	very low
Density (g/cm ³)	0.91	0.88	---
Crystallinity	crystalline	crystalline	amorphous



Polypropylene can Easily Copolymerize with Polyethylene

HOMOPOLYMER

-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-

RANDOM COPOLYMER

-A-A-B-B-A-B-B-B-A-B-B-B-A-A-A-B-B-A-B-A-B-

BLOCK COPOLYMER

-A-A-A-A-A-A-B-B-B-B-B-B-B-B-A-A-A-A-A-

A = propylene

B = ethylene

Melting Point of Polypropylene - The melting point of polypropylene occurs at a range.

1. Homopolymer: 160 - 165°C
2. Copolymer: 135 - 159°C

Density of Polypropylene - PP is one of the lightest polymers among all commodity plastics. This feature makes it a suitable option for lightweight\weight saving applications.

1. Homopolymer: 0.904 – 0.908 g/cm³
2. Random Copolymer: 0.904 – 0.908 g/cm³
3. Impact Copolymer: 0.898 – 0.900 g/cm³

Polypropylene can Easily Copolymerize with Polyethylene

Polypropylene Homopolymer is the most widely utilized as a general purpose grade. It contains only propylene monomer in a semi-crystalline solid form. Main applications include packaging, textiles, healthcare, pipes, automotive and electrical applications.

Polypropylene Copolymer family is further divided into random copolymers and block copolymers produced by polymerizing of propene and ethane:

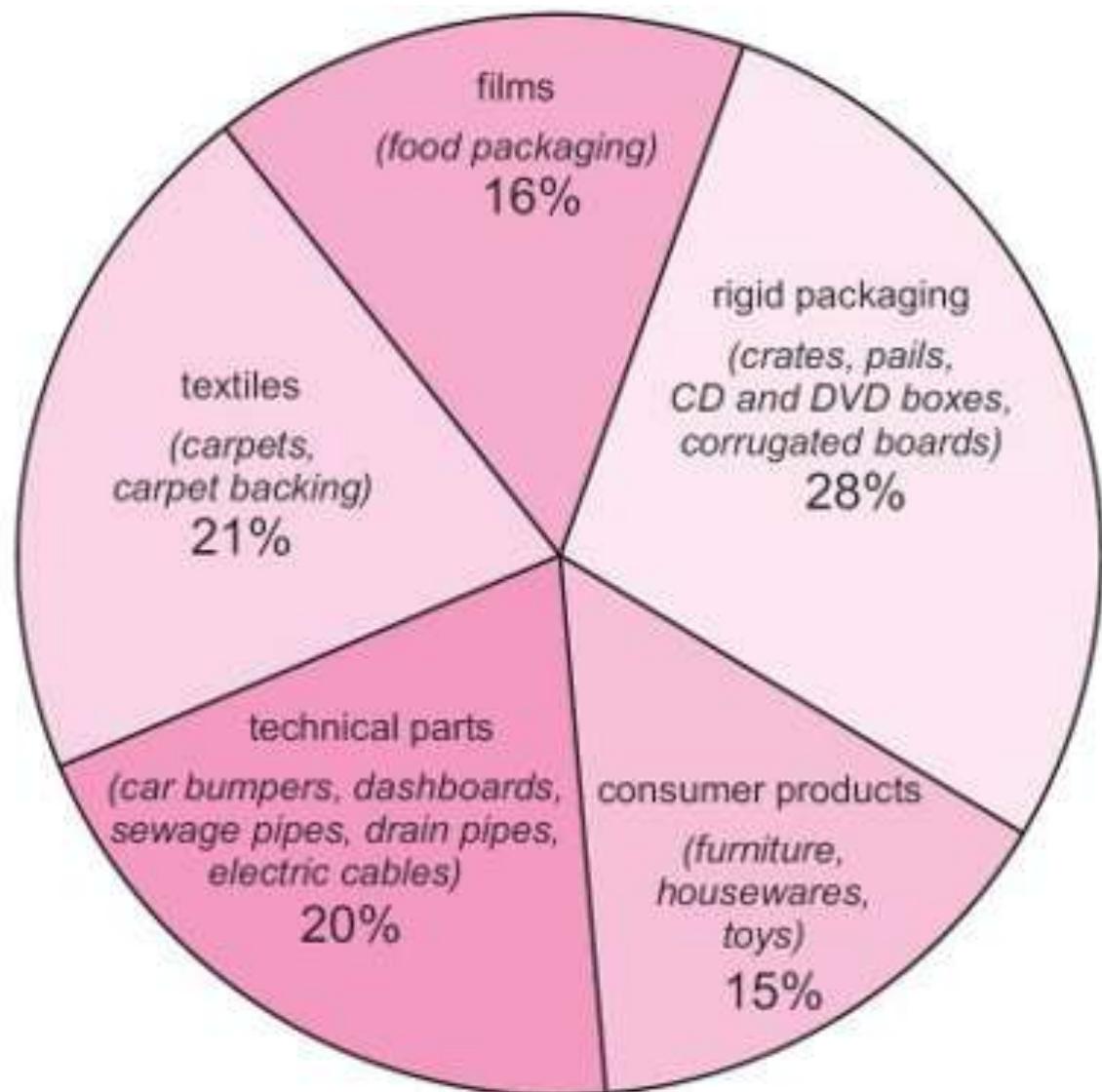
Polypropylene Random Copolymer is produced by polymerizing together ethene and propene. It features ethene units, usually up to 6% by mass, incorporated randomly in the polypropylene chains. These polymers are flexible and optically clear making them suitable of applications requiring transparency and for products requiring an excellent appearance.

While in **Polypropylene Block Copolymer**, ethene content is larger (between 5 and 15%). It has co-monomer units arranged in regular pattern (or blocks). The regular pattern hence makes thermoplastic tougher and less brittle than the random co-polymer. These polymers are suitable for applications requiring high strength, such as industrial usages.

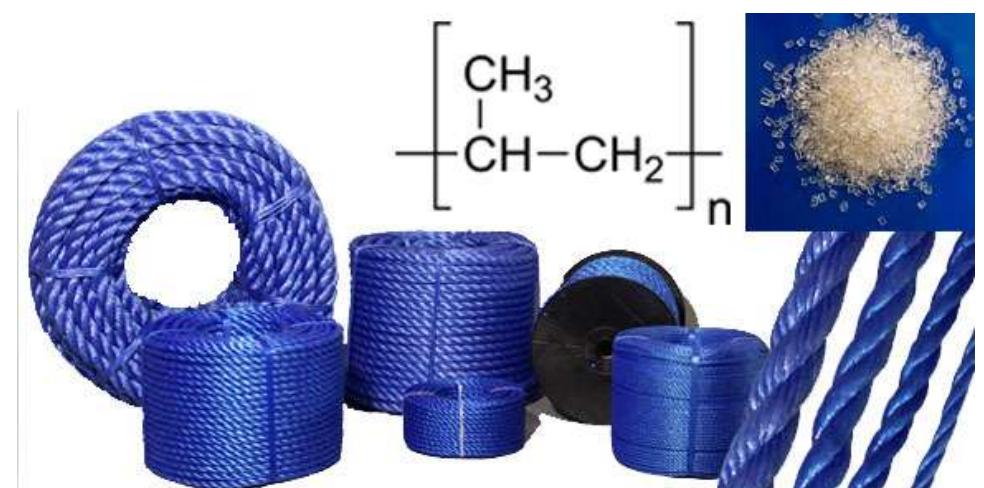
Property Comparison of Polypropylene Homopolymer and Copolymer

Property	Homopolymer			Copolymer	
Melt flow index	3	0.7	0.2	3	0.2
Tensile strength (MPa)	34	30	29	29	25
Elongation at break (%)	350	115	175	40	240
Flexural modulus (MPa)	1310	1170	1100	1290	1030
Brittleness temp. (°C)	-15	0	0	-15	-20
Vicat softening point (°C)	154-150	148	148	148	147
Rockwell hardness (R-scale)	95	90	90	95	88.5
Impact strength (ft lb)	10	25	34	34	42.5

Applications for Polypropylene



Typical PP Homopolymer Products



March 5, 1963

A. K. MELIN
HOOP TOY

3,079,728
Filed May 13, 1959

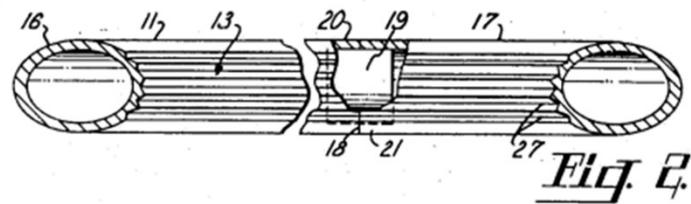


Fig. E.

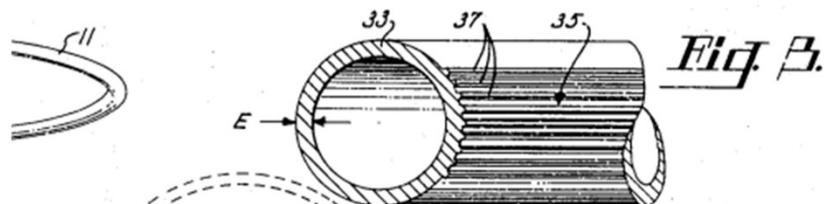


Fig. B.

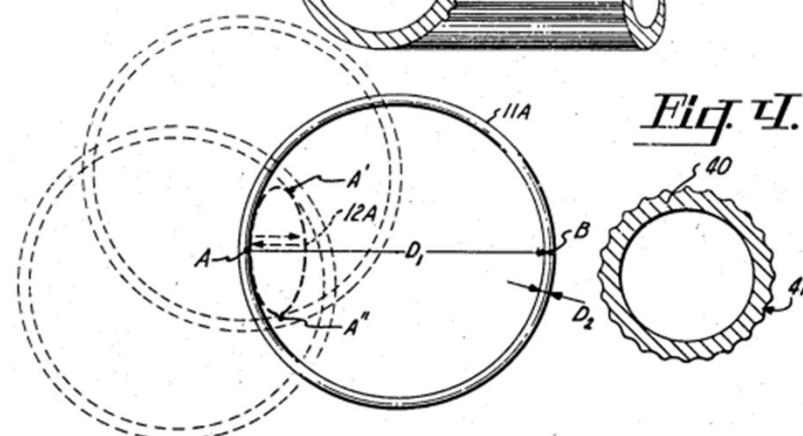


Fig. H.

The original polypropylene produced by Phillips Petroleum (Marlex) had very poor properties.

It was extremely brittle restricting any large volume sales. Phillips had a large stockpile of polypropylene which they could not move from inventory.

UNTIL: A new revolutionary product came along which utilized all of the overstock that Phillips had

Development of Wham-O and the Hula Hoop

In 1948, friends Arthur Melin and Richard Knerr founded a company in California to sell a slingshot they created to shoot meat up to falcons they used for hunting. The company's name, Wham-O, came from the sound the slingshots supposedly made.

Wham-O eventually branched out from slingshots, selling boomerangs and other sporting goods. Its first hit toy, a flying plastic disc known as the **Frisbee**, debuted in 1957. The Frisbee was originally marketed under a different name, the **Pluto Platter**, in an effort to capitalize on America's fascination with UFOs.

Melin and Knerr were inspired to develop the Hula Hoop after they saw a wooden hoop that Australian children twirled around their waists during gym class. Wham-O began producing a plastic version of the hoop, dubbed "Hula" after the hip-gyrating Hawaiian dance of the same name, and demonstrating it on Southern California playgrounds. Hula Hoop mania took off from there.

March 5, 1963

A. K. MELIN
HOOP TOY

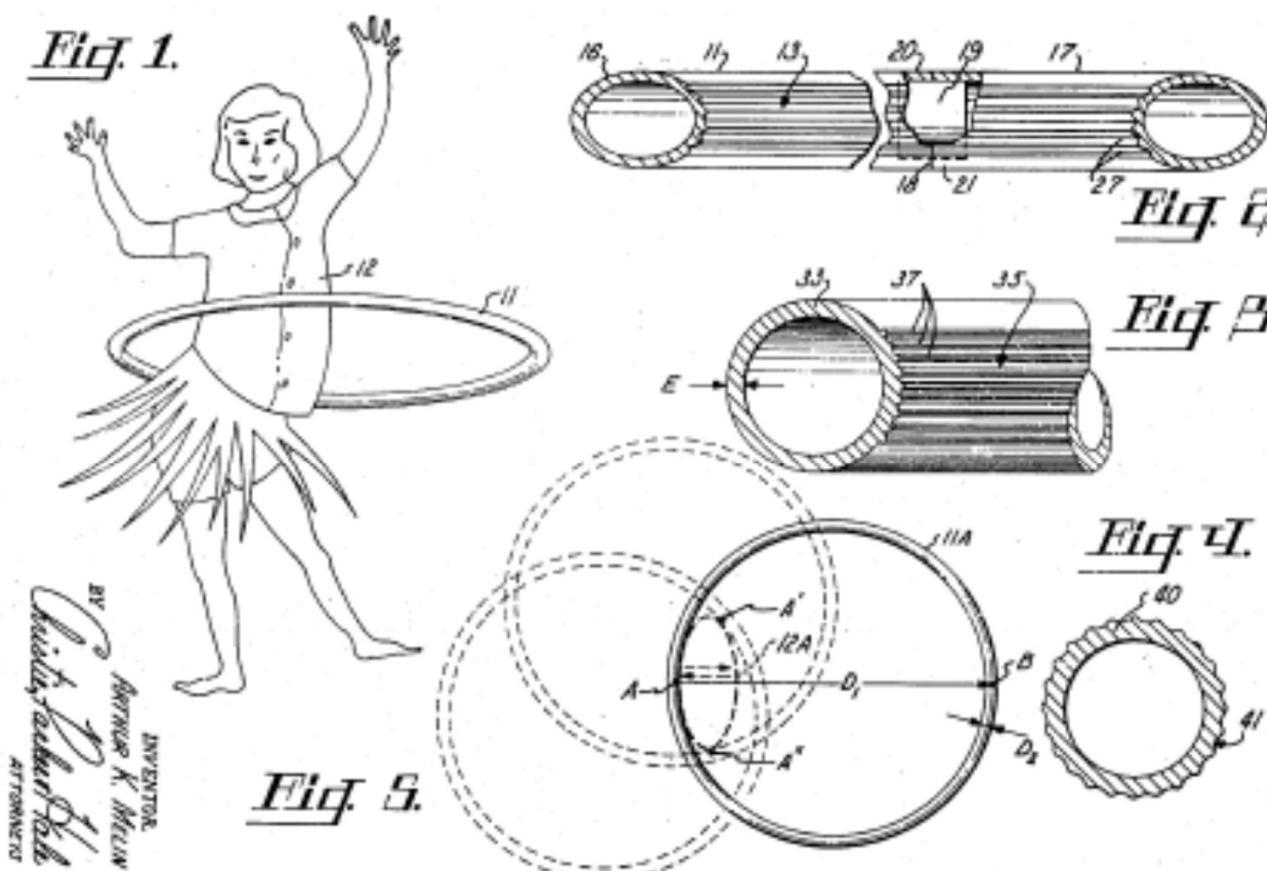
3,079,728

Filed May 13, 1959

An Original Use for a New Polymer - Polypropylene

US Patent - 3,079,728
HOOP TOY

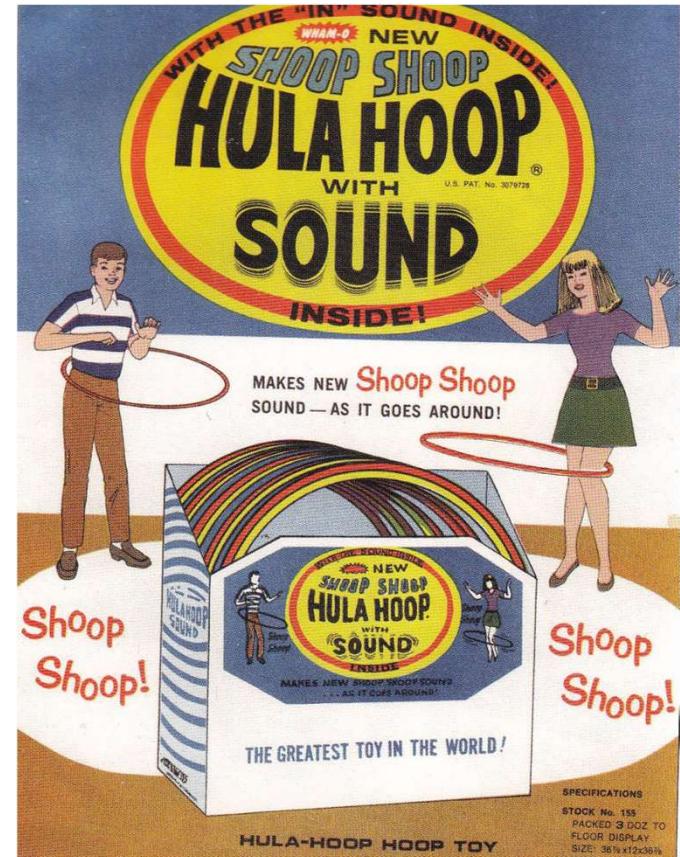
Arthur K. Melin, Pasadena, Calif.
Filed May 13, 1959 Ser. No. 813,030



The Hula Hoop Saved the Polypropylene Industry

Wham-O's nationwide daily production ultimately peaked at about 20,000 per day. There soon was not enough Grex and Phillips Petroleum's once ignored miracle polypropylene, Marlex, was suddenly very much in demand.

Plastic Hula-Hoop plants sprang up in Chicago, Newark and Toronto. Canada. The completely unanticipated demand for Marlex gave Phillips the time necessary to resolve initial production problems and position itself as a prime source of plastic resins.

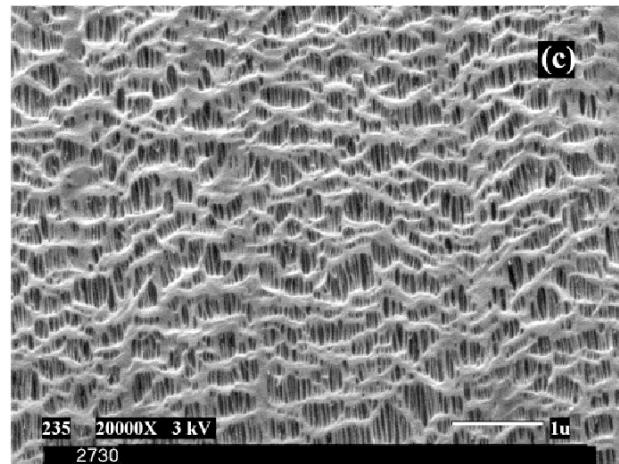
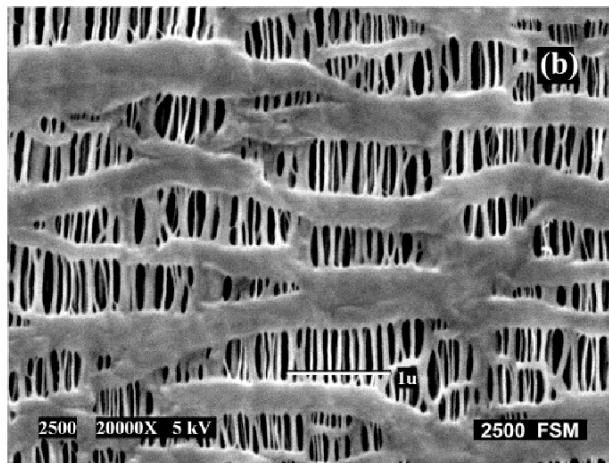
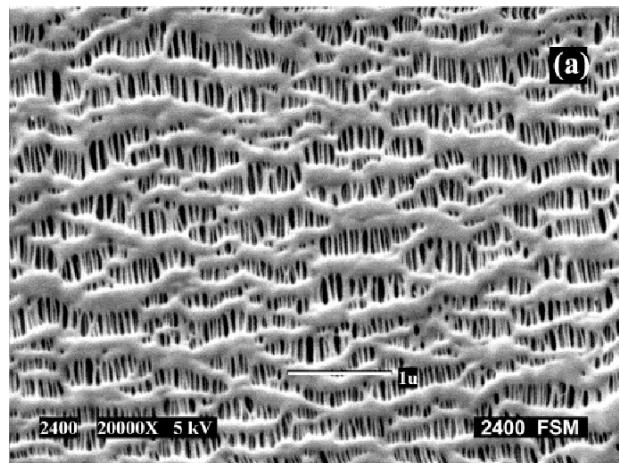


The **Shoop Shoop Hula Hoop** was nutty. Literally. Originally, Wham-O experimented with **walnut shells inside** the hoops to **make sound**. The shells were later replaced by **ball bearings**, which did the trick.

Advantages and Disadvantages of Polypropylene

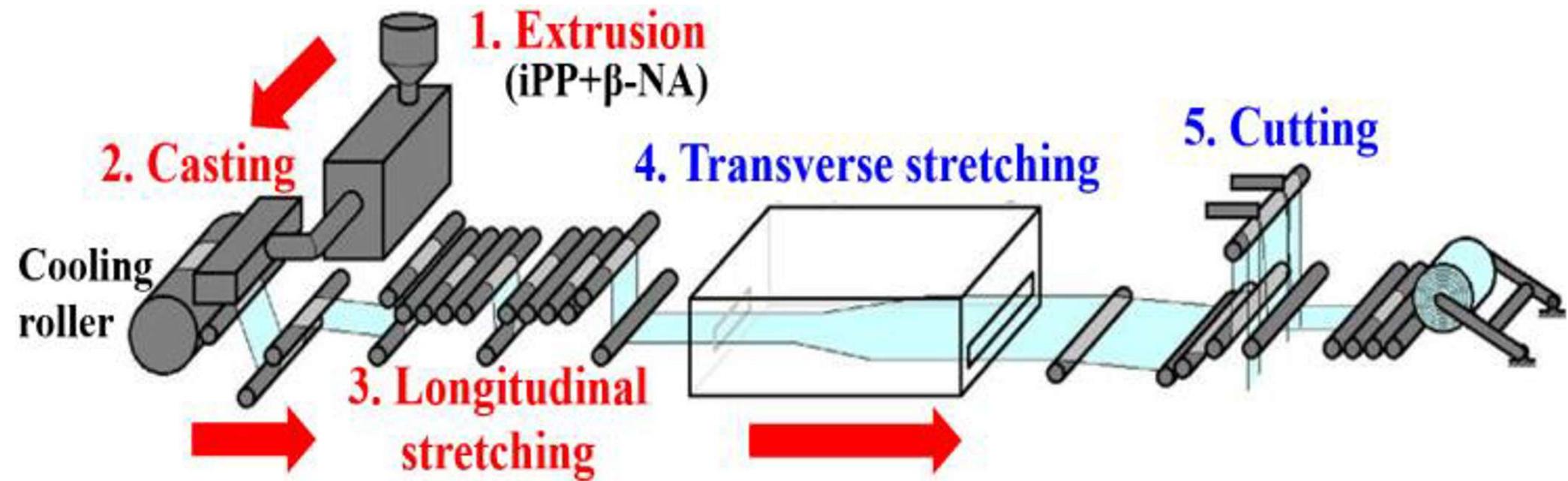
Advantages of PP		Disadvantages of PP
Homo-polymer	Copolymer	Degraded by UV (Ultraviolet)
Process ability, Good	Process ability, High	Flammable, but retarded grades available
Impact resistance, Good	Impact resistance, High	Attacked by chlorinated solvents and aromatics
Stiffness, Good	Stiffness, High	Difficult to bond
Food contact, Acceptable	Food contact, Not preferable	Several metals accelerate oxidative degrading Low temperature impact strength is poor

Polypropylene is the Basic Material in Celgard



The **Celgard** membrane is **made of PP**, which is a low-cost and quite inert polymer. It is resistant to extreme pH conditions and is insoluble in most solvents at room temperature. It swells in polar solvents such as carbon tetrachloride. No solvent is required for the preparation of the membrane.

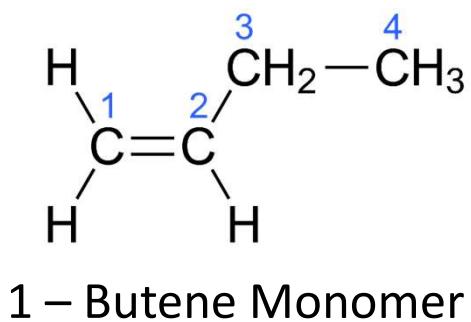
How is Celgard Made?



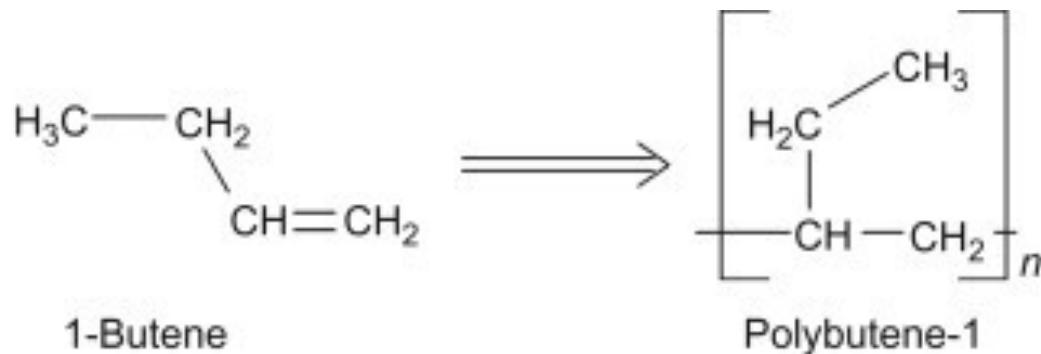
Importance of Celgard in Lithium Ion Batteries

MARKET	EDV		
CELGARD PRODUCT SOLUTIONS	Battery Electric Vehicles (BEV)	Plug-In Hybrid Electric Vehicles (PHEV)	Hybrid Electric Vehicles (HEV)
MARKET NEEDS	<ul style="list-style-type: none">• Vehicle Range• Long Battery Life• Safety	<ul style="list-style-type: none">• High Power for Acceleration• Long Battery Life• Consistent Energy Output over an Extended Period of Time	<ul style="list-style-type: none">• High Power for Acceleration• Ability to Withstand Frequent Charges and Discharges over the Life of the Battery
FEATURES	<ul style="list-style-type: none">• Low Ionic Resistance and High Porosity• PP Outer Layers Provide High Temperature Melt Integrity (HTMI) and Oxidative Resistance• PE Inner Layer Provides High-Speed Shutdown During a Thermal Event	<ul style="list-style-type: none">• Excellent Electrolyte Absorption for Fast Ion Transfer• Sustained Separator Mechanical Integrity over the Life of the Battery	<ul style="list-style-type: none">• High Cycle Life• Unparalleled Tolerance or Resistance to Electrochemical Oxidation at Elevated Temperatures and Voltages
APPLICATION/ BATTERY BENEFIT	<ul style="list-style-type: none">• Increased Battery Energy Density for Longer Driving Ranges• Increased Battery Longevity and Strength• Increased Battery Safety	<ul style="list-style-type: none">• High Battery Discharge Rate for Vehicle Acceleration• Ability to Withstand Deep Battery Discharges• Increased Battery Longevity and Strength	<ul style="list-style-type: none">• Fast Charge and Discharge Rates over the Life of the Battery• Increased Battery Longevity and Strength

Poly(butene-1) or Polybutylene



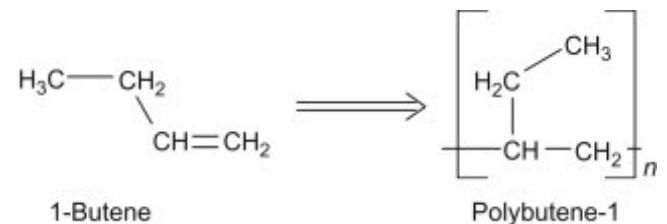
Polybutylene is produced by polymerisation of 1-butene using supported Ziegler–Natta catalysts. PB-1 is a high molecular weight, linear, isotactic, and semi-crystalline polymer. PB-1 combines typical characteristics of conventional polyolefins with certain properties of technical polymers.



History of Polybutylene

1974 - Invented by Witco Chemical

Ethyl side groups in a linear backbone structure



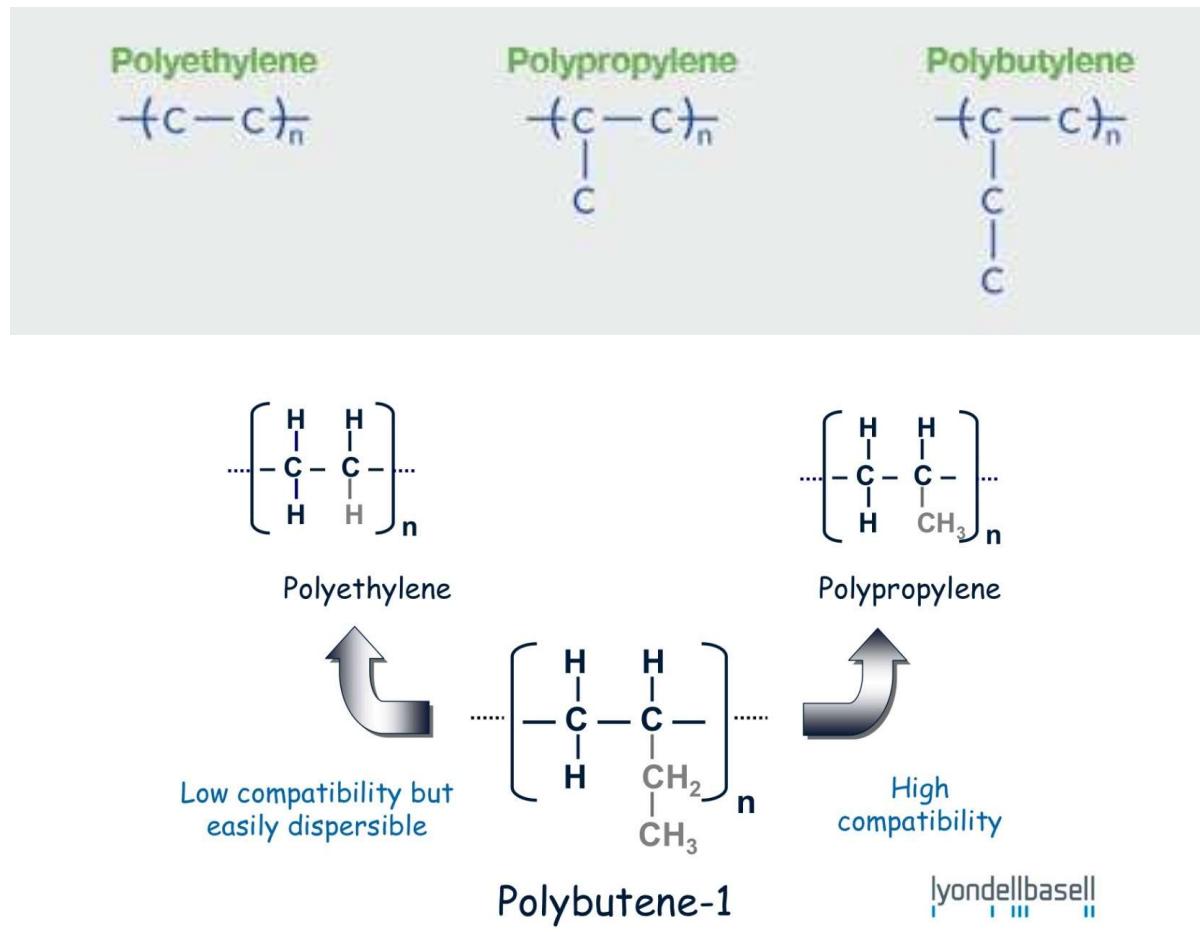
Linear isotactic material upon cooling the crystallinity is 30%

Post-forming can increase crystallinity to 55%

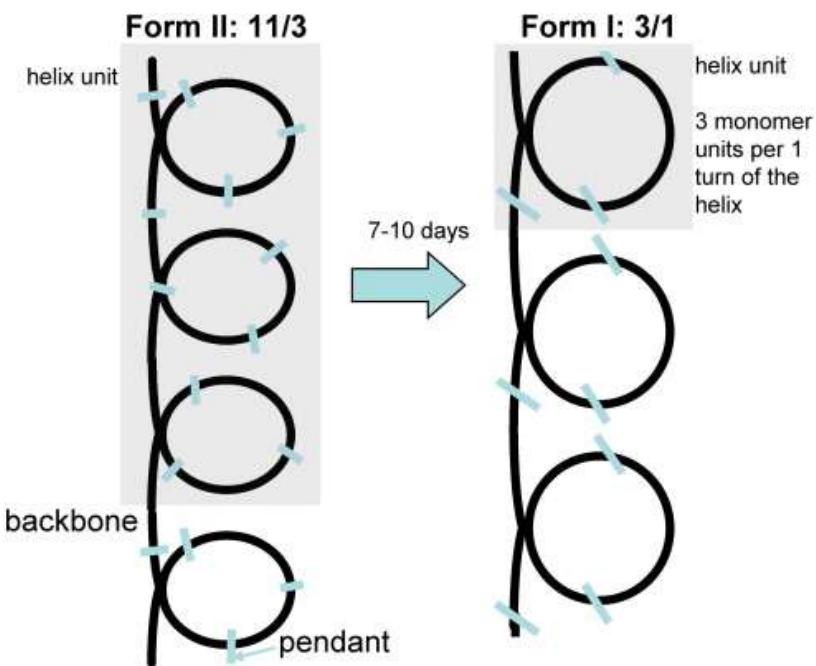
Processed by conventional thermoplastic techniques

Applications primarily in pipe and film; also, tank liners, hot melt adhesives, coextruded as a moisture barrier and heat sealable packaging

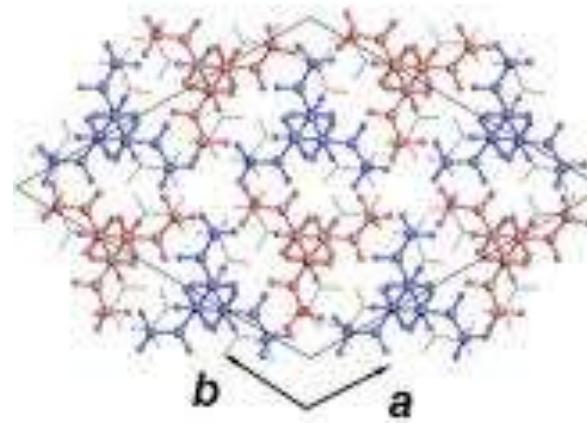
Polybutylene Comparison to Polyethylene and Polypropylene



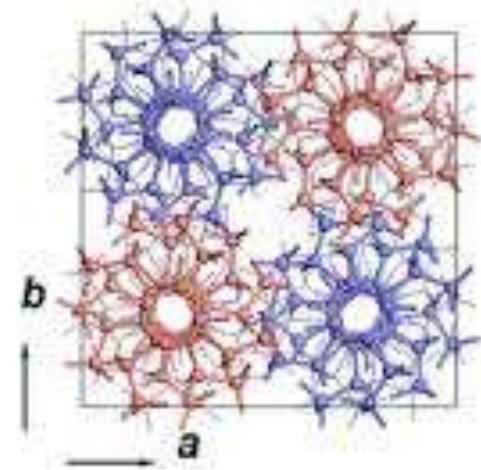
Two Crystal Forms Exist for Polybutylene



**isotactic Polybutene-1
Crystal Form I**



Crystal Form II



Each Form of Polybutylene Crystal has a Specific Melting Point and Density

Polymorph	Structure	How Obtained	Density (g/cm ³)	Melting point (°C)
Form I	Hexagonal (twined)	Stable form produced by transition from other forms	0.95	125-136
Form I'	Hexagonal (untwined)	Directly from solution	-	90-100
Form II	Tetragonal	Directly from the melt, and directly from solution at room temperature	0.88-0.90	118-126
Form III	Orthorhombic	Directly from solution	-	90-103

Properties of Polybutylene

Mechanical Properties of Polybutylene

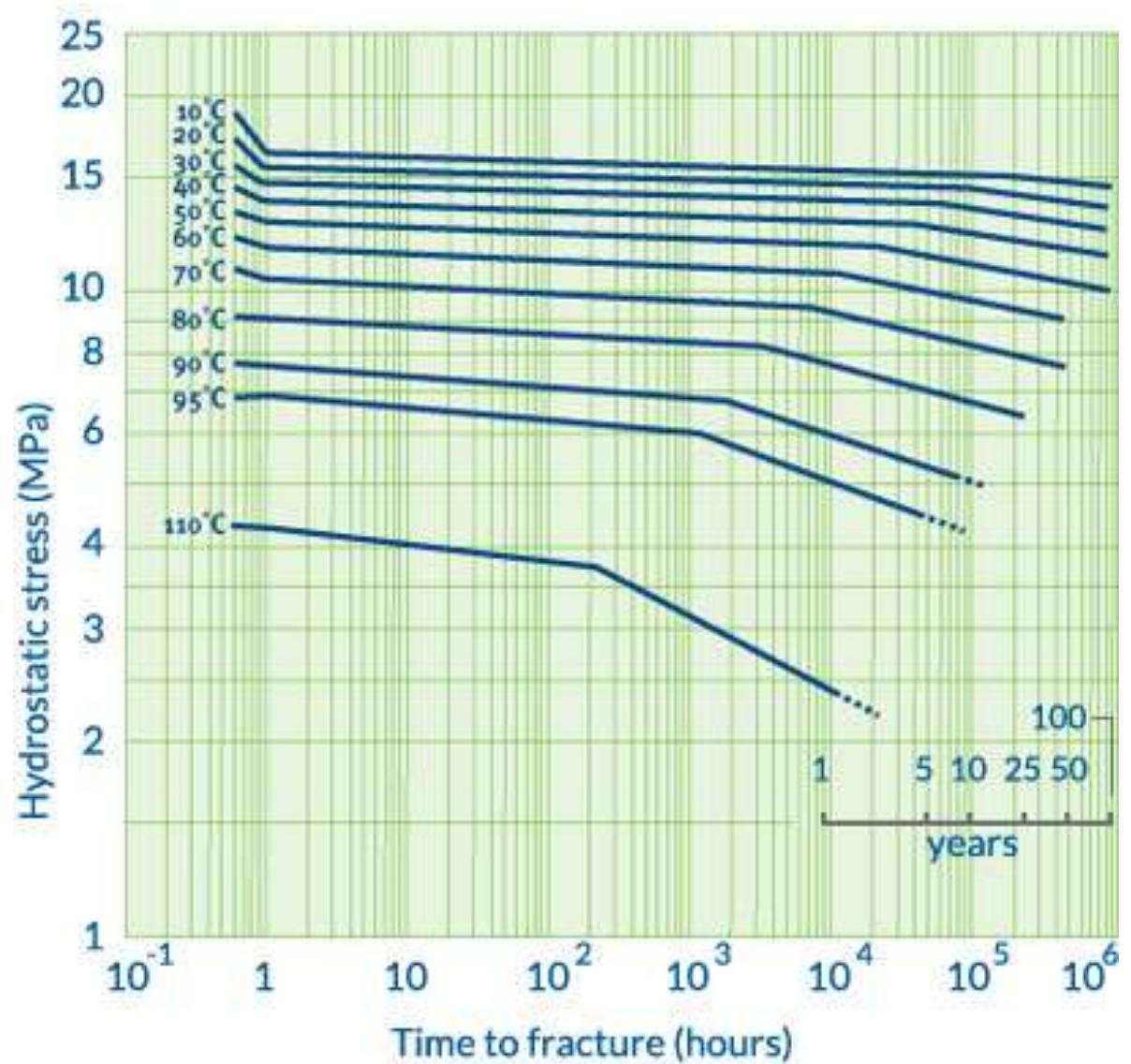
	Polybutylene	Polypropylene	LDPE (For Comparison)	HDPE (For Comparison)
Density	0.908 - .917	0.90	0.91- 0.925	0.959-0.965
Crystallinity	30% to 50%	30% to 50%	30% to 50%	80% to 91%
Tensile Strength, psi	4,000	4,500 – 5,500	600 - 2,300	5,000 – 6,000
Tensile Modulus, psi	10K – 40K	165K – 225K	25K – 41K	150K – 158 K
Tensile Elongation, %	300% - 400%	100% - 600%	100% - 650%	10% - 1300%
Impact Strength ft-lb/in	No break	0.4 – 1.2	No break	0.4 – 4.0
Hardness	Shore D 55 – D65	R80 - 102	D44 – D50	D66 – D73

Additional Properties of Polybutylene

Some properties:

•Elastic modulus	290–295 MPa
•Tensile strength	36.5 MPa
•Molecular weight	725,000 (g/mol)
•Crystallinity	48–55%
•Water absorption	<0.03%
•Glass transition temperature	–25 to –17 °C
•Thermal conductivity	0.22 W/(m*K)

Long Term Stress
Rupture
Performance
Indicated that
Polybutylene could
be a Good Hot- and
Cold-Water Piping
Material



Polybutylene Plumbing was Popular in North America between 1978 and 1997

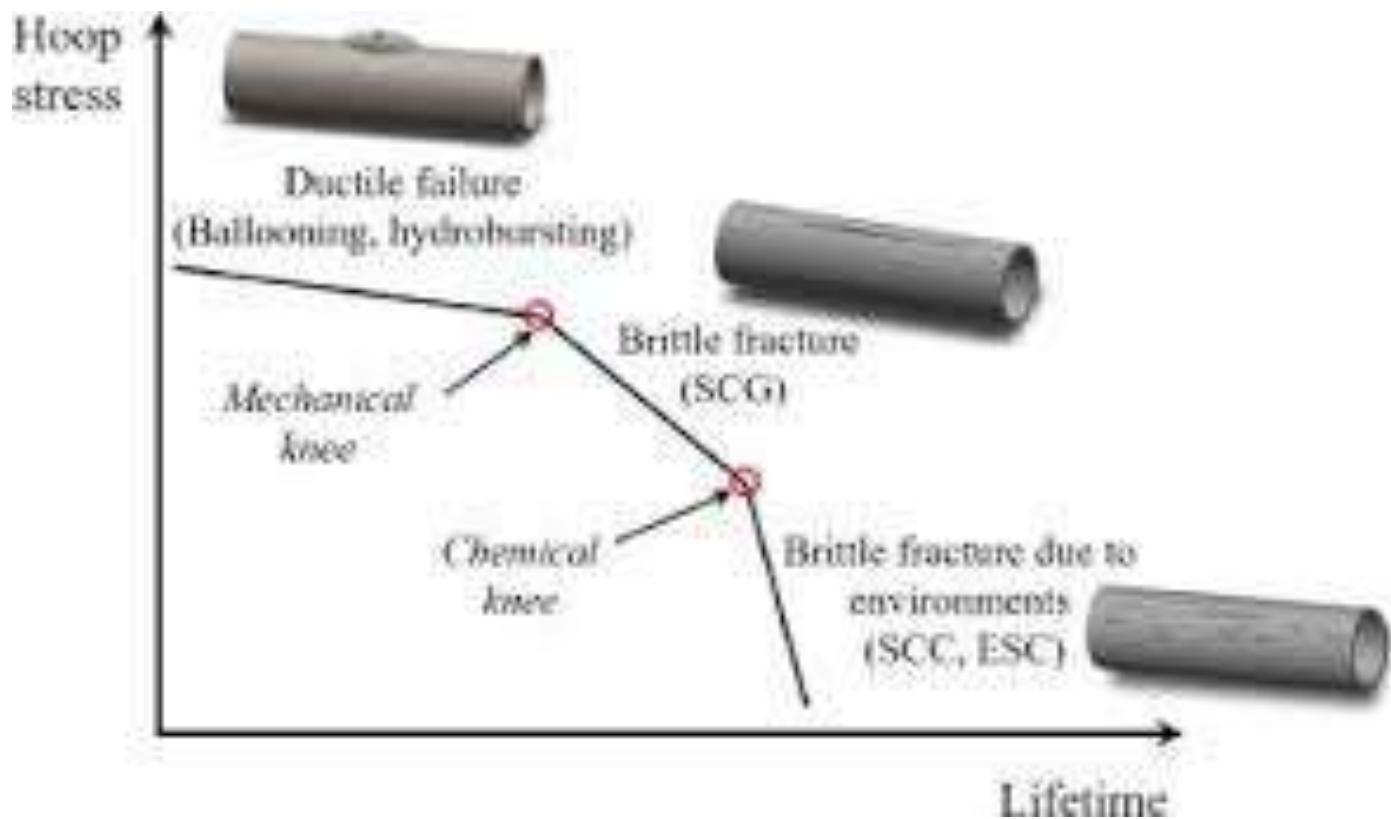


Polybutylene in Hot Water Piping Systems

The main use of PB-1 is in flexible pressure piping systems for hot and cold drinking water distribution, pre-insulated district heating networks and surface heating and cooling systems. ISO 15876 defines the performance requirements of PB-1 piping systems. The most striking features are weldability, temperature resistance, flexibility and high hydrostatic pressure resistance. The material can be classified PB 125 with a minimum required strength (MRS) of 12.5 MPa. Other features include low noise transmission, low linear thermal expansion, no corrosion and calcification.

PB-1 piping systems are no longer being sold in North America. The overall market share in Europe and Asia is rather small but PB-1 piping systems have shown a steady growth in recent years. In certain domestic markets, e.g. Kuwait, the United Kingdom, Korea and Spain, PB-1 piping systems have a strong position.

Illustration of the Environmental Degradation Failure on a Hoop Stress vs Failure Time Plot



Polybutylene Water Pipes Began Leaking



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Removal of Polybutylene Piping in North America

Polybutylene plumbing was used in several million homes built in the United States from around 1978 to 1997. Problems with leaks and broken pipes led to a class action lawsuit, Cox v. Shell Oil, that was settled for \$1 billion. The leaks were associated with degradation of polybutylene exposed to chlorinated water.

Polybutylene water pipes are no longer accepted by United States building codes and have been the subject of class action lawsuits in both Canada and the U.S. The National Plumbing Code of Canada 1995 listed polybutylene piping as acceptable for use with the exception of recirculation plumbing. The piping was removed from the acceptable for use list in the 2005 issue of the standard.

¹

There is evidence to suggest that the presence of chlorine and chloramine compounds in municipal water (often deliberately added to retard bacterial growth) will cause deterioration of the internal chemical structure of polybutylene piping and the associated acetal fittings. The reaction with chlorinated water appears to be greatly accelerated by tensile stress, and is most often observed in material under highest mechanical stress such as at fittings, sharp bends, and kinks.

Lesson 14: Polypropylene PP Poly(1-butene) – Polybutylene - PB

Questions?



Dr. Andy Olah, amo5@case.edu, O: 216-368-0606, C: 216-272-0505

“I don’t always go the extra mile, but when I do it’s because I missed my exit.”

EMAC 276

Lecture 16: Polydienes: from Natural Rubber to Synthetic Rubber

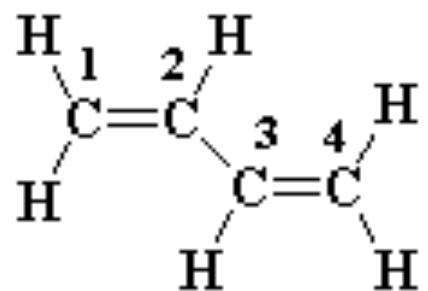
Part 2: Polychloroprene, Polybutadiene and Styrene-Butadiene Block Copolymers

Andy Olah, Ph.D.
February 26, 2025

What is a diene?

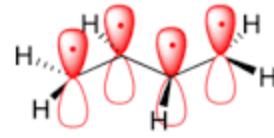
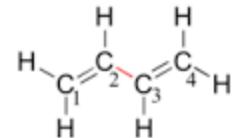
A diene is an unsaturated hydrocarbon containing two double bonds between carbon atoms.

Butadiene is the simplest diene:



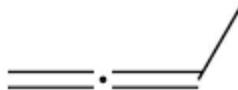
Butadiene has two carbon-carbon double bonds, in the 1 and 3 positions, that is, starting at the carbon atoms numbered 1 and 3.

Dienes and Polydienes can Adopt Numerous Configurations

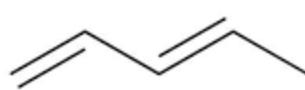


1,3-butadiene

The placement of the double bond.



Cumulated



Conjugated



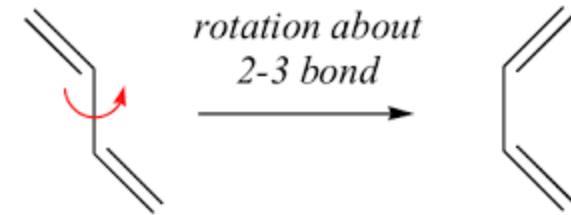
Isolated

Cumulated – pi bonds are adjacent.

Conjugated – pi bonds are separated by exactly ONE single bond.

Isolated – pi bonds are separated by any distance greater than ONE single bond.

Rotation around the single bond.



s-trans

Isolated

s-cis



s-trans

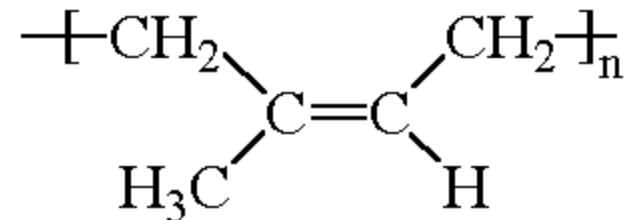


s-cis

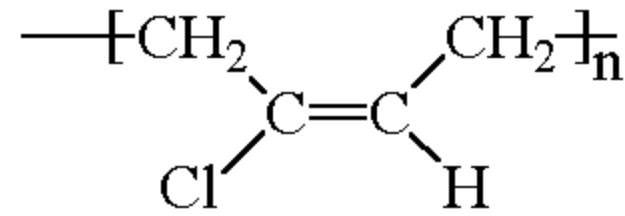
Monomer

Diene Based Polymers that We Will Consider

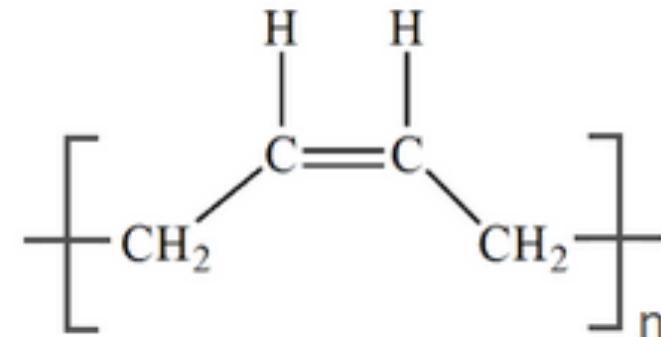
Polyisoprene



Polychloroprene (Neoprene)

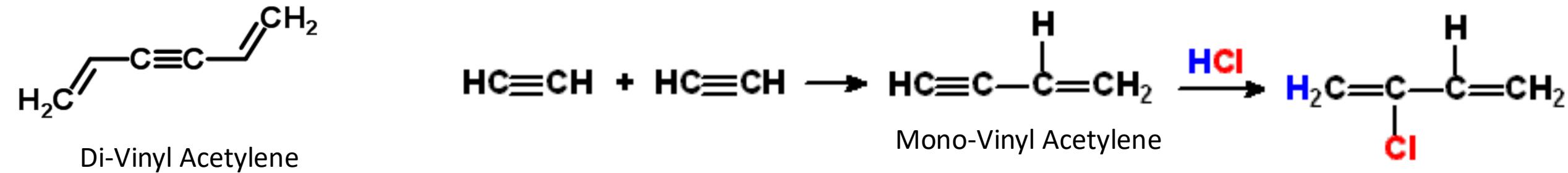


Polybutadiene



Synthesis of Chloroprene Monomer

Neoprene was invented by the DuPont Company on April 17, 1930. The research was focused on acetylene chemistry and during the course of this work he produced divinyl acetylene, a jelly that forms into an elastic compound similar to rubber when passed over sulfur dichloride. Collins at DuPont focused on mono-vinyl acetylene and allowed it to react with hydrogen chloride gas, manufacturing chloroprene.

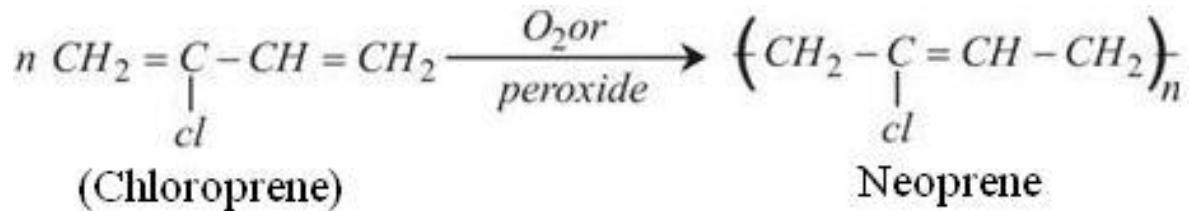


NOTE: Chloroprene commonly refers to the monomer and Neoprene refers to the polymerization of 1,3 chloroprene.

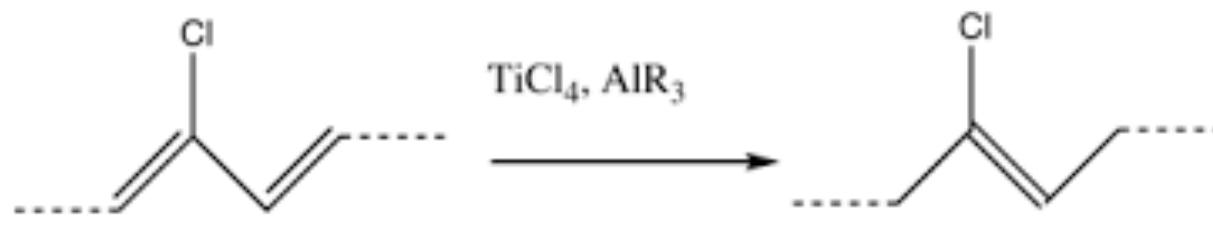
NOTE: The chemical designation of chloroprene monomer is “2-chloro, 1,3-butadiene”.

Synthesis of Neoprene

Neoprene Synthesis



Free Radical



Ziegler-Natta

DuPont first marketed the compound in 1931 under the trade name DuPrene, but its commercial possibilities were limited by the original manufacturing process, which left the product with a foul odor.

A new process was developed, which eliminated the odor-causing byproducts and halved production costs. The trademark was dropped in 1937 and replaced with a generic name, “neoprene”.

DuPont then worked extensively to generate demand for its product. By 1939, sales of neoprene were generating profits over \$300,000 for the company (equivalent to \$6,573,000 in 2024).

Commercialization of Neoprene

Neoprene was one of the first synthetic rubbers

Neoprene resists degradation more than natural or synthetic rubber. This relative inertness makes it well suited for applications such as gaskets, hoses, and corrosion-resistant coatings.

It resists burning better than exclusively hydrocarbon based rubbers, resulting in its appearance in weather stripping for fire doors. Because of its tolerance of extreme conditions, neoprene is used to line landfills. Neoprene's combustion occurs around 260 °C (500 °F).

In its native state, neoprene is a very pliable rubber-like material with insulating properties similar to rubber or other solid plastics.

Neoprene foam is used in many applications and is produced in either closed-cell or open-cell form. The closed-cell form is waterproof, less compressible and more expensive. The open-cell form can be breathable. It is manufactured by foaming the rubber with nitrogen gas, where the tiny enclosed and separated gas bubbles can also serve as insulation.

Commercialization of Neoprene

Chloroprene is used primarily for gaskets, cable jackets, tubing, seals, O-rings, tire-sidewalls, gasoline hoses and weather-resistant products such as wet suits and orthopedic braces. It is also used as a base resin in adhesives, electrical insulations and coatings.



Polybutadiene - History

1910 - The Russian chemist Sergei Vasilyevich Lebedev was the first to polymerize butadiene.

1926 - Lebedev invented a process for manufacturing butadiene from ethanol, and in 1928, developed a method for producing polybutadiene using sodium as a catalyst.

1936 - The Soviet Union built the world's first polybutadiene plant in which the butadiene was obtained from petroleum. By 1940, the Soviet Union was by far the largest producer of polybutadiene with 50,000 tons per year.

1930 – 1940 - Other industrialized countries such as Germany and the United States developed polybutadiene and SBR as an alternative to natural rubber.

Polybutadiene - History

1940 – 1950 - Although the Goodrich Corporation had successfully developed a process for producing polybutadiene in 1939, the government of the United States opted for the use of Buna-S to develop its synthetic rubber industry after its entry into the World War II, using patents of IG Farben obtained via Standard Oil.

1950- 1960 - After the war, the production of synthetic rubber was in decline due to the decrease in demand when natural rubber was available again. However, interest was renewed in the mid-1950s after the discovery of the Ziegler–Natta catalyst. The following year, Firestone Tire and Rubber Company was first to produce low *cis* polybutadiene using butyllithium as a catalyst.

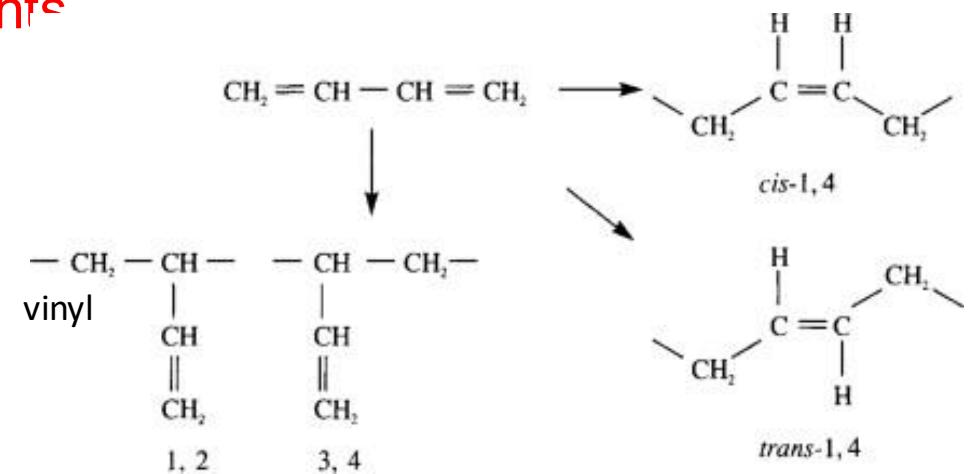


Polybutadiene

The monomer 1,3-butadiene is an organic compound that is a simple conjugated diene hydrocarbon (dienes have two carbon-carbon double bonds).

Polybutadiene forms by linking many 1,3-butadiene monomers to make a much longer polymer chain molecule. In terms of the connectivity of the polymer chain, butadiene can polymerize in three different ways, called *cis*, *trans* and *vinyl*. The *cis* and *trans* forms arise by connecting the butadiene molecules end-to-end, so-called 1,4-polymerisation.

The properties of the resulting isomeric forms of polybutadiene differ. For example, "high cis"-
polybutadiene has a high elasticity and is very popular, whereas the so-called "high *trans*" is a plastic crystal with few useful applications. The vinyl content of polybutadiene is typically no more than a few percent. In addition to these three kinds of connectivity, polybutadienes differ in terms of their branching and molecular weight^c

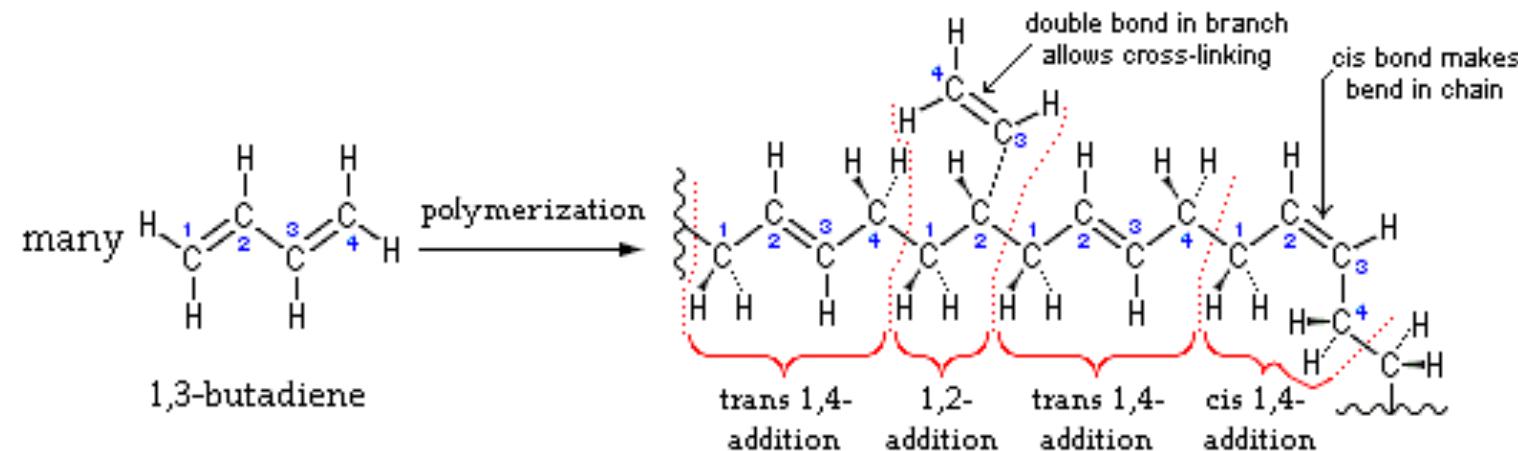


Polymerization of Butadiene

The *trans* double bonds formed during polymerization allow the polymer chain to stay rather straight, allowing sections of polymer chains to align to form microcrystalline regions in the material.

The *cis* double bonds cause a bend in the polymer chain, preventing polymer chains from aligning to form crystalline regions, which results in larger regions of amorphous polymer. It has been found that a substantial percentage of *cis* double bond configurations in the polymer will result in a material with flexible elastomeric (rubber-like) qualities.

In free radical polymerization, both *cis* and *trans* double bonds will form in percentages that depend on temperature. The polymerization catalysts influence the *cis* vs *trans* ratio.



Commercialization of Polybutadiene

Polybutadiene is largely used in various parts of automobile tires; the manufacture of tires consumes about 70% of the world production of polybutadiene, with a majority of it being high *cis*.

The polybutadiene is used primarily in the sidewall of truck tires, this helps to improve fatigue to failure life due to the continuous flexing. It is also used in the tread portion of giant truck tires to improve the abrasion, i.e. less wearing.

Its main competitors in this application are styrene-butadiene rubber (SBR) and natural rubber. Polybutadiene has the advantage compared to SBR in its lower glass transition temperature, which gives it a high resistance to wear and a low rolling resistance. This gives the tires a long life and low fuel consumption.

However, the lower transition temperature also lowers the friction on wet surfaces, which is why polybutadiene almost always is used in combination with any of the other two elastomers.

About 1 kg of polybutadiene is used per tire in automobiles, and 3.3 kg in utility vehicles.

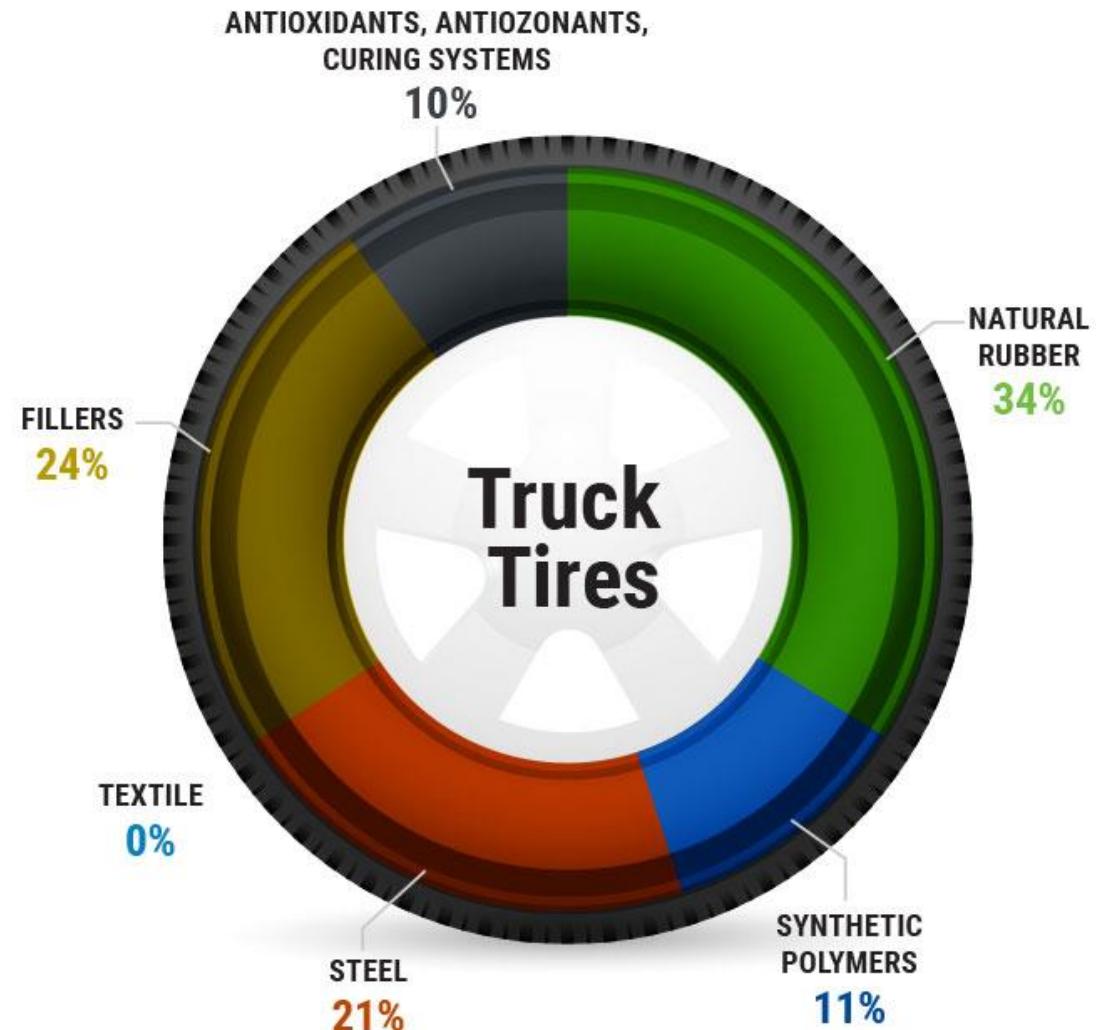
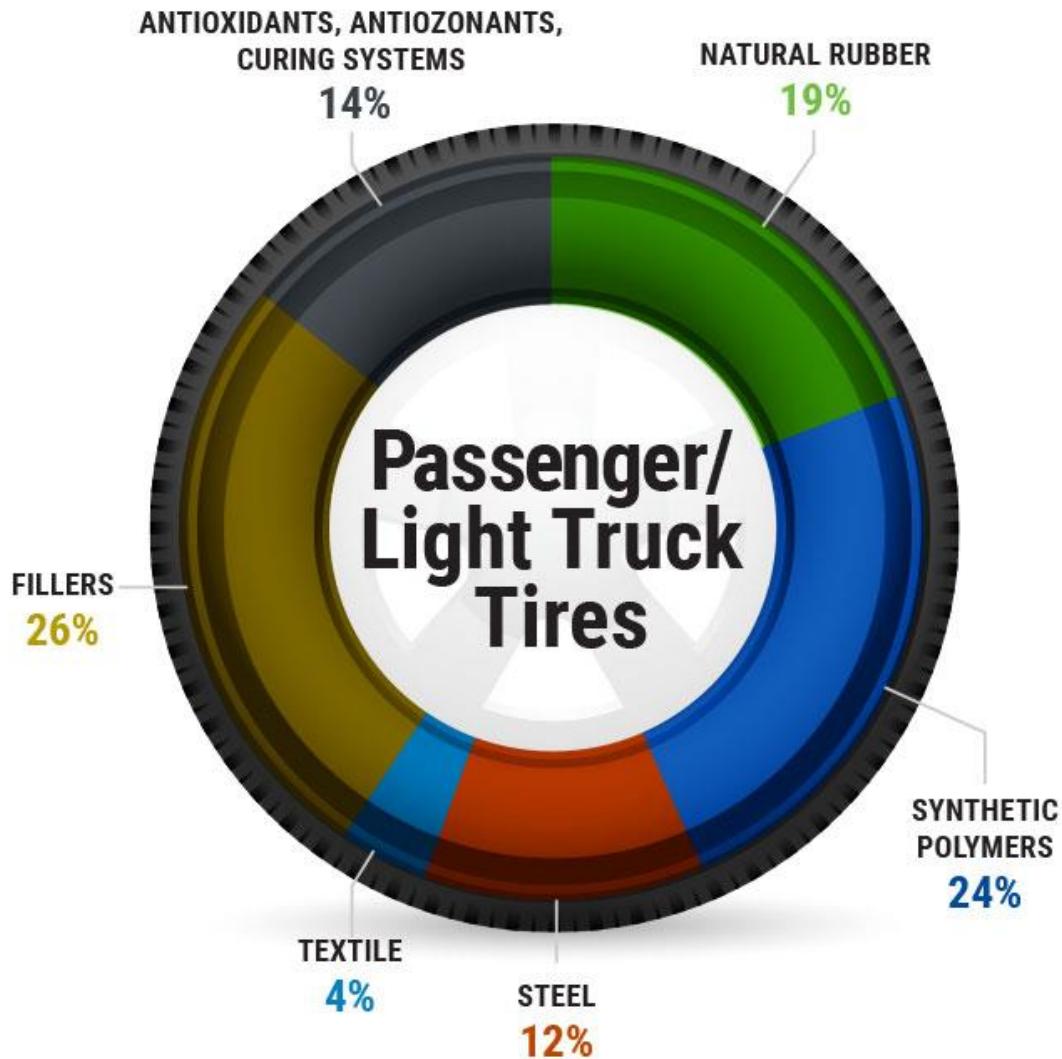
Commercialization of Polybutadiene

About 25% of the produced polybutadiene is used to improve the mechanical properties of plastics, in particular of high-impact polystyrene (HIPS) and to a lesser extent acrylonitrile-butadiene- styrene (ABS). The addition of between 4 and 12% polybutadiene to polystyrene transforms it from a fragile and delicate material to a ductile and resistant one.

The quality of the process is more important in the use in plastics than in tires, especially when it comes to color and content of gels which have to be as low as possible. In addition, the products need to meet a list of health requirements due to its use in the food industry



Material Composition of Tires



Composition & Source



Carbon black and silica are the basic tire fillers, providing the necessary “structure” to the compound



Other chemicals have various functions, like oils, zinc oxide or anti-degradants to protect the compound



Synthetic rubber is added to natural rubber to achieve the desired elasticity



High-strength steel cords are applied under the tread of passenger car tires (and in the carcass of truck tires) while other steel wires are located near the bead to assure adherence to the rim



Passenger car tires feature rayon or polyester cords radially disposed along the carcass (“radial tires”), while nylon cords are placed under the tread or near the bead area



Natural rubber has unique elastic properties and is an essential element of a tire. Truck tires have an even higher natural rubber content than passenger car tires

Polybutadiene is Used in Solid Fuel Rockets

HTPB - Hydroxyl-terminated polybutadiene is a telechelic polymer with more than two terminal hydroxyl groups according to its functionality mainly used for manufacturing adhesives and coatings from one side and as a binder for composite rocket propellant on the other side.

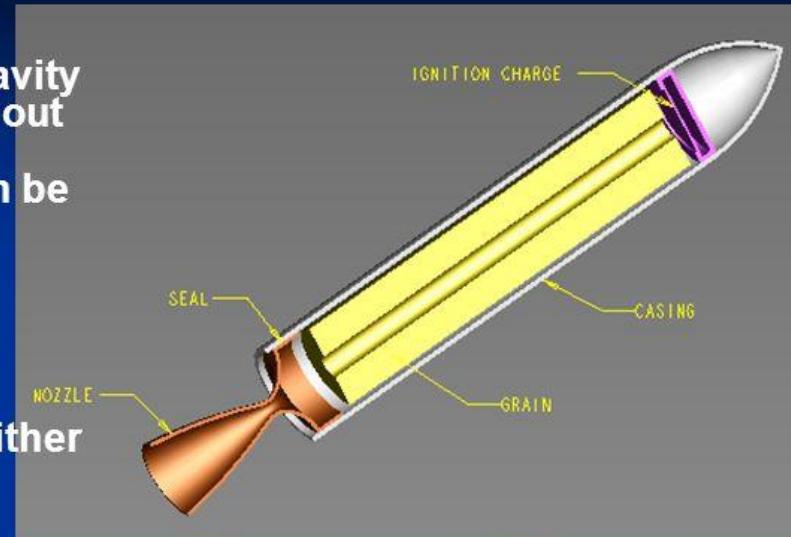
PBAN - Polybutadiene acrylonitrile copolymer, also noted as polybutadiene—acrylic acid—acrylonitrile terpolymer is a copolymer compound used most frequently as a rocket propellant fuel mixed with ammonium perchlorate oxidizer.

Solid Propellants

The cast fuel has a central cavity to allow burning throughout the length of the rocket motor, in shapes that can be anything from a simple cylinder to a star

Solid rocket fuel is typically identified by the type of chemical binder used - either HTPB or PBAN

Hydroxyl-terminated polybutadiene, or HTPB, is a rubber-like binder that is stronger, more flexible, and faster-curing than PBAN, but suffers from a slightly lower I_{sp} , and uses fast-curing, toxic isocyanates



Polybutadiene Core for Golf Balls

Polybutadiene is preferred to other elastomers due to its high resilience.

The core of the balls are formed by compression molding with chemical reactions.

First, polybutadiene is mixed with additives, then extruded, pressed using a calendar and cut into pieces which are placed in a mold. **The mold is subjected to high pressure and high temperature for about 30 minutes, enough time to vulcanize the material.**

The golf ball production consumes about **20,000 tons of polybutadiene per year.**



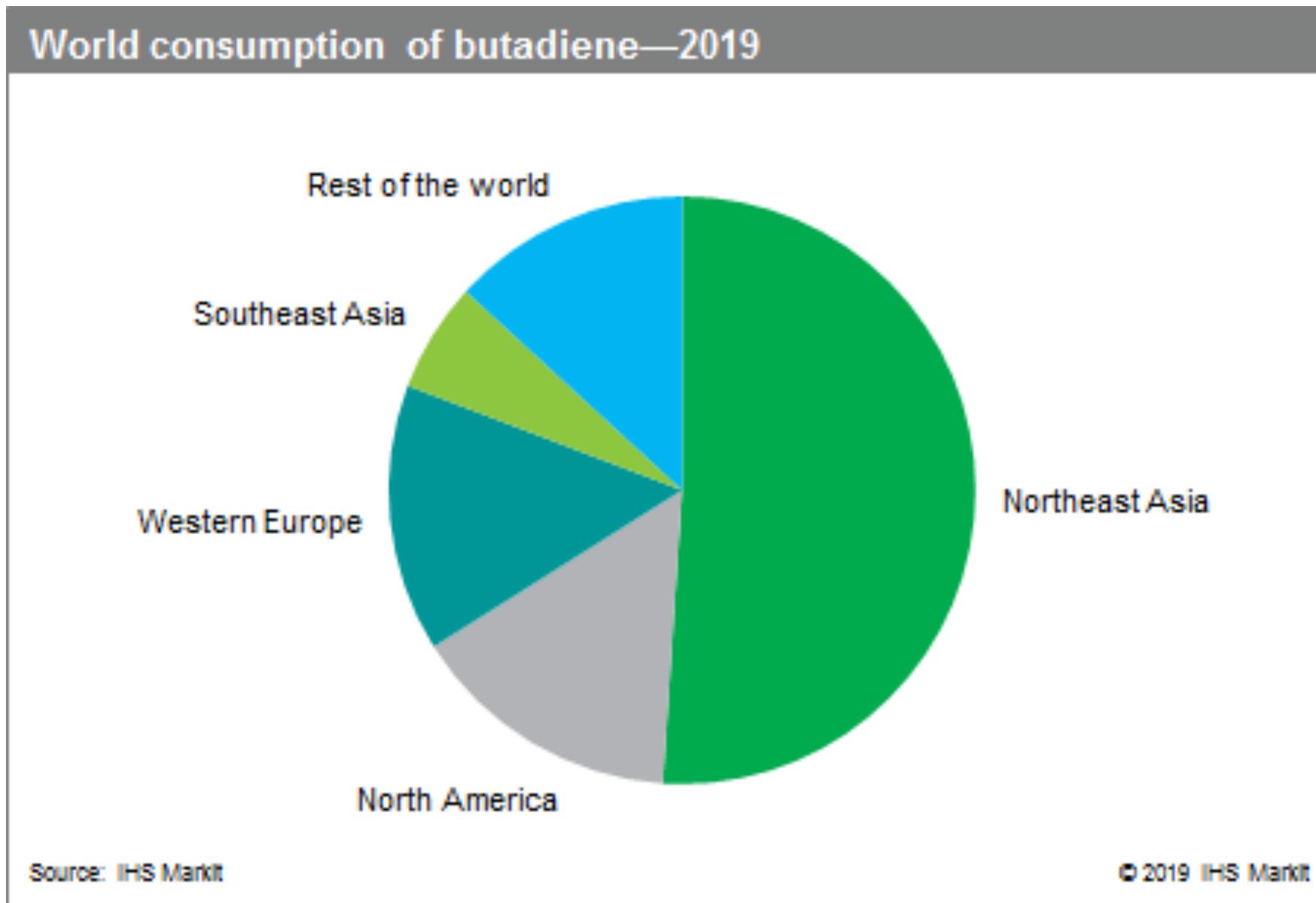
Commercial Uses of Polybutadiene

➤ APPLICATIONS AND USES

- Tire production (SBS)
- Conveyor belt
- Water hoses
- Gaskets
- Golf ball & super ball
- Engine belt
- As fuel in space shuttle for boosting rockets



World Consumption of Polybutadiene



March 22, 1966

N. H. STINGLEY

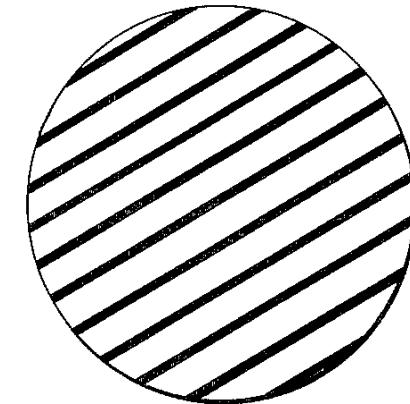
3,241,834

HIGHLY RESILIENT POLYBUTADIENE BALL

Filed Aug. 25, 1965

BALL MATERIAL:

SPECIFIC GRAVITY	-	1-1.3
POLYBUTADIENE	-	ABOUT 100 PARTS
SULFUR VULCAN. AGENT	-	0.5 to 15 PARTS
HYDRATED SILICA or CARBON BLACK or LITHIUM OXIDE	}	- 5 to 15 PARTS



This compound is vulcanized with sulfur at a temperature of 165 °C (329 °F) and formed at a pressure of 3,500 psi (24 MPa).

Stingley sought uses for his polybutadiene synthetic rubber, as well as someone to manufacture it. He first offered his invention to the Bettis Rubber Company, for whom he worked at the time, but they turned it down because the material was not very durable.

Polybutadiene Brought Us the “SuperBall”

So Stingley took it to toy company Wham-O; they worked on developing a more durable version which they still manufacture today.

A **SuperBall** is a bouncy ball based on a type of synthetic rubber invented in 1964 by chemist Norman Stingley.



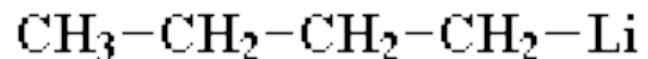
"It took us nearly two years to iron the kinks out of Super Ball before we produced it," said Richard Knerr, President of Wham-O in 1966. "It always had that marvelous springiness.... But it had a tendency to fly apart. We've licked that with a very high-pressure technique for forming it.

Synthesis of S-B-S Rubber via Anionic Polymerization

Anionic polymerization is a type of vinyl polymerization.

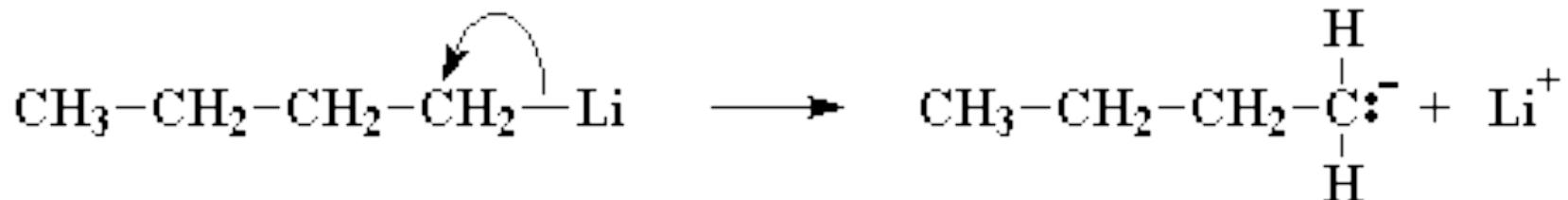
The initiator is an anion having a negative electrical charge.

The most common anionic initiator is n-butyl lithium:



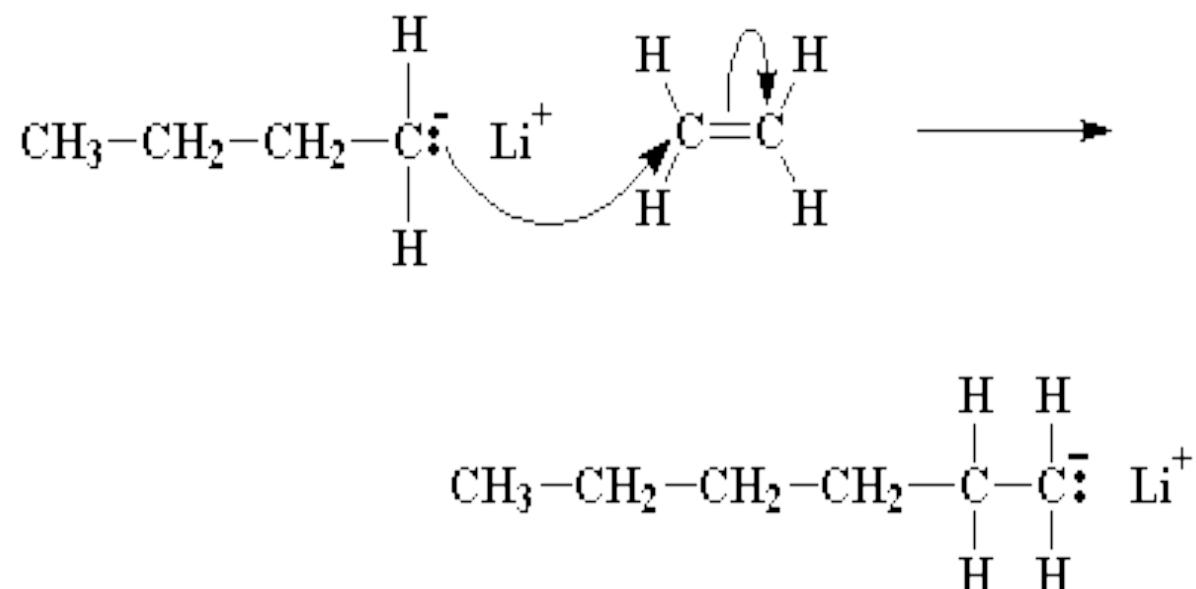
butyl lithium

The n-butyl lithium disassociates to a positive lithium cation and a negative anion with the negative charge on the terminal carbon (i.e., carbanion).



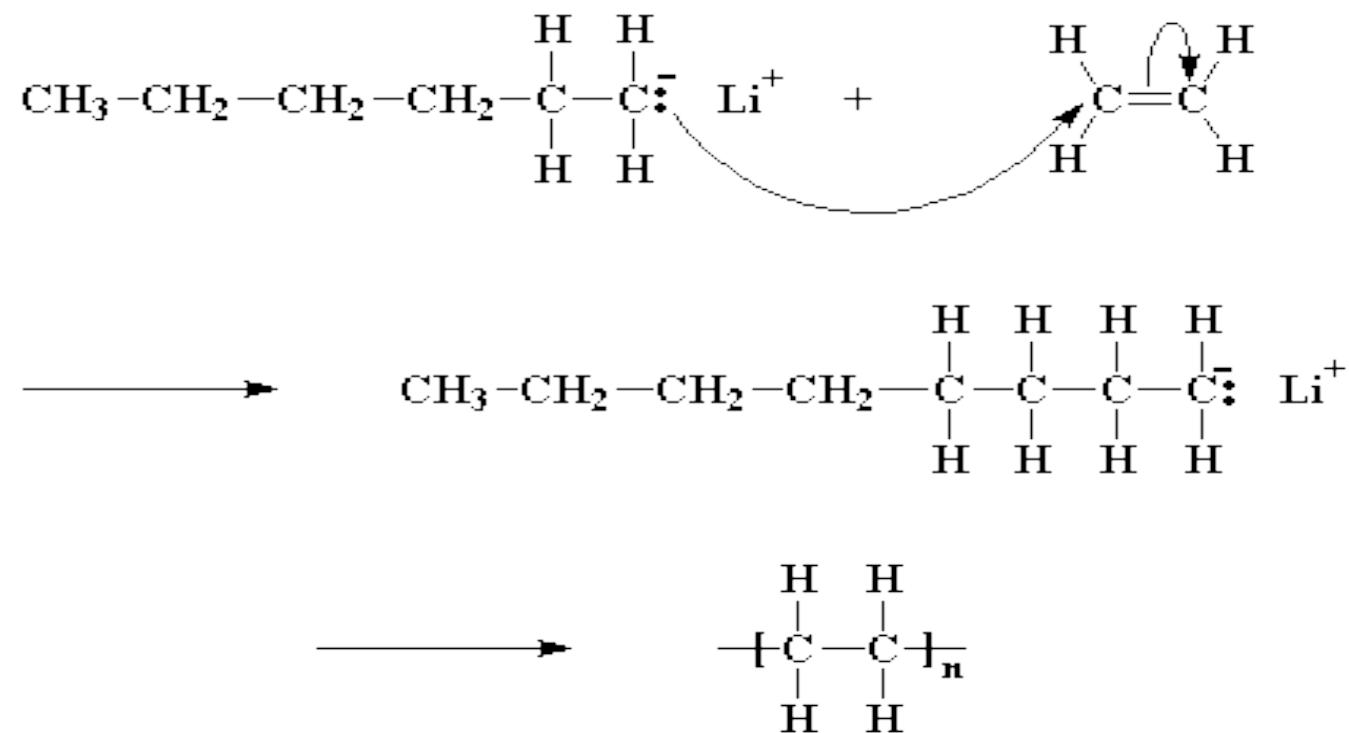
Synthesis of S-B-S Rubber via Anionic Polymerization

A pair of electrons from the butyl anion will be donated to one of the double bond carbon atoms of the monomer. This forms a new carbanion, with the negative charge resting on the new terminal carbon. The process in which the butyl lithium falls apart, and the butyl anion reacts with a monomer molecule is called *initiation*.



Synthesis of S-B-S Rubber via Anionic Polymerization

The new carbanion reacts with a new monomer molecule in the same manner and another carbanion is generated. This propagation step continues. In this way the polymer chain grows. This adding of monomer after monomer is called *propagation*.



Synthesis of S-B-S Rubber via Anionic Polymerization

Definition of a Living Polymer

This propagation step continues until the monomers in the reactor have been incorporated into the propagating chains.

If more monomers are introduced into the reactor the polymerization will continue.

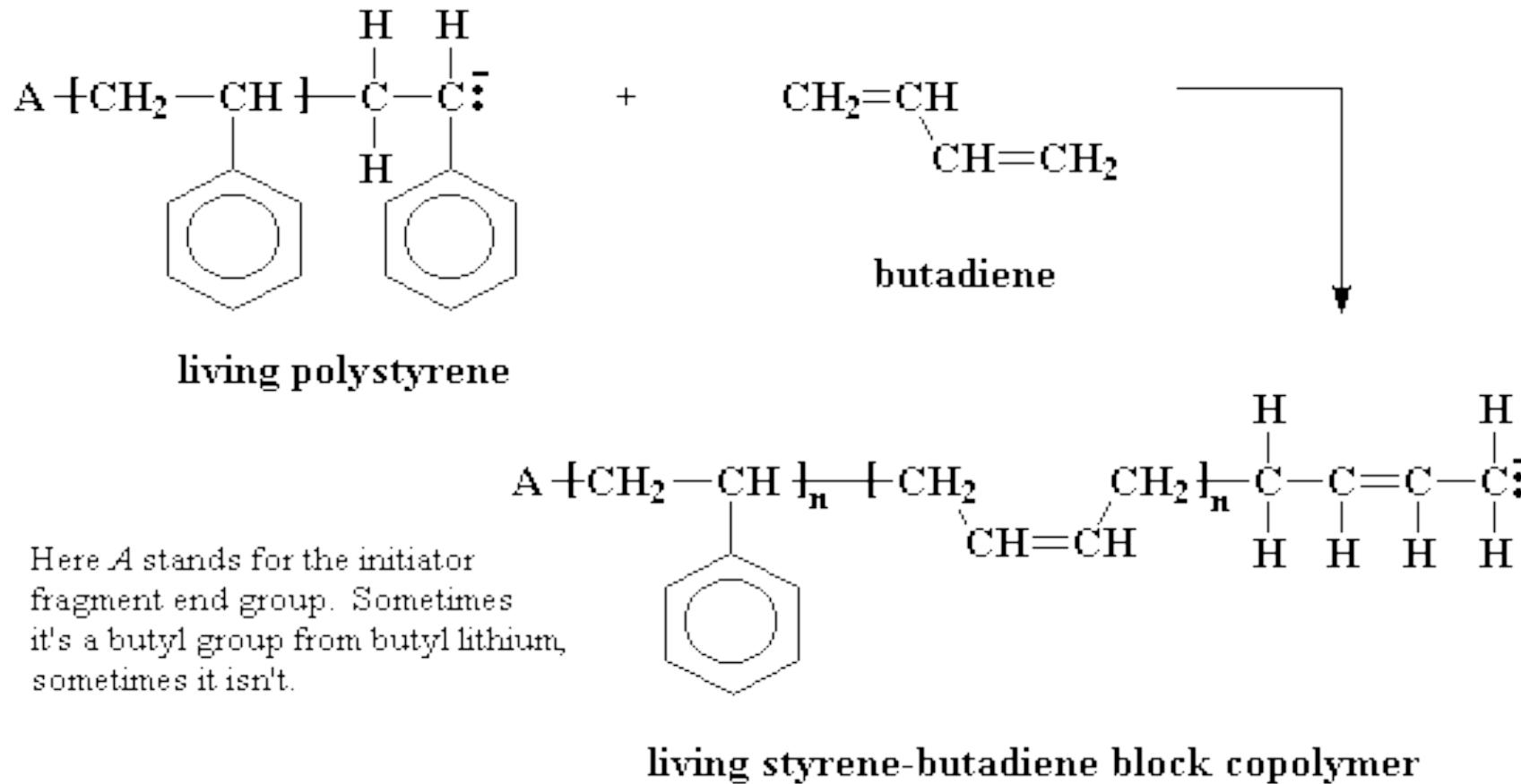
Only when a chemical terminator such as water is introduced will polymerization stop.

Hence the name: living anionic polymerization.

If after depletion of the styrene monomer in the reactor butadiene monomer is introduced a polymer is produced comprising a block of styrene followed by a block of butadiene.

Synthesis of S-B-S Rubber via Anionic Polymerization

After depletion of the styrene monomer in the reactor butadiene is introduced a polymer is produced comprising a block of styrene monomers and a block of butadiene monomers.



Here A stands for the initiator fragment end group. Sometimes it's a butyl group from butyl lithium, sometimes it isn't.

Also, described as:

Synthesis of S-B-S Rubber via Anionic Polymerization

Three methods exist to produce a styrene-butadiene-styrene triblock polymer:

- 1) Linear anionic polymerization of styrene monomer followed by butadiene monomer followed by styrene monomer:



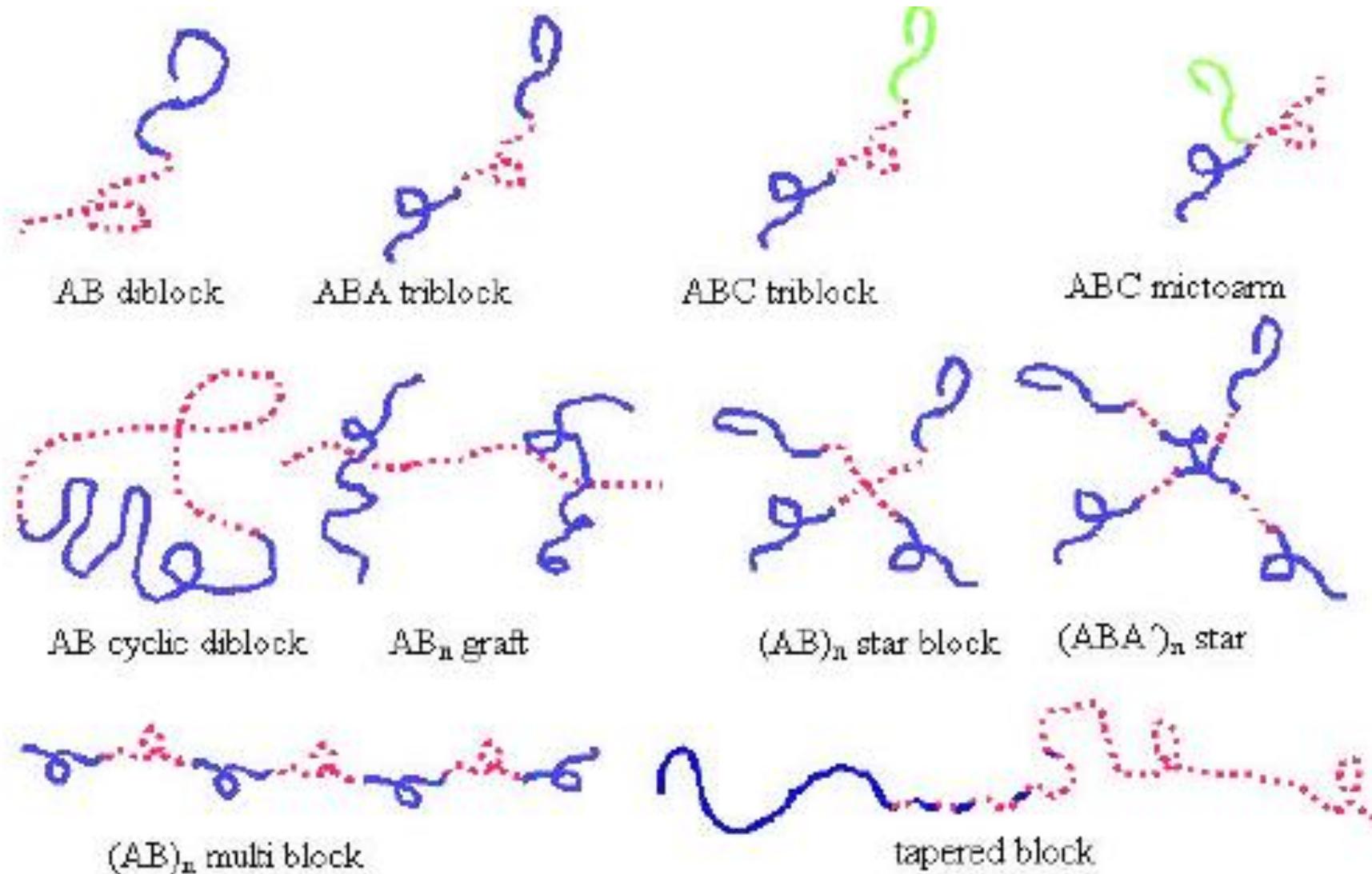
- 1) Reacting two styrene butadiene di-block polymers at the internal butadiene:



- 1) Employing a di-functional initiator and polymerizing butadiene then styrene:



Various Molecular Architectures can be Produced by Anionic Polymerization



Domain Formation by Block Copolymers

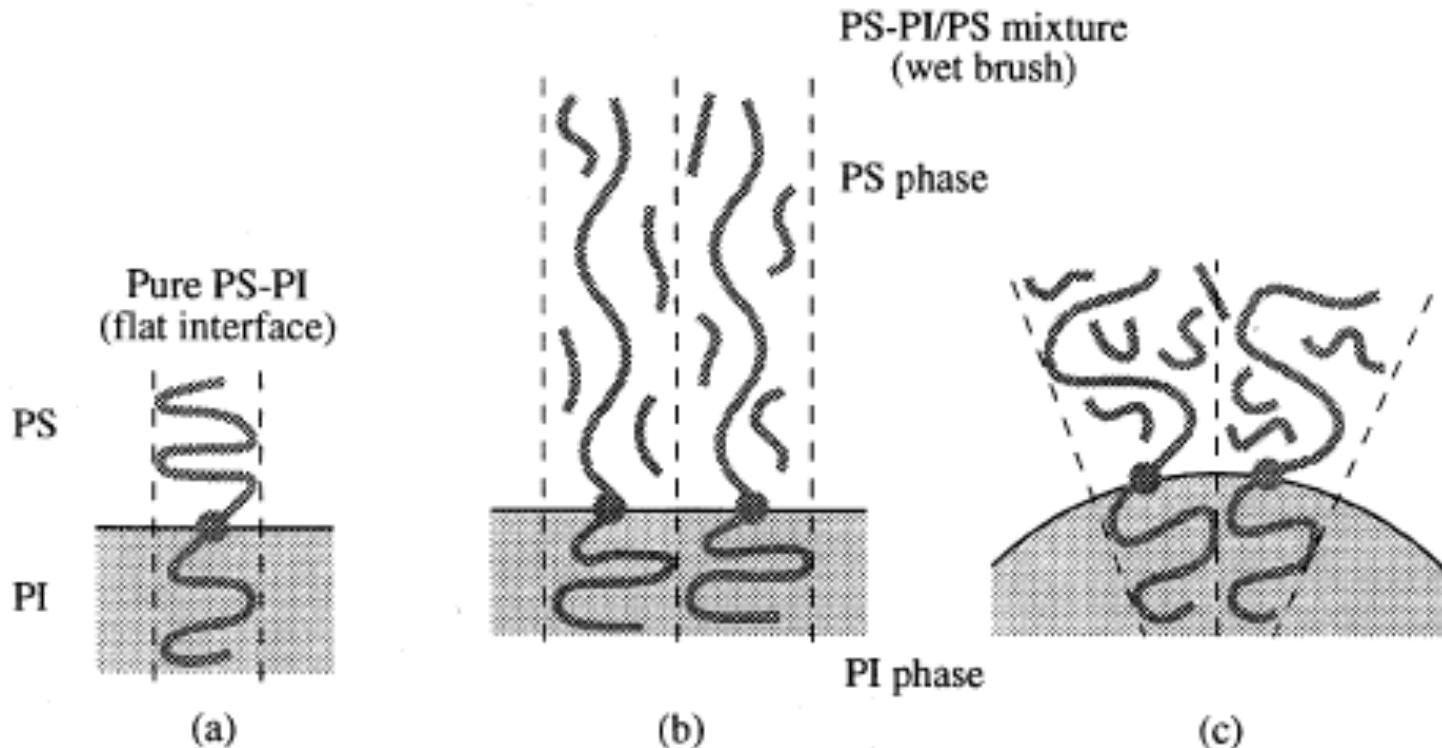
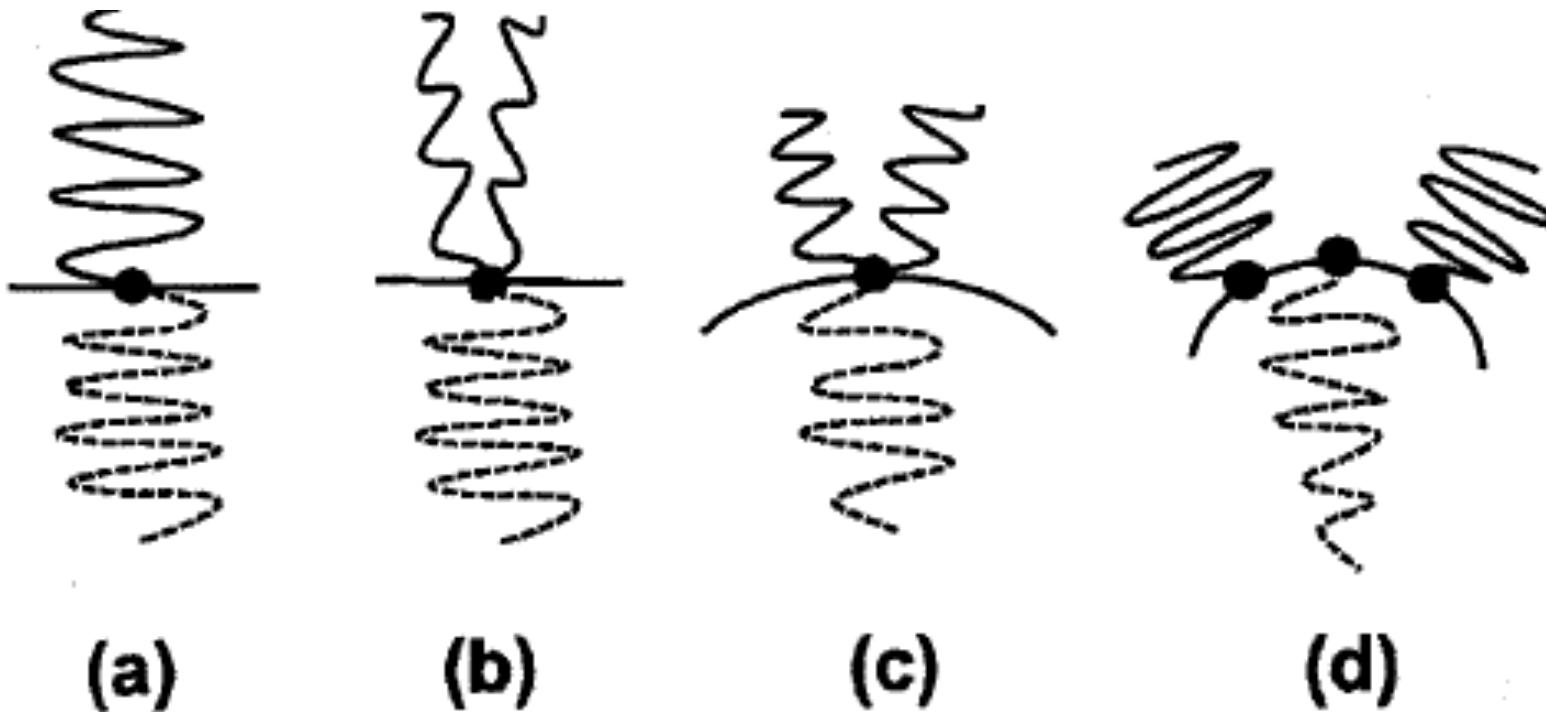


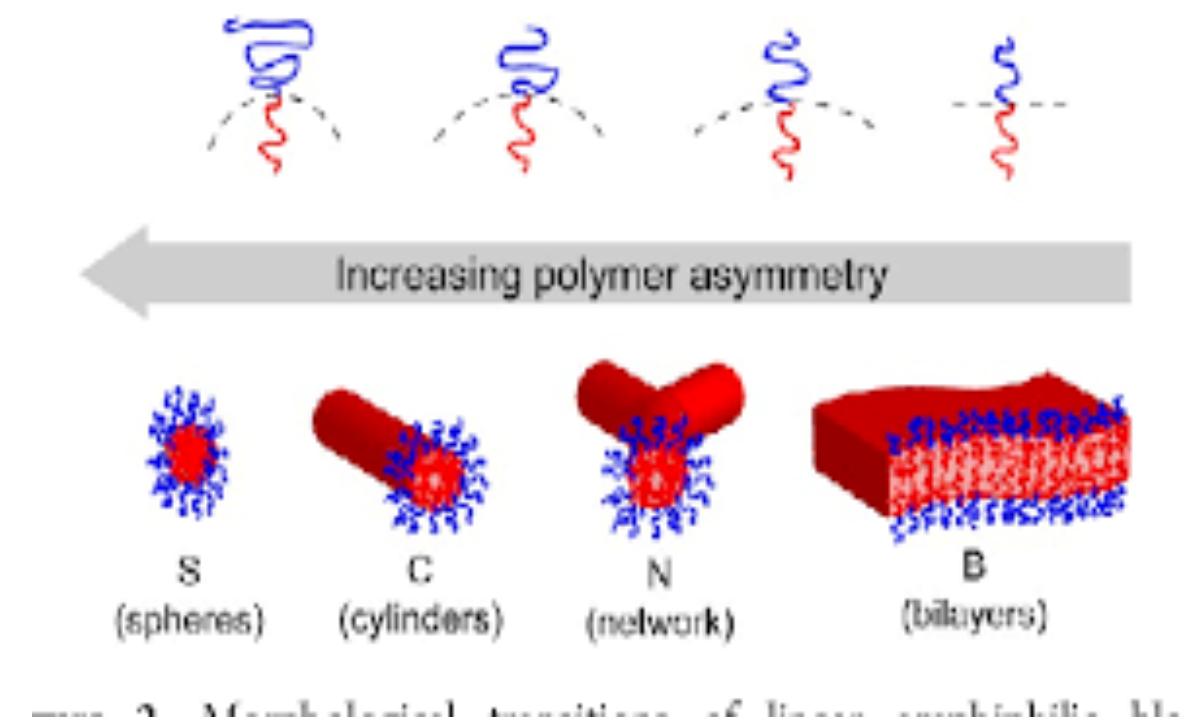
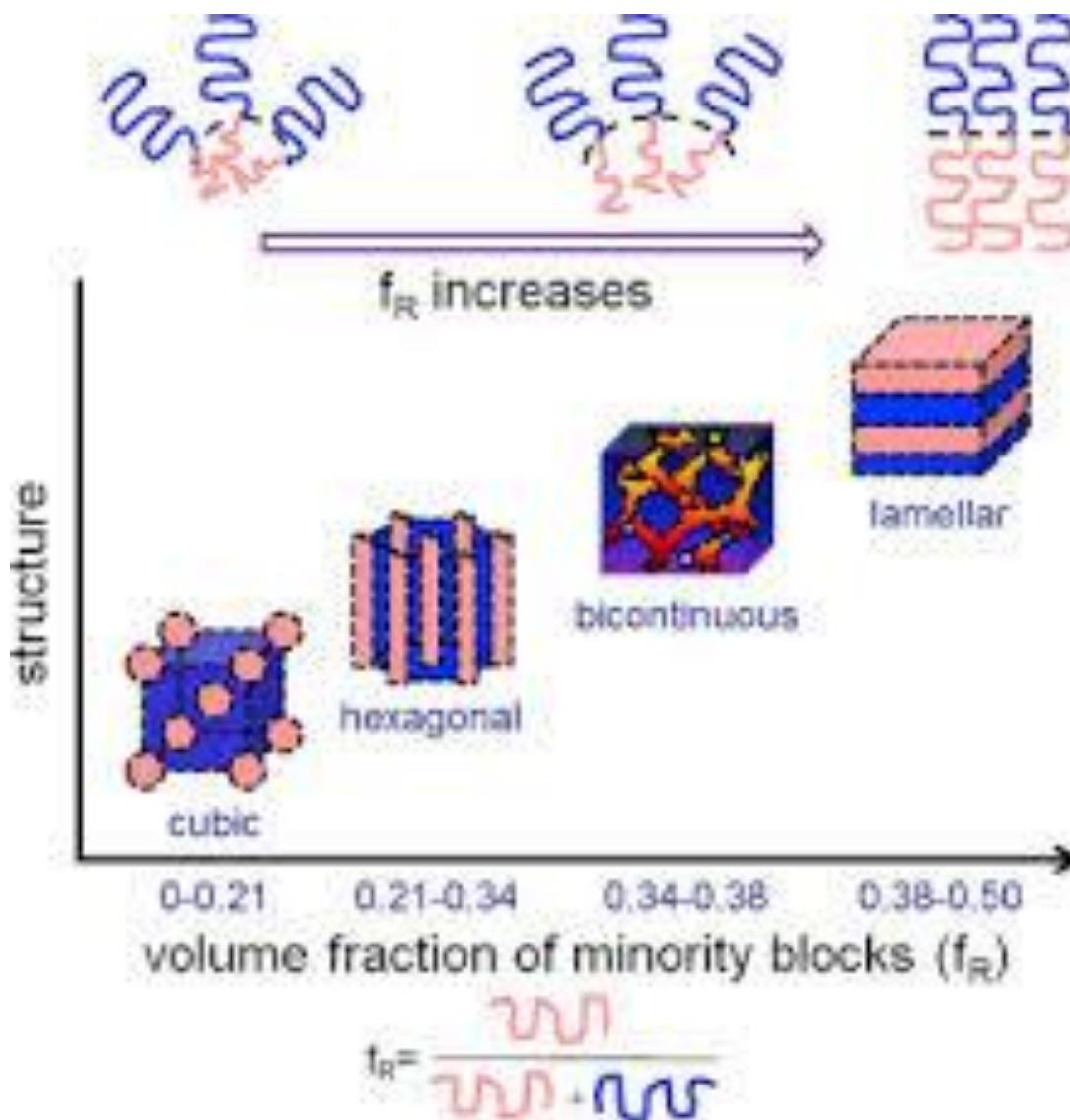
Figure 2.11: Schematic illustration of chain packing: a) pure SI diblock copolymer chain with symmetrical volume fraction forming a flat interface, b) swelling of PS lamellae by uniform solubilization of hPS molecules causes stretching of PS-block chains and/or compression of PI-block chains resulting in a decrease in conformational entropy, c) alternatively a curved interface is formed to gain entropy [76].

Domain Formation by Block Copolymers



2.6: Schematic of A-B junction points on an interface for a) (2A)B linear diblock copolymers, b) A₂B block copolymers with a trifunctional branch point at a flat interface, c) A₂B single graft block copolymer with a trifunctional branch point at a curved interface and d) A₂B block copolymers with approximation of equal spacing between the grafted A blocks. The curvature of the interface represents the shifts of the OOT lines towards higher B volume fractions on the morphology diagrams [30,32].

Domain Formation by Block Copolymers



Domain Morphology of Block Copolymers

Spheres



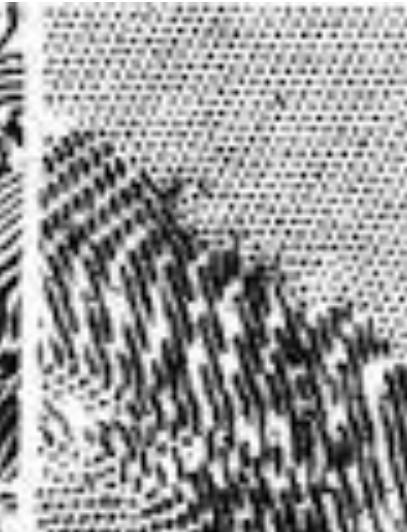
Cylinders



Lamella



Cylinders



Spheres



< 15%

15 – 35%

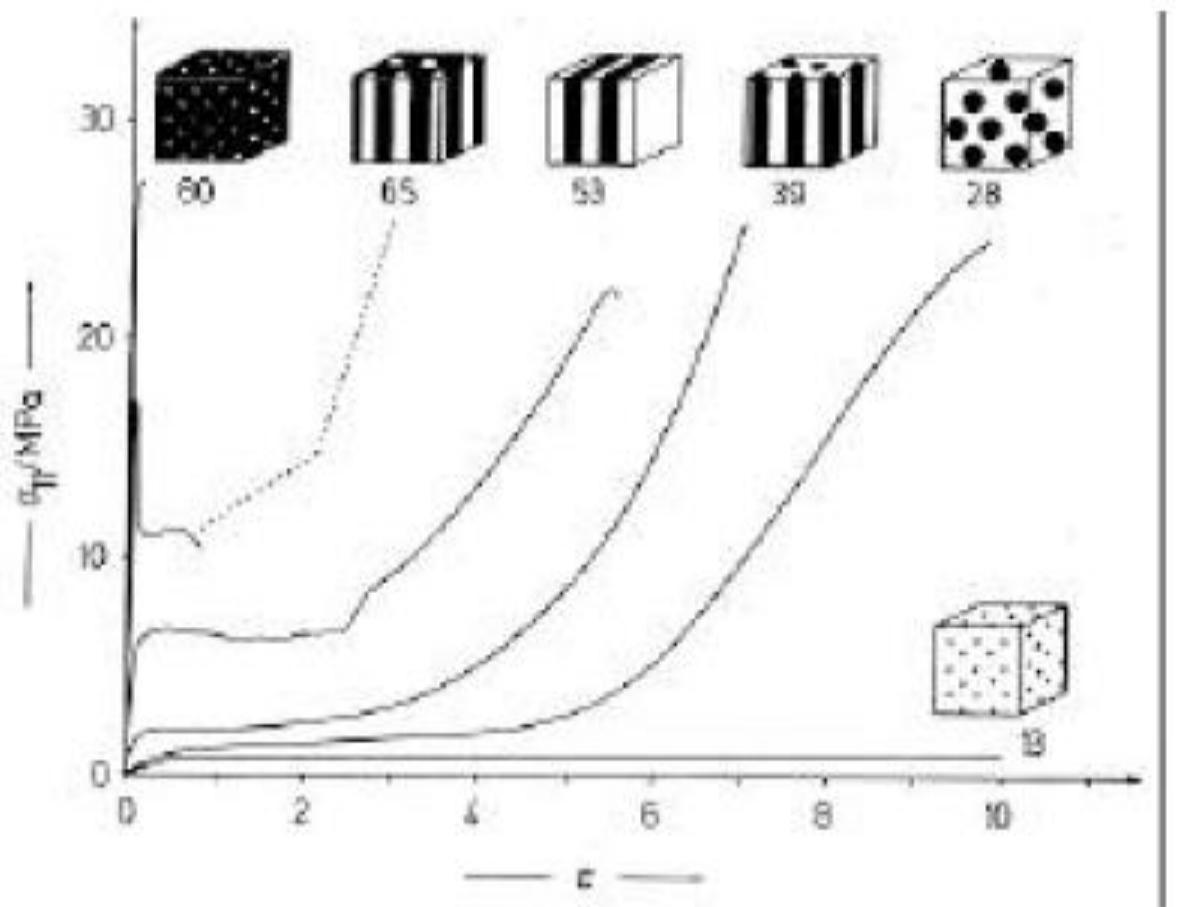
35 – 65%

65 – 85%

> 85%

0.5 μm

Phase Dependent Mechanical Properties

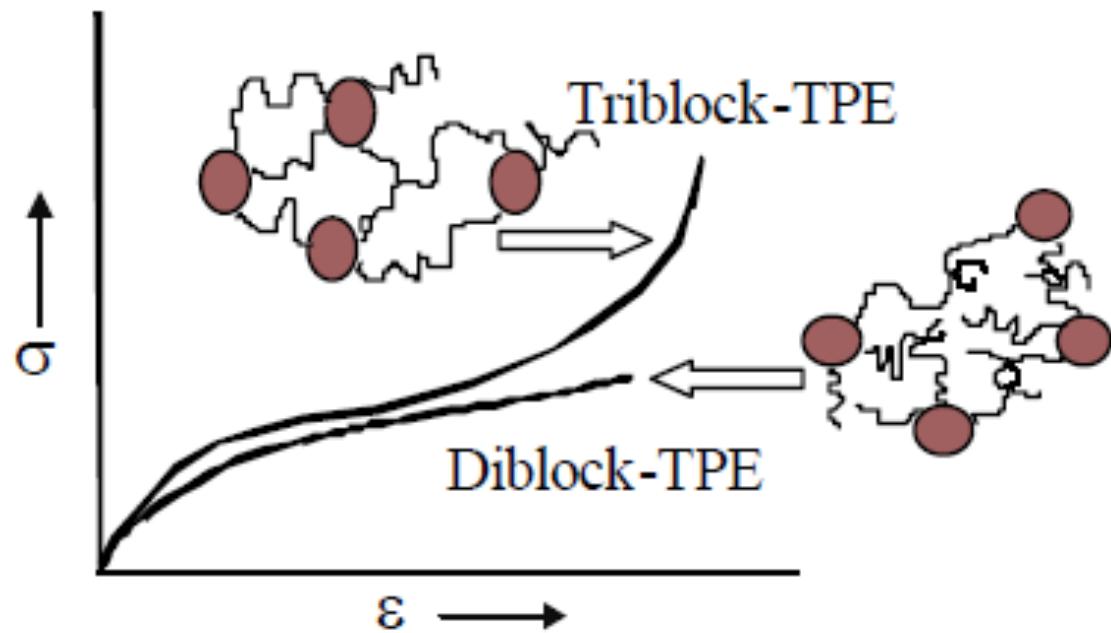


Phase Dependent Mechanical Properties

Styrene – Black Domain – Hard Phase

Butadiene – White Domain – Soft (Rubber) Phase

Elastomers are Derived from a Tri-block Copolymer



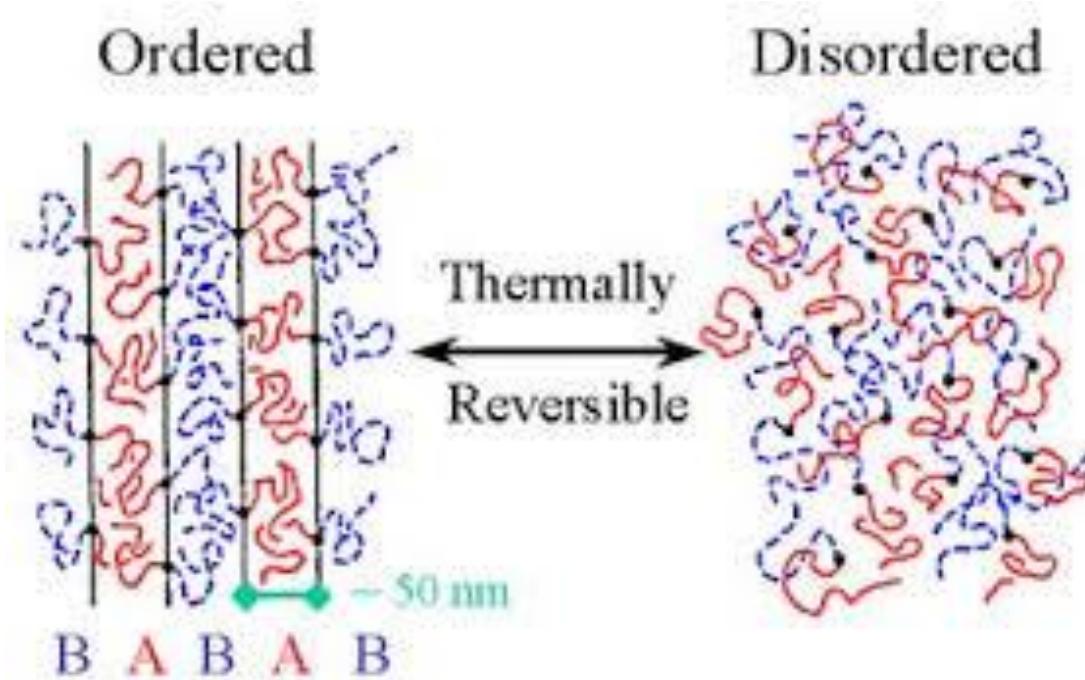
A styrene-butadiene-styrene copolymer defines the morphology of a thermoplastic elastomer.

The styrene segments are the minor component of the S-B-S copolymer and the butadiene segments are the major components.

The styrene components form the rigid spherical domains acting like crosslinks.

The butadiene segments form the elastomeric network.

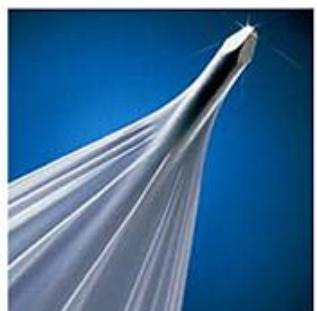
What defines a Thermoplastic Elastomer?



When the temperature is raised above the glass transition temperature of styrene (i.e., 100C) the styrene domains melt allowing the material to Become disordered and flow.

Once this melt is formed into the final form or geometry the material is cooled and the styrene domains are formed imparting the elastomeric properties.

Examples of S-B-S Thermoplastic Elastomer Products



Comparative Mechanical Properties of Elastomers

	Durometer hardness range	Tensile strength at room temp, psi	Elongation at room temp, %	Temp. range of service °C	Weather resistance
Natural rubber	20–100	1,000–4,000	100–700	-55–80	Fair
Styrene-butadiene rubber (SBR)	40–100	1,000–3,500	100–700	-55–110	Fair
Polybutadiene	30–100	1,000–3,000	100–700	-60–100	Fair
Polyisoprene	20–100	1,000–4,000	100–750	-55–80	Fair
Polychloroprene	20–90	1,000–4,000	100–700	-55–100	Very good
Polyurethane	62–95 A 40–80 D	1,000–8,000	100–700	-70–120	Excellent
Polyisobutylene	30–100	1,000–3,000	100–700	-55–100	Very good

Table 1 Selected properties of some elastomers.

Comparative Properties of Elastomers

ISOPRENE BASED RUBBERS

NATURAL (ISOPRENE) RUBBER AND POLYISOPRENE

ADVANTAGES:

NATURAL RUBBER exhibits high resilience, good tensile strength, and tear resistance. In addition to excellent wear resistance, NATURAL RUBBER also offers low permanent set characteristics plus good flexing qualities at low temperatures.

DISADVANTAGES:

NATURAL RUBBER does not perform well when exposed to chemicals and petroleum derivatives, including petrochemicals. It is not recommended for outdoor applications where maximum resistance to sunlight, ozone, oxygen or heat aging is major factors.

TYPICAL APPLICATIONS: Boots, belts, bumpers, tubing.

Comparative Properties of Elastomers

BUTADIENE BASED RUBBERS

SBR (STYRENE BUTADIENE RUBBER) RUBBER AND POLYBUTADIENE

ADVANTAGES:

SBR provides good abrasion, wear, and tensile qualities. SBR can be readily substituted for NATURAL RUBBER in many applications with significant cost savings. Resilience is about the same as NATURAL RUBBER.

DISADVANTAGES:

Like its natural counterpart, SBR offers little resistance to oils and chemicals. SBR must be specially compounded to provide resistance to ozone, sunlight, and heat.

TYPICAL APPLICATIONS:

Washers, gaskets, grommets.

Comparative Properties of Elastomers

NEOPRENE® (POLYCHLOROPRENE) RUBBER

ADVANTAGES:

NEOPRENE® is resistant to ozone, sunlight, oxidation and many petroleum derivatives. Added advantages include good resistance to water, many chemicals, good resilience characteristics and high tensile strength properties.

DISADVANTAGES:

NEOPRENE® has few practical limitations. While NEOPRENE® is slightly higher in price than general purpose synthetic rubbers, its resistance to ozone, oil and chemicals make it cost effective in many applications. It is generally attacked by strong oxidizing acids, esters, ketones, chlorinated, aromatic and nitro hydrocarbons.

TYPICAL APPLICATIONS:

Plumbing fixtures; gaskets; hose; mechanical seals; mechanical belts; solid rocket propellant; garden hose; inner tubes; laboratory tubing.

Lesson 15: Polydienes – From Natural Rubber to Synthetic Rubber Part 2: Polychloroprene, Polybutadiene and Styrene-Butadiene Block Copolymers

Questions?



Dr. Andy Olah, amo5@case.edu, O: 216-368-0606, C: 216-272-0505

“There are three signs of “old age”. The first is memory loss and . . . I forget the other two.”

EMAC 276

Lecture 17: The Importance of Standardization The Importance of Patents

February 28, 2025

Andy Olah, Ph.D.; amo5@case.edu

The Importance of Standardization

What's the Difference Between an Oil, a Wax and a Polymer?

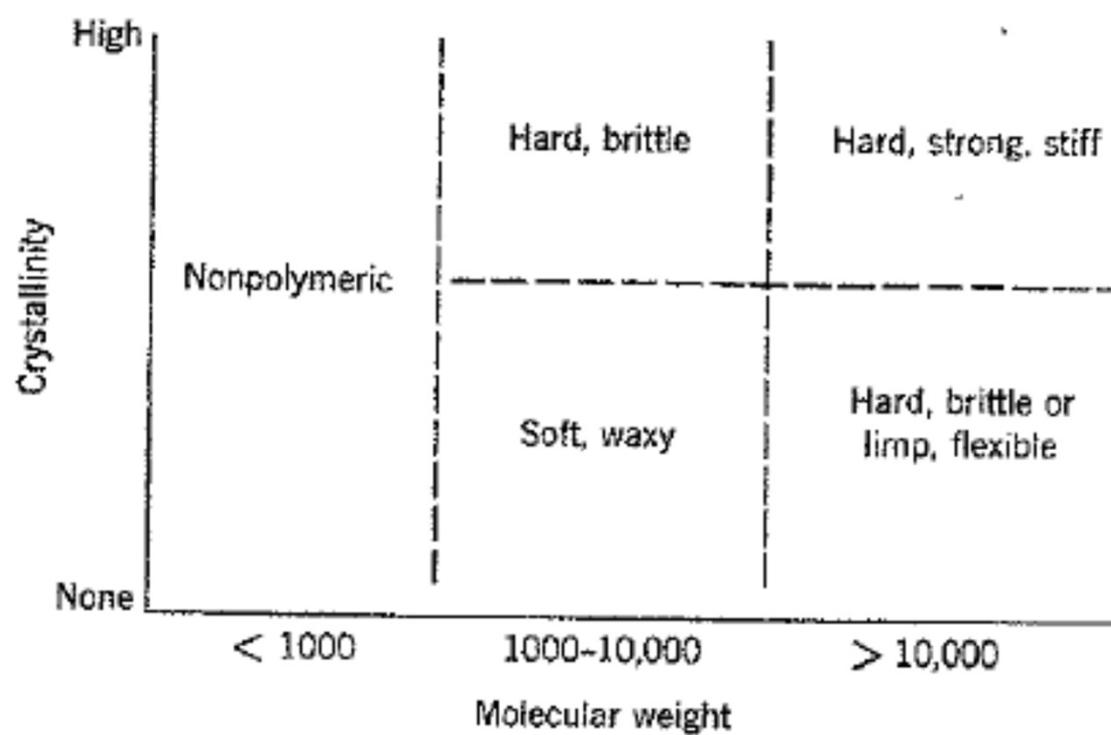


Fig. 1-3. Classification of the expected properties of materials on the basis of molecular weight and crystallinity.

What's the Difference Between an Oil, a Wax and a Polymer?

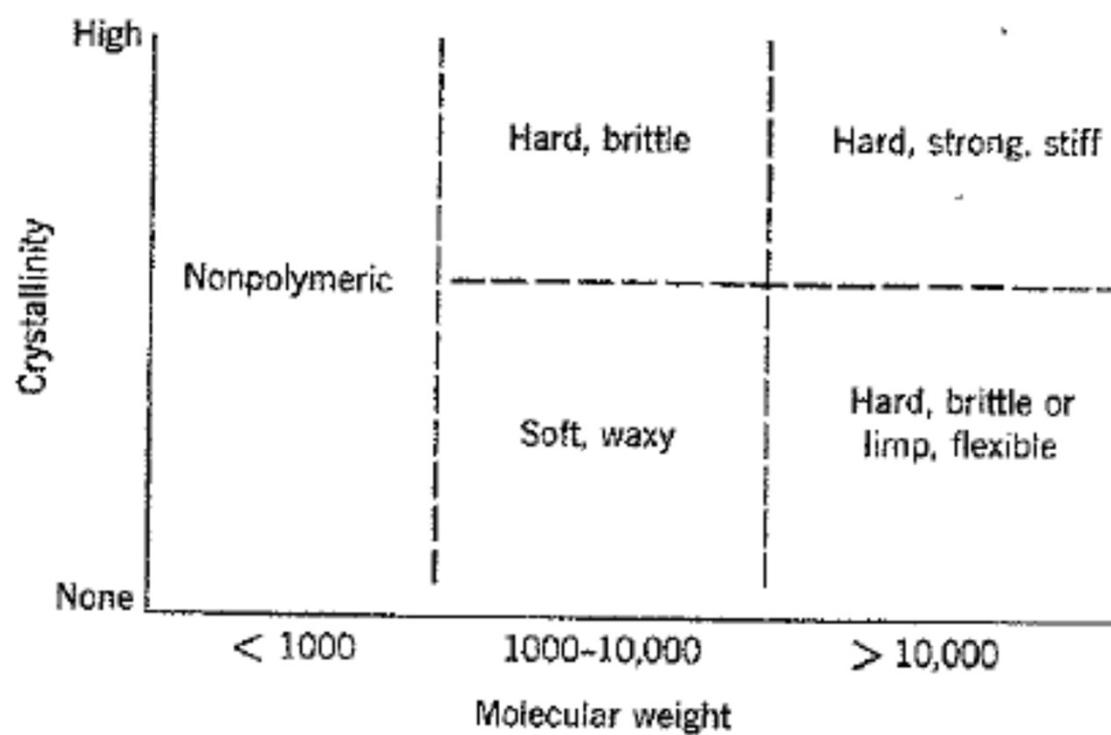


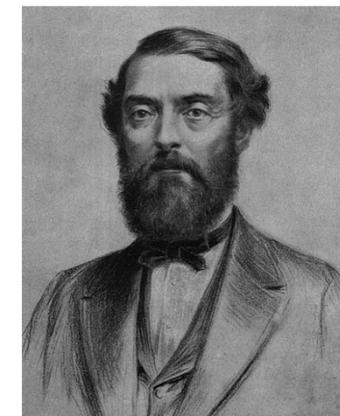
Fig. 1-3. Classification of the expected properties of materials on the basis of molecular weight and crystallinity.

Answer: Molecular Weight. Remember polyethylene and polydimethylsiloxane.

On August 27, 1859, Drake Struck Oil in Pennsylvania



Western Pennsylvania and Eastern Ohio were original locations for the early production of crude oils.



Edwin Drake

BTW: Melrose, in Nacogdoches County, was the site in 1866 of the first drilled well to produce oil in Texas.

Pennsylvania Based Crude Oils were High in Paraffin Content

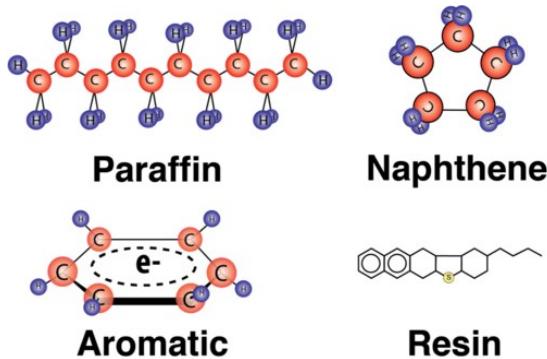
Element	Weight %	Hydrocarbon	Weight %
Carbon	83-87	Paraffins	30
Hydrogen	10-14	Naphthenes	49
Nitrogen	0.1-2	Aromatics	15
Oxygen	0.1-1.5		
Sulfur	0.5-6		
Metals	< 0.1	Asphalts	6

The hydrocarbon weight % values are averages.



Does not hold true today since most motor oils are multiblends.

Basic Composition of Crude Oil



PROPERTIES OF HEAVY CRUDE OILS

- Heavy crude oil is asphaltic. It is "heavy" (dense and viscous).
- heavy crude oils with a high content of naphthenic compounds, such as asphaltenes.
- Asphaltic crude oils are also known as naphthene-based crude oil when the paraffin wax content is low (< 10%)
- Heavy oil has over 60 carbon atoms and hence a high boiling point and molecular weight.

Oil Lamps and Lamp Oil

Oils that were commonly used in lamps:

- Vegetable oil
- Olive oil
- Corn oil
- Sunflower Oil
- Mustard Seed Oil
- Whale Oil
- Petroleum Based - Kerosene



The quality of oils from different companies varied, some didn't light, others were sooty, and still others nearly exploded when lit.

One Man Marketed an Oil that was Very Uniform in Performance



Being invested in the newly discovered crude oil production in Pennsylvania and Ohio he utilized these high paraffinic content oils to produce a high quality lamp oil that wasn't sooty and was consistent in performance.

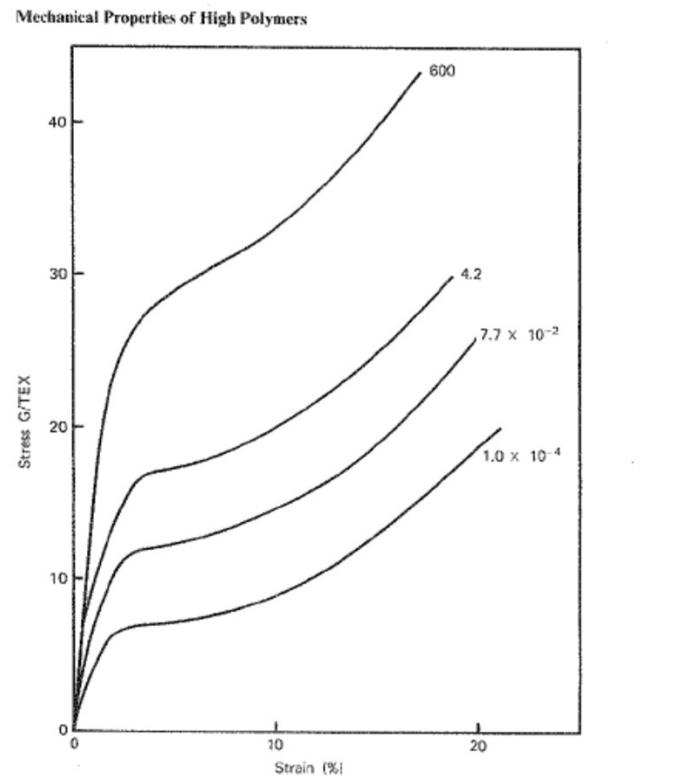
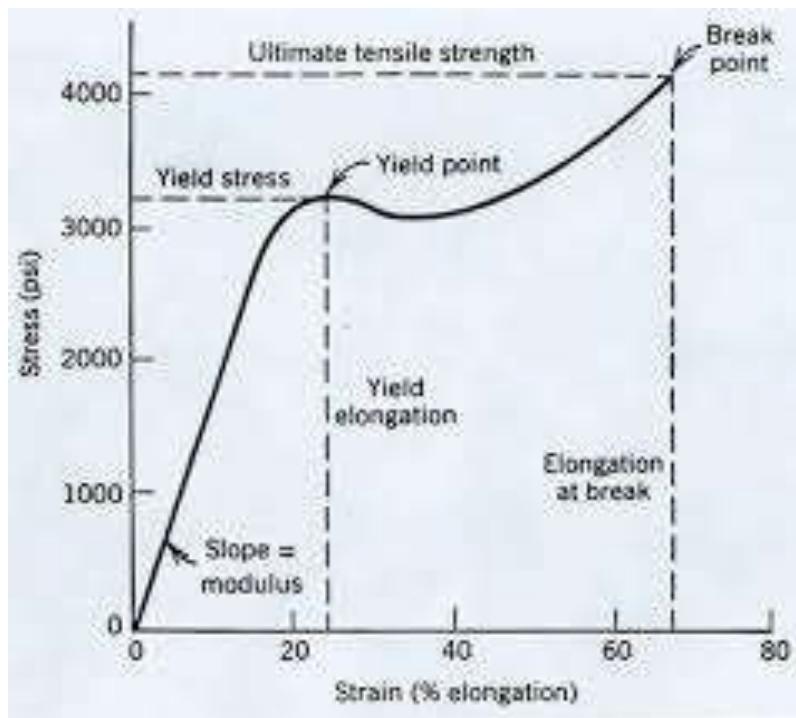
In order to represent the performance and consistency of this ***oil in 1870 he decided to call his company the Standard Oil Company.***

This man was John D. Rockefeller, and he started this company in Cleveland, Ohio.

J.D. Rockefeller recognized the importance of standardization of quality in the marketing of a product.

Why Develop Standards?

Use the simple stress-strain curve for a polymer as an example.



A lot of information can be obtained from a single stress-strain curve.

It can differ relative to strain rate.

: 27 Effect of strain rate on tensile stress-strain curves of polyacrylonitrile (77). Tex = weight in grams of 1000 m of yarn. G = applied force/g.

Use the simple stress-strain curve for a polymer as an example.

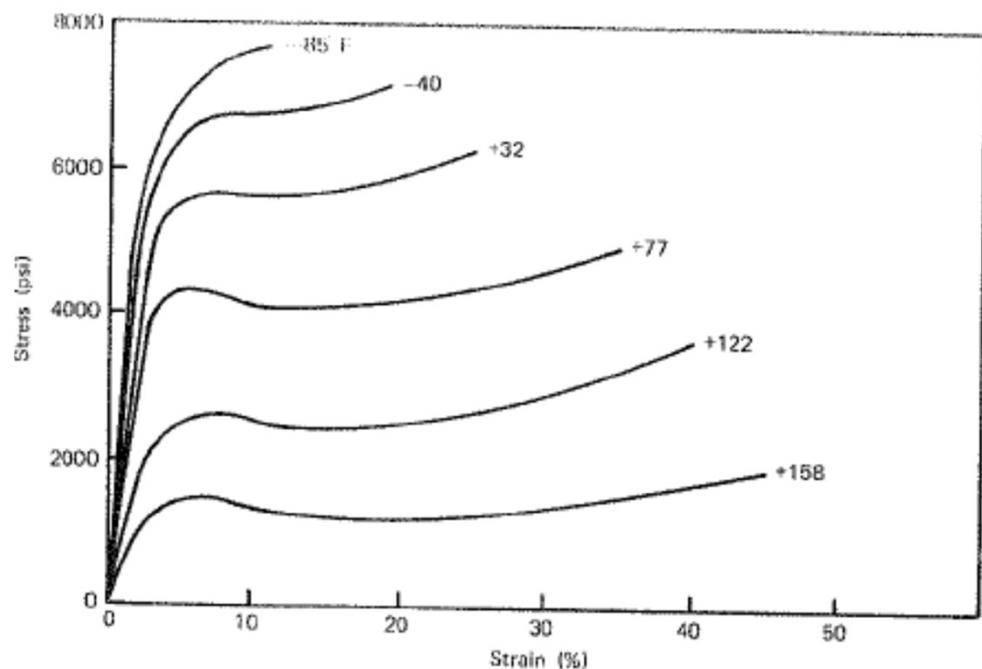


Figure 29 Effect of temperature on tensile stress-strain curves of cellulose acetate (20).

It can differ relative to temperature.

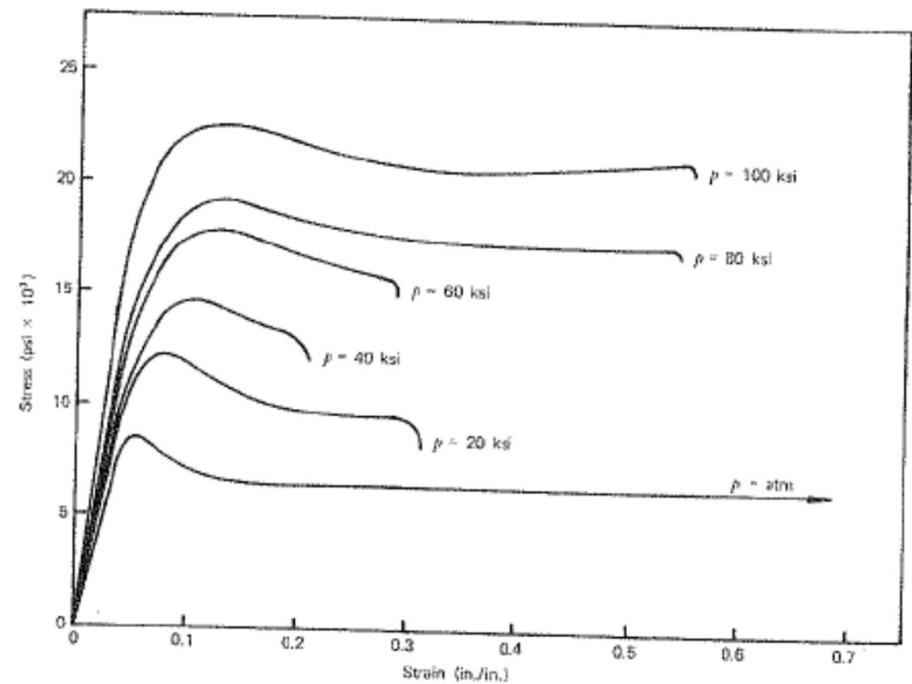


Figure 30 Effect of pressure on tensile stress-strain curves of polyvinyl chloride.

It can differ relative to pressure.

Without Standardization

- Lab-to-Lab Variation and Characterization
 - Sample Geometry
 - Sample Preparation and Conditioning
 - Sample Testing
 - Data Reporting
- Misrepresentation of Performance
- Reporting Deficiencies and Inconsistencies
- Harmonization of Testing around the World



 Designation: D638 - 14

**Standard Test Method for
Tensile Properties of Plastics¹**

This standard is issued under the fixed designation D638; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript symbol (a) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the U.S. Department of Defense.

DOW™ HDPE DMDA-8920 HEALTH+™ Technical Data Sheet

Additive	• Antiblock: No	• Slip: No	• Processing Aid: No
Physical			
Density	0.954 g/cm ³	0.954 g/cm ³	ASTM D792
Base Density ¹	0.954 g/cm ³	0.954 g/cm ³	Dow Method
Melt Index (190°C/2.16 kg)	20 g/10 min	20 g/10 min	ASTM D1238
Environmental Stress-Cracking Resistance (ESCR) 122°F (50°C), 100% Igepal, F50	3.00 hr	3.00 hr	ASTM D1693
Mechanical	Nominal Value (English)	Nominal Value (SI)	Test Method
Tensile Strength			ASTM D638
Yield	4100 psi	28.3 MPa	
Break	2000 psi	13.8 MPa	
Tensile Elongation			ASTM D638
Yield	7.0 %	7.0 %	
Break	250 %	250 %	
Flexural Modulus - 2% Secant	167000 psi	1150 MPa	ASTM D790B
Impact	Nominal Value (English)	Nominal Value (SI)	Test Method
Tensile Impact Strength ²	20.0 ft-lb/in ²	42.0 kJ/m ²	ASTM D1822
Hardness	Nominal Value (English)	Nominal Value (SI)	Test Method
Durometer Hardness (Shore D)	57	57	ASTM D2240
Thermal	Nominal Value (English)	Nominal Value (SI)	Test Method
Deflection Temperature Under Load 66 psi (0.45 MPa), Unannealed	163 °F	72.8 °C	ASTM D648
Brittleness Temperature	< -105 °F	< -76.1 °C	ASTM D746
Vicat Softening Temperature	261 °F	127 °C	ASTM D1525
Melting Temperature (DSC)	266 °F	130 °C	Dow Method
Peak Crystallization Temperature (DSC)	243 °F	117 °C	Dow Method
Additional Information			

Plaque molded and tested in accordance with ASTM D4976.

Global Standard Organizations

- ISO - International
 - CEN – European Community
 - ASTM – North American*
 - CSA – Canadian
 - GB – China (PRC)
 - BIS – India
 - NSF – Drinking Water Systems (N. America)*
 - UL – Fire Protection*
- * Currently active
- Harmonization – Correspondence (similarity) of standards between different standard organizations; i.e., ASTM and ISO.

How to Develop or Change an ASTM Standard

- Take out a project obtaining a project number (WK #). Get Sub-committee Chairman's approval.
- Assemble a Task Group with other member having common interest.
- Develop a “draft” for balloting.
- Ballot to Subcommittee only
 - If any Negative Vote is received resolve Negative and reballot to Subcommittee.
 - If No Negative Votes are received move draft up for a Main Committee Ballot.
 - If any Negative Vote is received resolve Negative and reballot to Main Committee.
- When no further Negative Votes are received project undergo's Standards review, Editorial review and becomes a formal new standard or modification to an existing standard.

Terminology

- Consensus Process – The standard development, change and renewal process requires the full approval of all members on the committee.
 - The ASTM process is the only full consensus process today.
 - All others are by a simple majority vote or 2/3 vote.
 - Any one “negative” vote will stop the ASTM process.
 - ASTM “Negative” handling.
 - Incorporate the “negative” concern and ballot again.
 - Get the negative voter to withdraw negative vote.
 - Take the “Negative” to Sub and Main committee in full session (Meets two times/year).
 - Find “Persuasive” – Must change document.
 - Find “Non-Persuasive” – Negative fails.
 - Find “Non-Related” – Negative fails.
 - Ballot the “Negative” to full committee by letter ballot.
- Hard Language (must, shall, etc.) vs Soft Language (can, could, may, etc.)

Current ASTM Committees – Full Vote

D 20 – Plastics

F 17 – Plastic Piping Systems

Chairman for 25 years F 17.25: Vinyl Pipe Subcommittee

E 5 – Fire Protection and Safety Standards

E 60 – Sustainability

As a “Fellow” of the ASTM Society, I have been requested to assist
in a brand new committee:

Current ASTM Committees – Full Vote

D 20 – Plastics

F 17 – Plastic Piping Systems

Chairman for 20 years F 17.25: Vinyl Pipe Subcommittee

E 5 – Fire Protection and Safety Standards

E 60 – Sustainability

As a “Fellow” of the ASTM Society, I have been requested to assist in a brand new committee:

D 37 - Cannabis

I highly recommend students become active in ASTM. There is a benefit to become involved early.
Visit: astm.org and type in “Student Membership” in search box.

The Importance of Patents

Why Patent?

Protect against copying

You will need to share your concepts with investors and other partners so that you can get your idea to the market. By having a provisional patent, no one will be able to steal your idea or concept.

Protect the company's ability to do business

If you don't patent your invention, someone will copy it and enter the market with your product. So, you will have competition in the market. You may also lose the right to compete if that person files a patent for the product.

Increase market position

If you have a patent portfolio, you will increase the market position by preventing other companies from competing in your specific niche.

Get licensing fees

You may not be able to commercialize your concept finally. But there might be others who have resources to turn your idea into a commercial commodity. Your company can then get licensing fees for using your concept.

Improves CV

If you have a patent portfolio, it shows that you have a technical expertise and the commitment to inventing something. Investors and partners will appreciate it and might want to work with you.

Basic Steps for Obtaining a Patent

Step 1: Determine the type of Intellectual Property protection that you need: Trademark, Copyright, Patent, etc.

Step 2: Determine if your invention is patentable:

Search to see if your invention has already been publicly disclosed.

Step 3: Get ready to apply: By Yourself or Outside Legal Help

There will be fees: filing, search and examination fees

Step 4: Prepare and submit your initial application

Step 5: Work with your examiner

There may be additional fees: examiner, extension of time, etc.

Step 6: Receive your approval

There will be additional fees: publishing and over time maintenance fees.

Basic Terminology

What is “Prior Art”:

Anything in the Public Domain that describes your Invention, such as:

1. Another invention
2. A published scholarly article
3. A device or product already marketed (US 72X, 3-14-1794)
4. A disclosed manufacturing practice
5. A presentation that has been recorded in some manner

When are you formally protected to discuss your invention?

Only when you have formally filed your invention application with the patent office (USPTO) and have an application number and filing date may you then discuss your invention/idea/etc.

NOTE: You are protected based on your filing date.

Claims – The most important part of a patent

4. CLAIMS

The most important part of the patent is the claims; the claims set forth and define the patent's scope of exclusive rights. In other words, they describe what the patent does or does not cover. Each claim element should be shown in the drawings and described in the detailed description.

There are two different ways to categorize the types of claims you'll find in a typical patent.

INDEPENDENT VS. DEPENDENT CLAIMS

Another way to categorize claims is independent claims versus dependent claims. As the names suggest, each independent claim stands on its own, whereas dependent claims always refer back to (and “depend” from) another claim.

INFORMATION CONTAINED WITHIN A PATENT

Broadly, the typical patent consists of four main parts:

- 1.Front page(s)
- 2.Drawings
- 3.Specification
 1. A background section
 2. A list of drawings
 3. A detailed description
- 4.Claims

The specification may also include the following other sections, though these are generally not required:

- A summary section
- A cross-reference to related applications
- A statement of government support

WHAT A PATENT WON'T TELL YOU

:

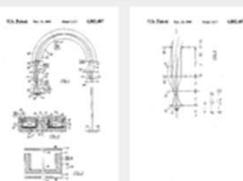
- Have the maintenance fees been paid?
- Has the patent expired?
- Who is the current owner of the patent?
- Has the patent been invalidated, enforced, licensed, or sold?
- Have any further applications (like continuations or divisionals) been filed for this subject matter after this patent was granted?

Direct imaging monochromatic electron microscope

Abstract

A direct-imaging, monochromatic electron microscope includes an objective lens for collecting a substantial portion of emitted electrons from an area across a sample surface, and focusing the electrons through an image plane. A collimating lens for collimating the electrons into beams is located at its focal distance from the image plane. An energy filter with an entrance aperture is receptive of the beams to transit monochromatic beams, and a transfer lens is receptive of the monochromatic beams for refocusing the same through a projection lens to effect an image of the plurality of spots in a projection plane. The objective lens is formed of a magnetic toroidal coil having a central hole therein with a dish-shaped magnetically permeable member cupped coaxially over the toroidal coil. The permeable member has a neck portion protruding through the central hole. The sample surface is interposed proximate the objective lens between the objective lens and the energy filter. The entrance aperture is positioned from the transfer lens by approximately a distance optically conjugate to the distance between the objective lens and the collimating lens.

Images (2)



Classifications

H01J37/26 Electron or ion microscopes; Electron or ion diffraction tubes

US4882487A

United States

Download PDF

Find Prior Art

Similar

Inventor: Robert L. Gerlach

Current Assignee : Applied Biosystems Inc , Nova Measuring Instruments Inc , First Bank NA

Worldwide applications

1988 · US

Application US07/268,440 events ⑦

1988-11-08 • Application filed by Perkin Elmer Corp

1988-11-08 • Priority to US07/268,440

1989-11-21 • Application granted

1989-11-21 • Publication of US4882487A

2007-06-05 • Anticipated expiration

Status • Expired - Lifetime

Show all events ▾

United States Patent [19]
Gerlach

[11] **Patent Number:** **4,882,487**
[45] **Date of Patent:** **Nov. 21, 1989**

- [54] **DIRECT IMAGING MONOCHROMATIC ELECTRON MICROSCOPE**
[75] Inventor: **Robert L. Gerlach**, Minnetonka, Minn.
[73] Assignee: **The Perkin-Elmer Corporation**, Norwalk, Conn.
[21] Appl. No.: **268,440**
[22] Filed: **Nov. 8, 1988**

Related U.S. Application Data

- [63] Continuation-in-part of Ser. No. 58,437, Jun. 5, 1987, Pat. No. 4,810,880.
[51] Int. Cl.⁴ H01J 37/285
[52] U.S. Cl. 250/306; 250/305;
250/310
[58] Field of Search 250/306, 305, 307, 310

[56] **References Cited**

U.S. PATENT DOCUMENTS

- 4,758,723 7/1988 Wardell et al. 250/307
4,810,880 3/1989 Gerlach 250/305

OTHER PUBLICATIONS

- Wincott et al., J. Phys. E: Sci. Instrum. 22 (1989) pp. 42-47.

*Primary Examiner—Jack I. Berman
Attorney, Agent, or Firm—E. T. Grimes; H. S. Ingham*

[57] **ABSTRACT**

A direct-imaging, monochromatic electron microscope includes an objective lens for collecting a substantial portion of emitted electrons from an area across a sample surface, and focusing the electrons through an image plane. A collimating lens for collimating the electrons into beams is located at its focal distance from the image plane. An energy filter with an entrance aperture is receptive of the beams to transit monochromatic beams, and a transfer lens is receptive of the monochromatic beams for refocusing the same through a projection lens to effect an image of the plurality of spots in a projection plane. The objective lens is formed of a magnetic toroidal coil having a central hole therein with a dish-shaped magnetically permeable member cupped coaxially over the toroidal coil. The permeable member has a neck portion protruding through the central hole. The sample surface is interposed proximate the objective lens between the objective lens and the energy filter. The entrance aperture is positioned from the transfer lens by approximately a distance optically conjugate to the distance between the objective lens and the collimating lens.

9 Claims, 2 Drawing Sheets

Independent Claims vs Dependent Claims

or

Main Claims vs Sub Claims

4,882,487

7

plurality of spots generally will approach a continuum. However, it may be desirable to collect all electrons from the entire area of the multiplier 108 in order to analyze the entire surface area with a high intensity beam resulting in a high total signal. Alternatively the energy source 16, such as an electron beam, may be focused into a spot on the surface and, for example, may be scanned over the surface in a scanning mode. In either event, the microscope of the present invention is advantageously utilized as an analysis device without direct imaging, with high collection efficiency and, therefore, sensitivity.

While the invention has been described above in detail with reference to specific embodiments, various changes and modifications which fall within the spirit of the invention and scope of the appended claims will become apparent to those skilled in this art. The invention is therefore only intended to be limited by the appended claims or their equivalents.

What is claimed is:

1. A direct imaging, monochromatic electron microscope comprising emitting means for emitting electrons from a plurality of spots on a sample surface, objective lens means for collecting a substantial portion of the emitted electrons and focusing the same at an image plane, collimating lens means for collimating the substantial portion of the emitted electrons into beams, an energy filter having an entrance aperture receptive of the beams to transit monochromatic beams having a selected energy, imaging means receptive of the monochromatic beams for focusing the same to effect an image of the spots, and detector means for detecting the image, the objective lens means having a first effective position plane, the collimating lens means having a second effective position plane and a focal length relative to the second plane, the second plane being positioned at a first distance from the image plane equal to the focal length and at a second distance from the first

5 plane, and the entrance aperture being positioned from the second plane by approximately a third distance optically conjugate to the second distance with respect to the second plane of the collimating lens means.

2. An electron microscope according to claim 1 wherein the objective lens means includes a magnetic objective lens.

3. An electron microscope according to claim 2 wherein the objective lens means comprises a magnetic field generating toroidal coil and a dish-shaped magnetically permeable member cupped coaxially over the toroidal coil.

4. An electron microscope according to claim 3 wherein the coil has a central hole therein and the permeable member has a neck portion extending substantially through the central hole.

5. An electron microscope according to claim 1 wherein the objective lens means is situated to collect the substantial portion of the emitted electrons from a 10 sample surface interposed between the objective lens and the energy filter proximate the objective lens.

6. An electron microscope according to claim 1 wherein the energy filter comprises a spherical analyzer of hemispherical configuration with a slotted exit aperture located diametrically opposite the entrance aperture.

7. An electron microscope according to claim 1 further comprising means for selecting the energy for the monochromatic electron beams.

8. An electron microscope according to claim 1 wherein the emitting means comprises an electron gun directed at the sample surface to cause Auger electron emission from the sample surface.

9. An electron microscope according to claim 1 wherein the emitting means comprises an X-ray source directed at the sample surface to cause photoelectron emission from the sample surface.

* * * *

Provisional vs Non-provisional Application

A provisional application is a quick and inexpensive way for inventors to establish a U.S. filing date for their invention which can be claimed in a later filed nonprovisional application.

A **provisional patent application** will never get a patent issued for your invention. It only lasts for one year and gives the inventor an opportunity to conduct more research or finish the invention before filing a non-provisional patent application. A provisional patent application also costs a lot less to file.

From the day you file, you will have a year to convert your provisional application.
Conversion involves filing a non-provisional patent application that includes a reference to your provisional patent application. In that way, a good provisional patent definition is a placeholder. It holds a place in line for your future non-provisional application.

Provisional vs Non-provisional Application

The provisional only holds the line for the invention as you described it in your provisional application. Anything new that goes into your non-provisional application will have to go to the back of the line.

What is a Non-Provisional Patent?

If a provisional patent application is simple, informal and quick to file then a non-provisional patent is the opposite: long, complicated and difficult to file. The non-provisional application form is very long. It contains many parts and the parts have many rules.

Unlike a provisional patent application, a non-provisional patent can issue into an enforceable claims. Your invention is only protected once your non-provisional patent is issued by the United States Patent and Trademark Office (USPTO). Then, if anyone tries to produce a similar product they are infringing your patent.

Which one Should You File? . . . File both. But don't write too specifically (i.e., preferred, more preferred, most preferred).

EMAC 276 – Homework
Assignment #3 – *Dr. Olah*
Due: Friday, March 21, 2025

We have reviewed the patent search engine “patents.google.com”, illustrating how patents can be found and pertinent aspects of those patents can be obtained.

I. Your assignment is to look up US 4,234,204 and list the following: **(1 Point Each)**

- a. Item invented:
- b. Filing date and Issue date:
- c. Inventor(s):
- d. Number of Main (Independent) claims:
- e. Number of Sub (dependent) claims:

II. Also, look up the following patents and list only the: a) inventor(s), b) date issued, and c) the item invented.

(1 Point Each)

- a. US 223,898
- b. US 174,465
- c. US 821,393
- d. US 1,773,980
- e. US 3,501,586

III. (X-tra Credit, 1 Point) What was the patent object, the date, and inventor for patent US X72

Lecture 19: The Importance of Standardization The Importance of Patents

Questions?



Dr. Andy Olah, amo5@case.edu, O: 216-368-0606, C: 216-272-0505

“Regular naps prevent old age, especially if you take them while driving.”

EMAC 276

Lecture 17: Continuation of Elastomers

Part 1: SBR (Cont'd)

Part 2: Polyisobutylene

Part 3: Polydimethylsiloxane

Andy Olah, Ph.D. amo5@case.edu

March 3, 2025

Domain Formation by Block Copolymers

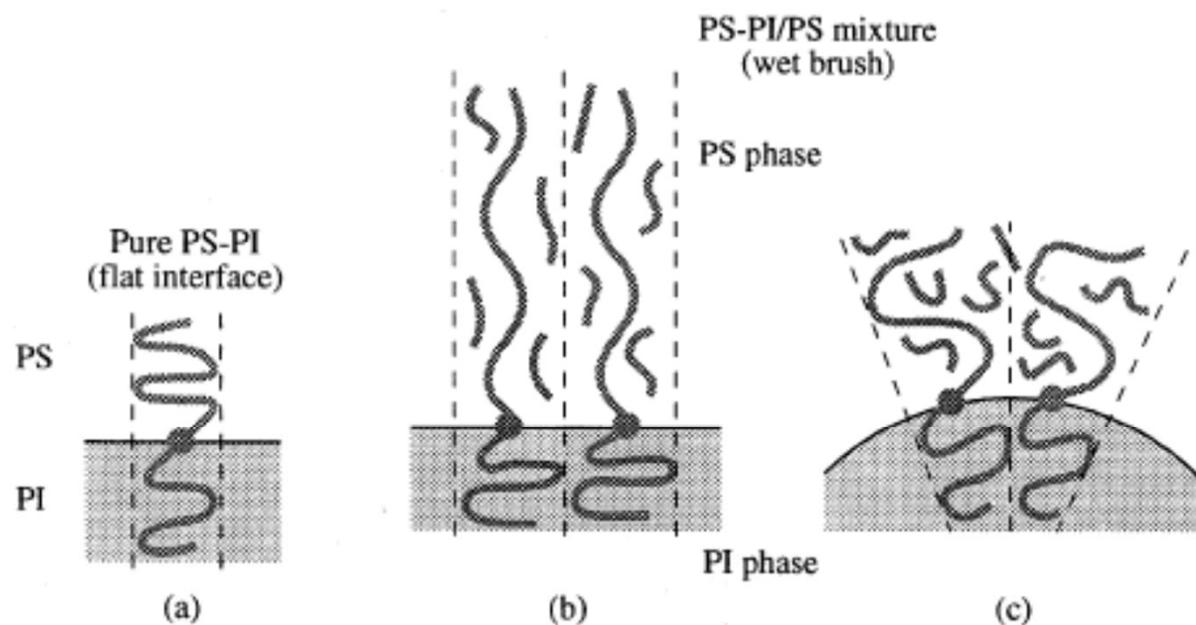
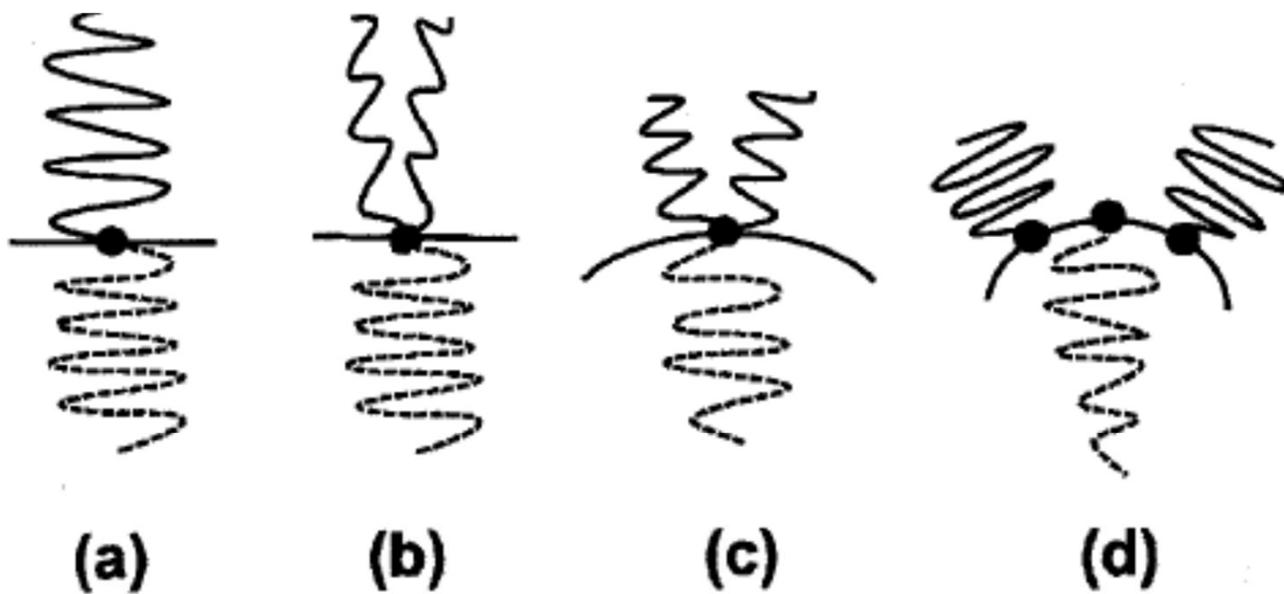


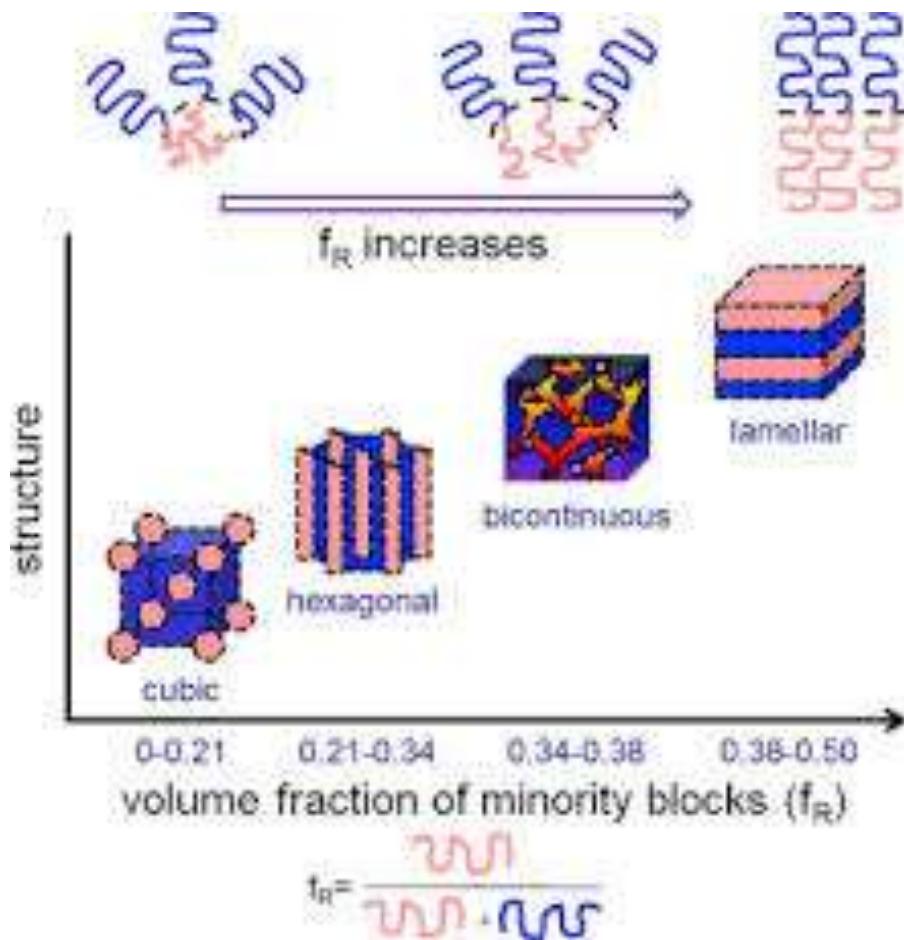
Figure 2.11: Schematic illustration of chain packing: a) pure SI diblock copolymer chain with symmetrical volume fraction forming a flat interface, b) swelling of PS lamellae by uniform solubilization of hPS molecules causes stretching of PS-block chains and/or compression of PI-block chains resulting in a decrease in conformational entropy, c) alternatively a curved interface is formed to gain entropy [76].

Domain Formation by Block Copolymers

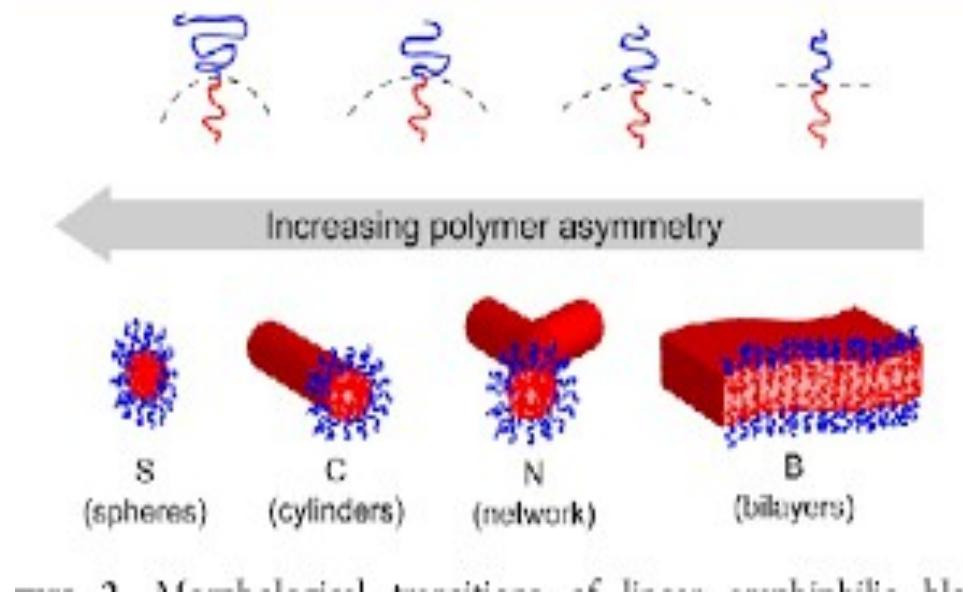


2.6: Schematic of A-B junction points on an interface for a) (2A)B linear diblock copolymers, b) A₂B block copolymers with a trifunctional branch point at a flat interface, c) A₂B single graft block copolymer with a trifunctional branch point at a curved interface and d) A₂B block copolymers with approximation of equal spacing between the grafted A blocks. The curvature of the interface represents the shifts of the OOT lines towards higher B volume fractions on the morphology diagrams [30,32].

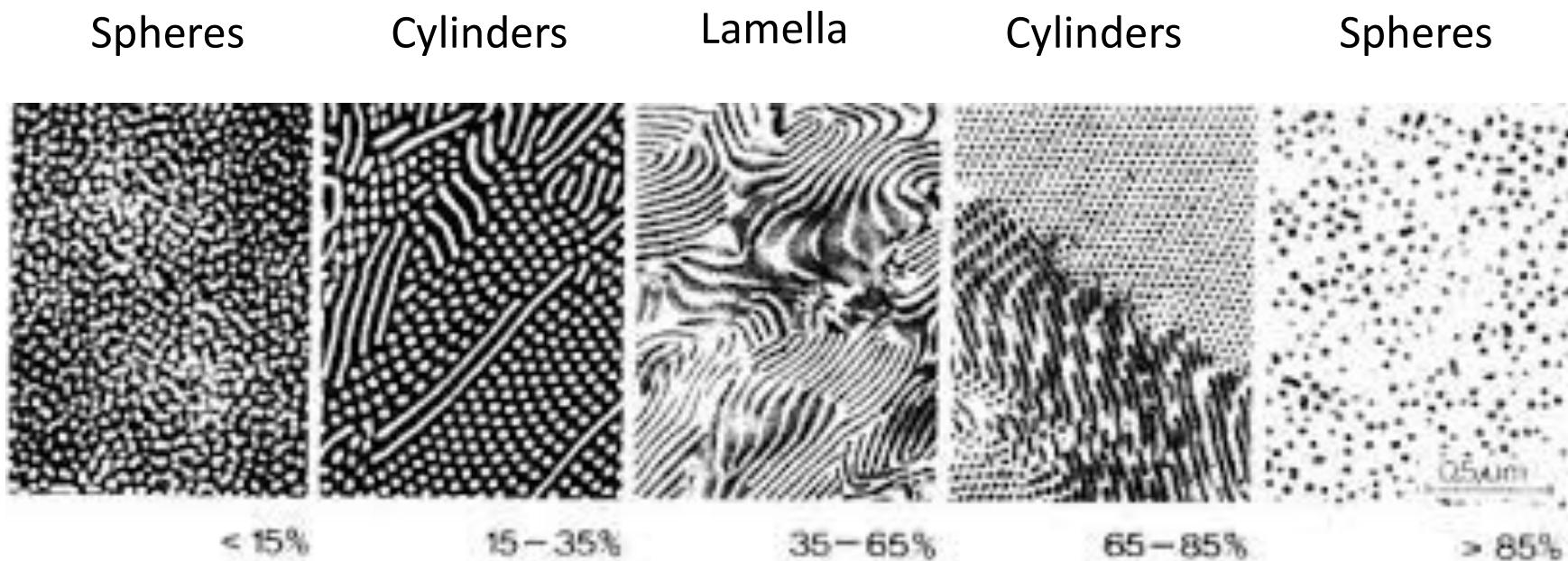
Domain Formation by Block Copolymers



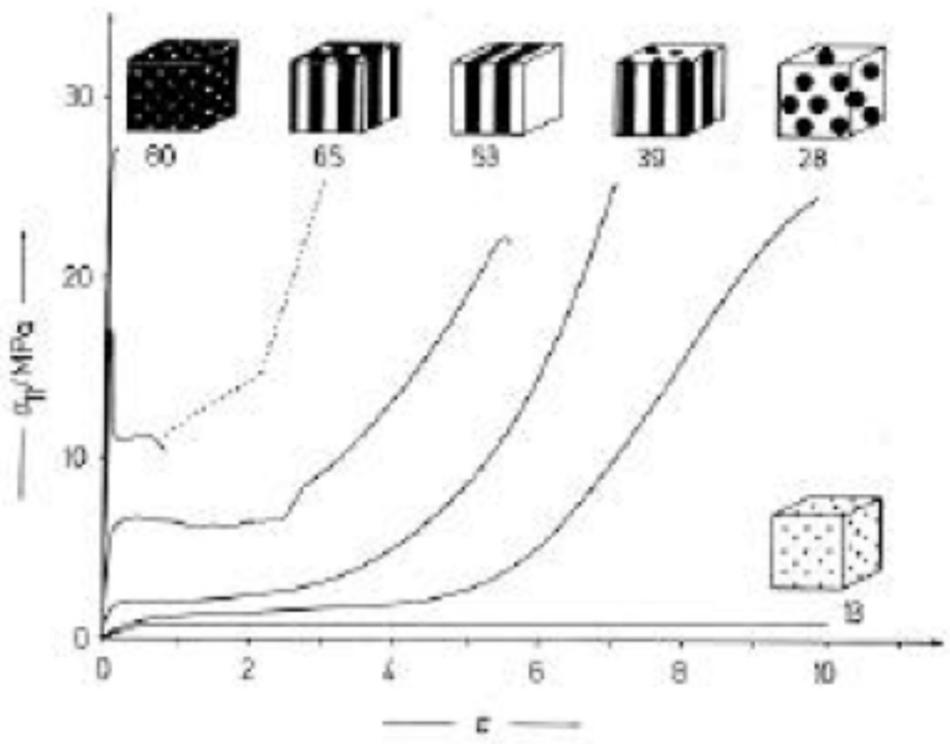
Curvature of the interface is based upon the ratio between the styrene and the butadiene segments and is critical in determining the morphology of the domains.



Domain Morphology of Block Copolymers



Phase Dependent Mechanical Properties

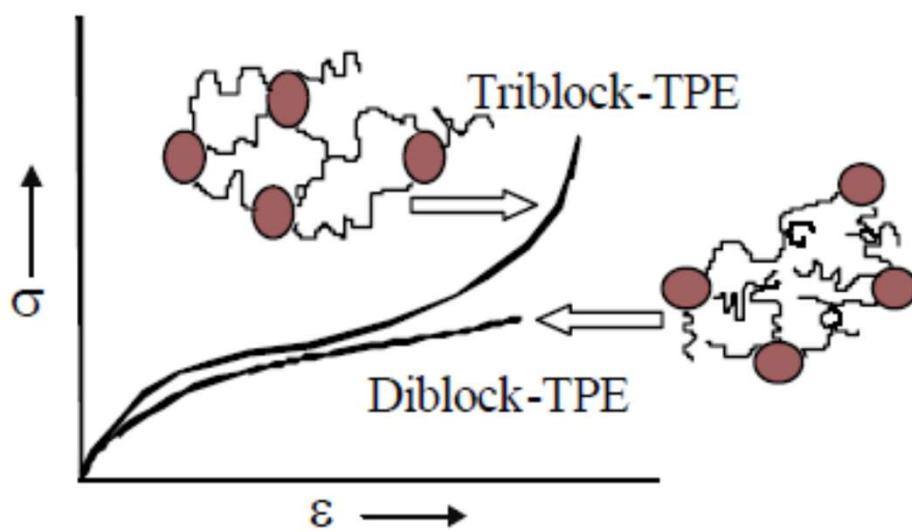


Phase Dependent Mechanical Properties

Styrene – Black Domain – Hard Phase

Butadiene – White Domain – Soft (Rubber) Phase

Elastomers are Derived from a Tri-block Copolymer



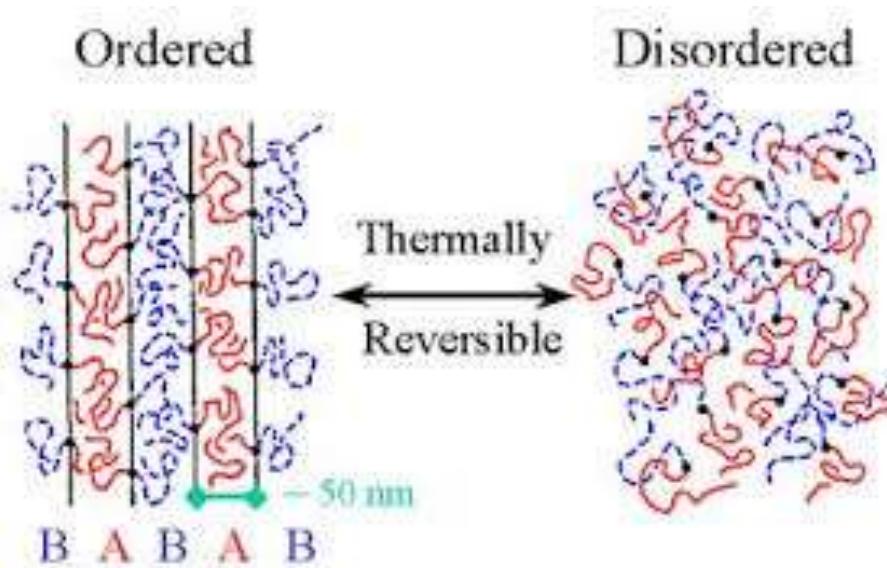
A styrene-butadiene-styrene copolymer defines the morphology of a thermoplastic elastomer.

The styrene segments are the minor component of the S-B-S copolymer and the butadiene segments are the major components.

The styrene components form the rigid spherical domains acting like crosslinks.

The butadiene segments form the elastomeric network.

What defines a Thermoplastic Elastomer?

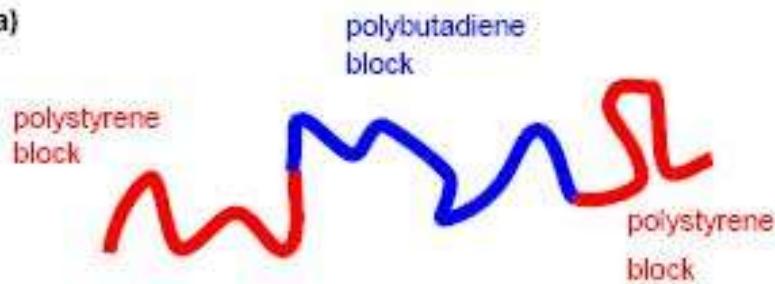


When the temperature is raised above the glass transition temperature of styrene (i.e., 100C) the styrene domains melt allowing the material to Become disordered and flow.

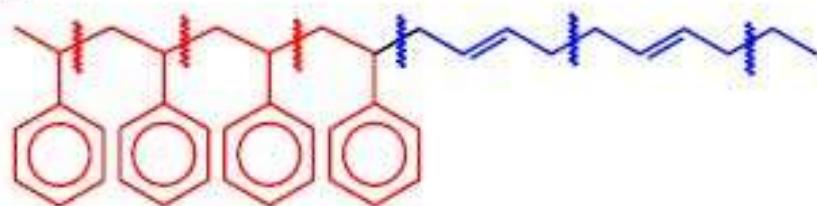
Once this melt is formed into the final form or geometry the material is cooled and the styrene domains are formed imparting the elastomeric properties.

Formation of a TPE by SBS Polymers

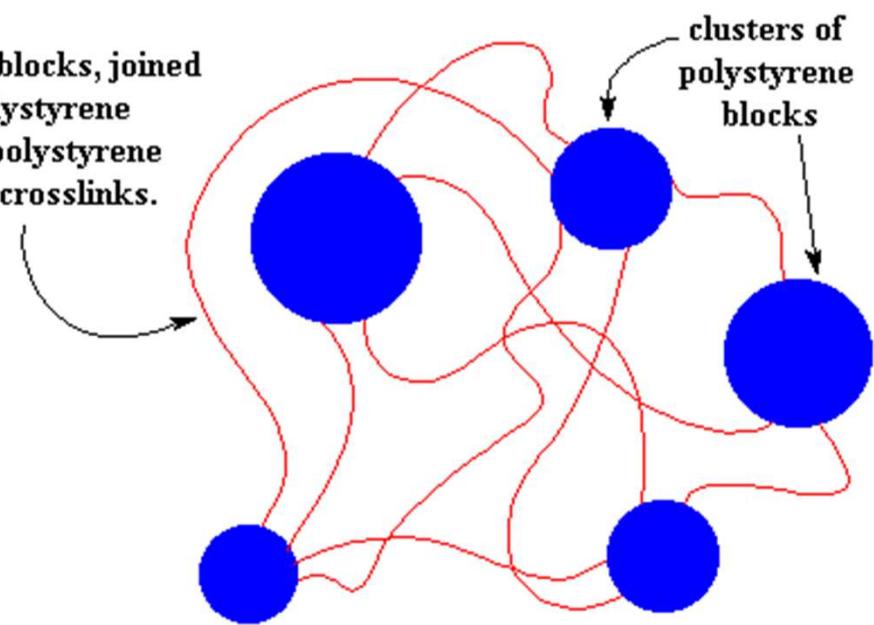
(a)



(b)



Polybutadiene blocks, joined together by polystyrene clusters. The polystyrene clusters act as crosslinks.



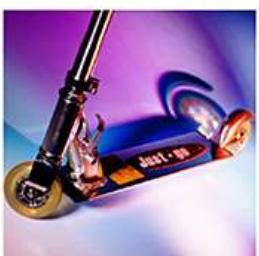
Polystyrene domain morphology is amorphous and glassy.

Comparative Mechanical Properties of Elastomers

	Durometer hardness range	Tensile strength at room temp, psi	Elongation at room temp, %	Temp. range of service °C	Weather resistance
Natural rubber	20–100	1,000–4,000	100–700	–55–80	Fair
Styrene-butadiene rubber (SBR)	40–100	1,000–3,500	100–700	–55–110	Fair
Polybutadiene	30–100	1,000–3,000	100–700	–60–100	Fair
Polyisoprene	20–100	1,000–4,000	100–750	–55–80	Fair
Polychloroprene	20–90	1,000–4,000	100–700	–55–100	Very good
Polyurethane	62–95 A 40–80 D	1,000–8,000	100–700	–70–120	Excellent
Polyisobutylene	30–100	1,000–3,000	100–700	–55–100	Very good

Table 1 Selected properties of some elastomers.

Examples of S-B-S Thermoplastic Elastomer Products



From: Science, Volume 96, Number 2490, Page 10, September 18, 1942

BUTYL RUBBER TIRES

BUTYL rubber tires in actual tests on New Jersey highways have shown a life of 20,000 miles if kept below a maximum of 40 miles an hour, was reported by J. P. Haworth and F. P. Baldwin, of the Esso Laboratories, before the Buffalo meeting of the American Chemical Society.

Possibilities of "tailor-made" rubber for the different parts of a tire were pointed out. In the average light car tire, weighing about 12 pounds, only about four pounds is in the conspicuous part, the tread. Requirements for tread are different from those of side wall, and these in turn differ from those of carcass and inner tube. Synthetic rubbers can be given properties to suit the uses to which they will be put, which is not possible with natural rubber.

Comparative Properties of Elastomers

BUTADIENE BASED RUBBERS

SBR (STYRENE BUTADIENE RUBBER) RUBBER AND POLYBUTADIENE

ADVANTAGES:

SBR provides good abrasion, wear, and tensile qualities. SBR can be readily substituted for NATURAL RUBBER in many applications with significant cost savings. Resilience is about the same as NATURAL RUBBER.

DISADVANTAGES:

Like its natural counterpart, SBR offers little resistance to oils and chemicals. SBR must be specially compounded to provide resistance to ozone, sunlight, and heat.

TYPICAL APPLICATIONS:

Washers, gaskets, grommets.

Comparative Properties of Elastomers

ISOPRENE BASED RUBBERS NATURAL (ISOPRENE) RUBBER AND POLYISOPRENE

ADVANTAGES:

NATURAL RUBBER exhibits high resilience, good tensile strength, and tear resistance. In addition to excellent wear resistance, NATURAL RUBBER also offers low permanent set characteristics plus good flexing qualities at low temperatures.

DISADVANTAGES:

NATURAL RUBBER does not perform well when exposed to chemicals and petroleum derivatives, including petrochemicals. It is not recommended for outdoor applications where maximum resistance to sunlight, ozone, oxygen or heat aging is major factors.

TYPICAL APPLICATIONS: Boots, belts, bumpers, tubing.

Comparative Properties of Elastomers

NEOPRENE® (POLYCHLOROPRENE) RUBBER

ADVANTAGES:

NEOPRENE® is resistant to ozone, sunlight, oxidation and many petroleum derivatives. Added advantages include good resistance to water, many chemicals, good resilience characteristics and high tensile strength properties.

DISADVANTAGES:

NEOPRENE® has few practical limitations. While NEOPRENE® is slightly higher in price than general purpose synthetic rubbers, its resistance to ozone, oil and chemicals make it cost effective in many applications. It is generally attacked by strong oxidizing acids, esters, ketones, chlorinated, aromatic and nitro hydrocarbons.

TYPICAL APPLICATIONS:

Plumbing fixtures; gaskets; hose; mechanical seals; mechanical belts; solid rocket propellant; garden hose; inner tubes; laboratory tubing.

Polyisobutylene

What does this elastomer have to do with baseball, Wrigley Field, or Chicago?



Polyisobutylene

What does it have to do with motor oil?



Polyisobutylene

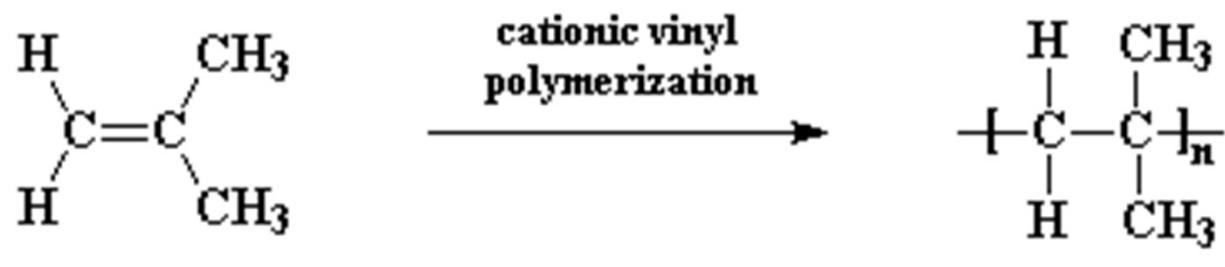
Polyisobutylene is a major component of chewing gum.

The Wrigley Company is a major purchaser of this elastomer.



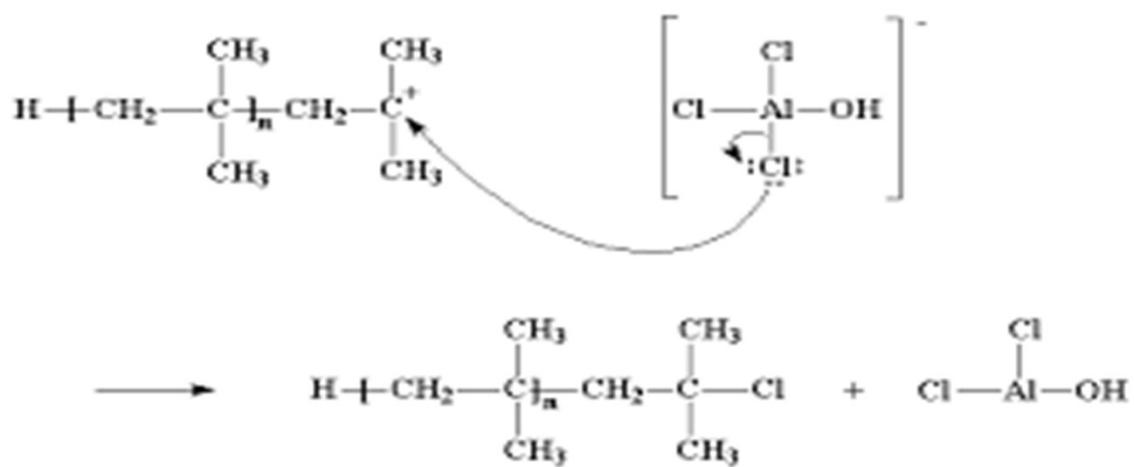
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Polyisobutylene (PIB)

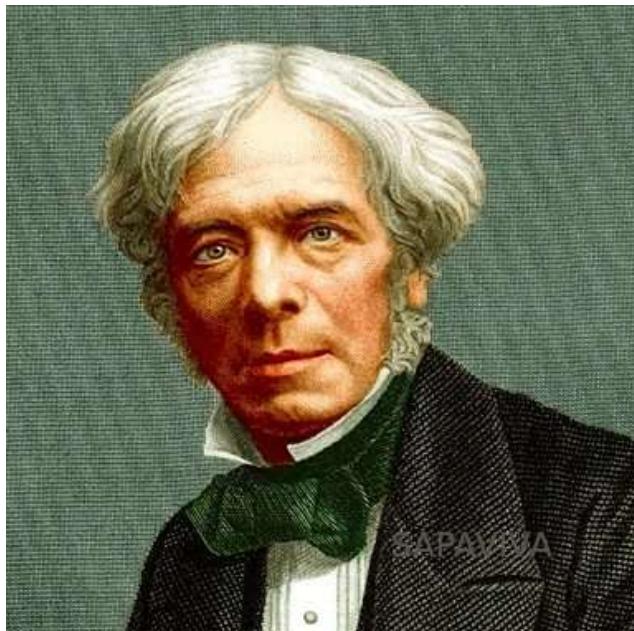


isobutylene

polyisobutylene



Polyisobutylene



Isobutylene was discovered by Michael Faraday in 1825.

Polyisobutylene (PIB) was first developed by the BASF unit of IG Farben in 1931 using a boron trifluoride catalyst at low temperatures.

PIB remains a core business for BASF to this day.

PIB homopolymers of high molecular weight (100,000–400,000) are polyolefin elastomers: tough extensible rubber-like materials over a wide temperature range; with low density (0.913–0.920), low permeability and excellent electrical properties.

Polyisobutylene and Butyl Rubber

Polyisobutylene is 100% isobutylene monomer.

Butyl Rubber is 98% isobutylene and 2% isoprene.

PIB was developed into butyl rubber in 1937, by researchers William J. Sparks and Robert M. Thomas, at Standard Oil of New Jersey's Linden, N.J., laboratory. Today, the majority of the global supply of butyl rubber is produced by two companies, ExxonMobil (one of the descendants of Standard Oil) and Polymer Corporation, a Canadian federal crown corporation established in 1942.

Properties and Applications

Butyl rubber (IIR) is the copolymer of isobutylene and a small amount of isoprene. First commercialized in 1943, the primary attributes of butyl rubber are excellent impermeability/air retention and good flex properties, resulting from low levels of unsaturation between long polyisobutylene segments. Tire innertubes were the first major use of butyl rubber, and this continues to be a significant market today.

Polyisobutylene/Butyl Rubber

Butyl rubber is impermeable to air and used in many applications requiring an airtight rubber.

The first major application of butyl rubber was tire inner tubes.

This remains an important segment of its market even today in addition to other similar applications.



Polyisobutylene and Butyl Rubber Uses

- the manufacture of adhesives,
- agricultural chemicals,
- fiber optic compounds,
- ball bladders (i.e., basketball, football, soccer, etc.) ,
- O-rings,
- caulk and sealants,
- cling film,
- electrical fluids,
- lubricants (2 stroke engine oil) paper and pulp,
- personal care products,
- pigment concentrates,
- for rubber and polymer modification,
- for protecting and sealing certain equipment for use in areas where chemical contamination is present,
- as a gasoline/diesel fuel additive.

And, also in chewing gum!



Polyisobutylene in Chewing Gum

Composition of Chewing Gum

	<u>Weight Percent</u>
Isobutylene-Isoprene L polymer	8.82%
Polyisobutylene	20.15%
Hydrogenated Vegetable Oil	36.83%
Hydroxylated Lecithin	3.60%
Calcium Carbonate	10.20%
Polyvinyl Acetate	16.20%
Glyceryl Monostearate	1.70%
Glyceryl Ester of Partially Hydrogenated Wood Rosin	2.50%

Polyisobutylene in Chewing Gum

Most modern chewing gum uses food-grade butyl rubber as the central gum base, which contributes not only the gum's elasticity but an obstinate, sticky quality which has led some municipalities to propose taxation to cover costs of its removal.

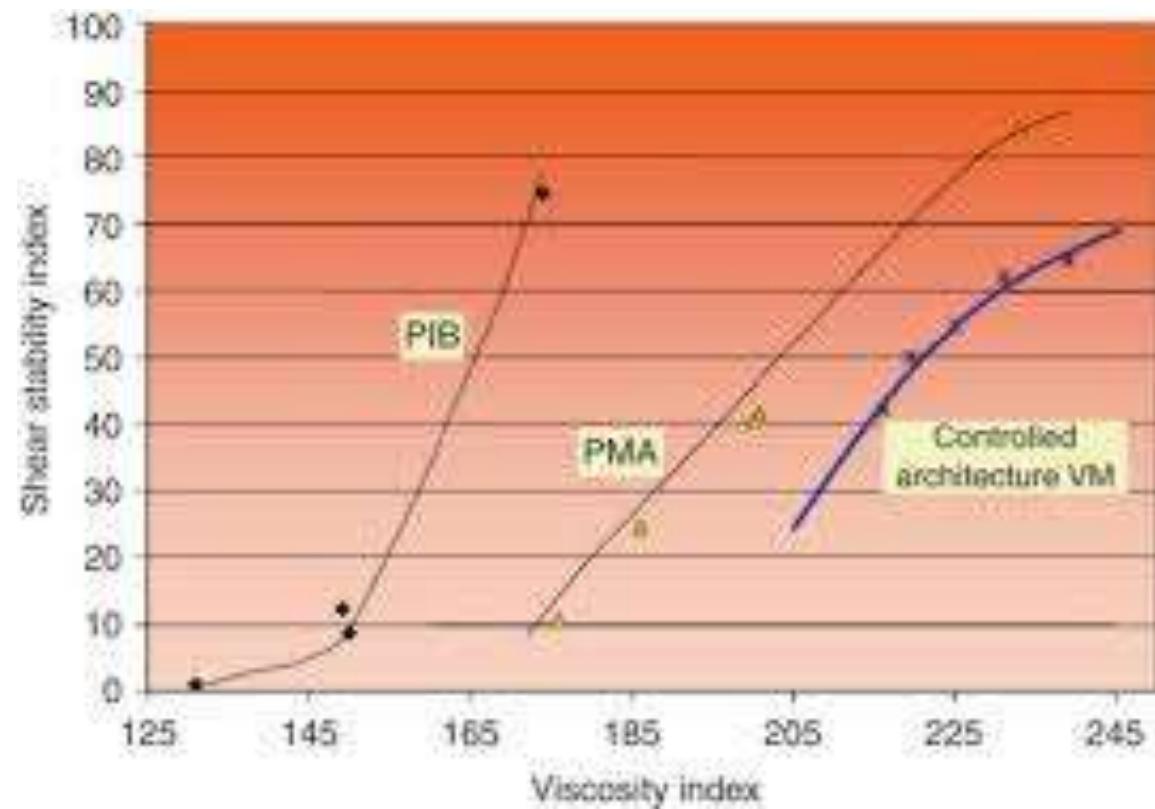
Recycled chewing gum has also been used as a source of recovered polyisobutylene. Amongst other products, this base rubber has been manufactured into coffee cups and 'Gumdrop' gum-collecting bins. When filled, the collecting bins and their contents are shredded together and recycled again.



Gumdrop bin made from polyisobutylene for recycling polyisobutylene.

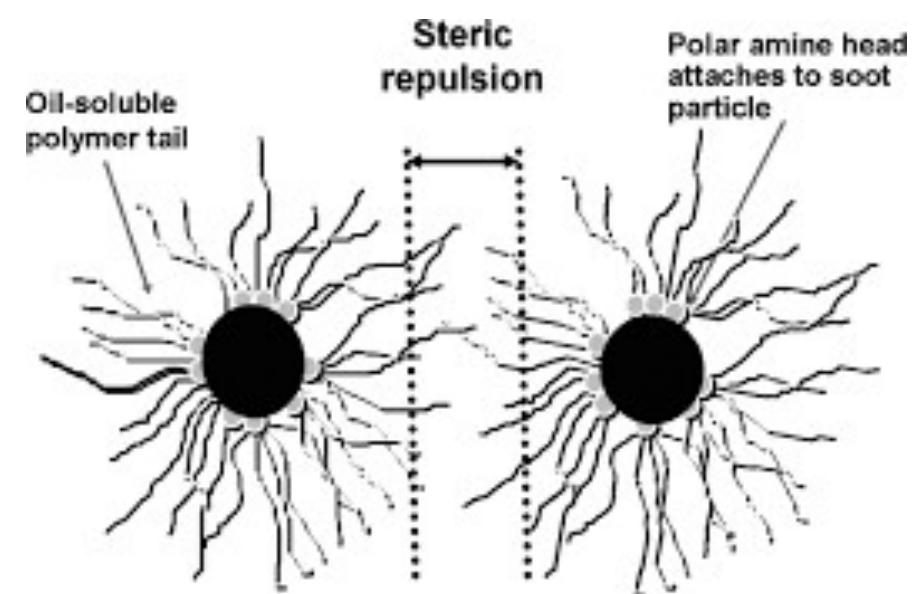
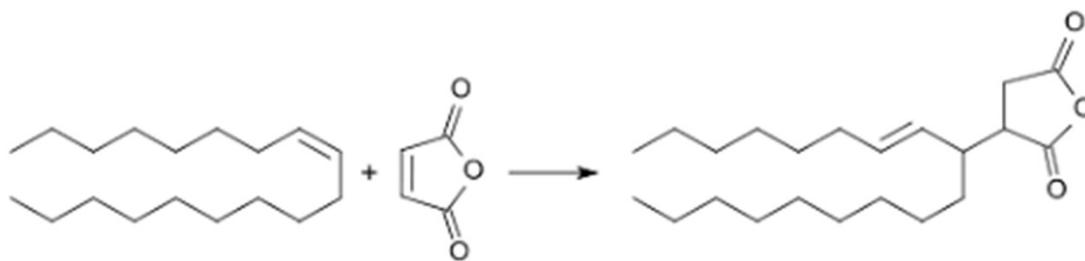
Polyisobutylene is a Major Component in Engine Oils as a Viscosity Modifier

base-oil-containing lubricant	
highly-reactive polyisobutene (1200-1600 mm ² /s [100°C], Mn 2000 to 2500 g/mol, GPC)	15-30 wt%
ester	7-13 wt%
additive component	2-6 wt%
base oil	45-60 wt%
antioxidant	0.5-2 wt%



Polyisobutylene(Succinic Anhydride) - PIBSA

Alkenyl succinic anhydrides (ASA) are modified five-membered succinic anhydrides bearing a branched iso-alkenyl chain (C_{14} to C_{22}):



Carbon polymer tails maintain separation between particles

Polyisobutylene Succinic Anhydride - PIBSA

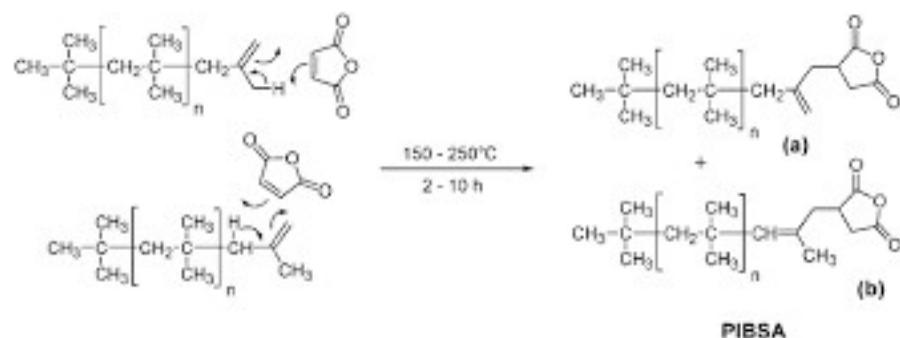
Polyisobutylene succinimides (PIBSA) are used to make dispersants that are used in tailor-made formulations to meet the challenging demands of engine oils.

Polyisobutylene succinimides are critical engine oil additives that keep engines clean by dispersing harmful debris generated during operation that can thicken the oil, and cause wear.

They reduce the formation of deposits on metal surfaces and inhibit soot agglomeration via stable micelle formation.

Their dispersant action helps keep small particles suspended so that they can be removed by the oil filter and not build up in the engine.

Lubrizol (Wickliffe, OH) is a leading manufacturer of PIBSA in the world.



Comparative Mechanical Properties of Elastomers

	Durometer hardness range	Tensile strength at room temp, psi	Elongation at room temp, %	Temp. range of service °C	Weather resistance
Natural rubber	20–100	1,000–4,000	100–700	–55–80	Fair
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Polyisoprene	20–100	1,000–4,000	100–750	–55–80	Fair
Polychloroprene	20–90	1,000–4,000	100–700	–55–100	Very good
Polyurethane	62–95 A 40–80 D	1,000–8,000	100–700	–70–120	Excellent
Polyisobutylene	30–100	1,000–3,000	100–700	–55–100	Very good

Table 1 Selected properties of some elastomers.

Polydimethylsiloxane

What does a B-29: Superfortress have to do with this polymer?



First Flight: December 30, 1942

Production of First Operational
Planes: April 15, 1944

Produced: 1945 – 1955(?)

Number Build: <4,000

Speed: 220 – 365 mph

Range: 5800 miles

Altitude: >32,000 feet

Load: 20,000 lbs

Polydimethylsiloxane

What does a B-29: Superfortress have to do with this polymer?

Answer: A lot!



First Flight: December 30, 1942

Production of First Operational Planes: April 15, 1944

Produced: 1945 – 1955(?)

Number Build: <4,000

Speed: 220 – 365 mph

Range: 5800 miles

Altitude: >32,000 feet

Load: 20,000 lbs

NOTE: The IX Center in Cleveland, OH was one of the initial manufacturing facilities for the B-29.

Polydimethylsiloxane

The B-29 Superfortress was a “state-of-the-art” airplane having a pressurized cabin for high altitude flight and the first ever rudimentary (computer) controlled fire control system.

The load capacity of the B-29 over two-times that of the B-17 requiring high performance state-of-the-art radial piston engines.

The period between December 1942 and April 1944 was a period of developmental problems and the need for necessary resolutions to these problems.

One major problem identified during this period was the limitations of the hydrocarbon-based oils, lubricants and gaskets in the high horsepower, high altitude engines.

These problems required a new material.

Polydimethylsiloxane



Polymer Chemistry



Silicone Chemistry



Silicone Based Oils and Polymers

The Dow Corning Corporation was formally established in 1943 as a joint venture between the American conglomerates The Dow Chemical Company and The Corning Glass Company to explore the potential of silicone based lubricants and polymers.

The Dow Corning Corporation was a manufacturer of products for use by the U.S. military in World War II. The company began operating its first plant, in Midland, MI, in 1945.

Polydimethylsiloxane

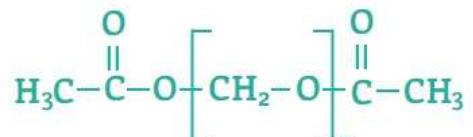
Why silicone based materials – Similarity to carbon in the periodic table – But Heavier.

elements

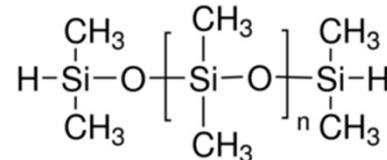
13	14	15	16	17	18	
5 B boron 10.81 [10.805, 10.821]	6 C carbon 12.011 [12.009, 12.012]	7 N nitrogen 14.007 [14.006, 14.008]	8 O oxygen 15.999 [15.999, 16.000]	9 F fluorine 18.998 [18.998]	2 He helium 4.0026	
12	13 Al aluminium 26.982 [26.981, 26.983]	14 Si silicon 28.085 [28.084, 28.086]	15 P phosphorus 30.974 [30.959, 32.076]	16 S sulfur 32.06 [32.059, 32.076]	17 Cl chlorine 35.45 [35.446, 35.457]	18 Ar argon 39.95 [39.952, 39.953]
30 Zn zinc 65.38(2) [65.38, 65.39]	31 Ga gallium 69.723 [69.72, 69.725]	32 Ge germanium 72.630(8) [72.63, 72.631]	33 As arsenic 74.922 [74.92, 74.923]	34 Se selenium 78.971(8) [78.97, 78.972]	35 Br bromine 79.904 [79.901, 79.907]	36 Kr krypton 83.798(2) [83.798, 83.799]
48 Cd cadmium 112.41 [112.41, 112.42]	49 In indium 114.82 [114.82, 114.83]	50 Sn tin 118.71 [118.71, 118.72]	51 Sb antimony 121.76 [121.76, 121.77]	52 Te tellurium 127.60(3) [127.6, 127.61]	53 I iodine 126.90 [126.9, 126.91]	54 Xe xenon 131.29 [131.29, 131.30]
80 Hg	81 Tl	82 Dy	83 Ri	84 Pa	85 At	86 Rn

Carbon and silicon share many characteristics. Each has a so-called valence of four--meaning that individual atoms make four bonds with other elements in forming chemical compounds. Each element bonds to oxygen. Each forms long chains, called polymers, in which it alternates with oxygen. **Silicon yields polymeric silicones, which we use to waterproof cloth or lubricate metal and plastic parts.**

Polydimethylsiloxane

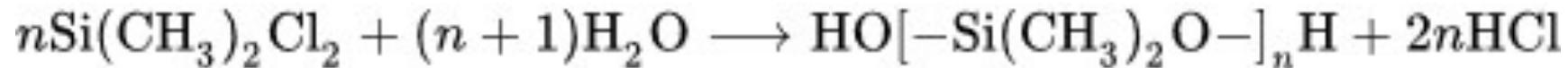


Polyoxymethylene

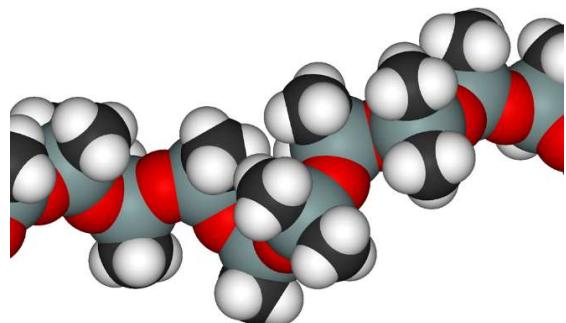


Polydimethylsiloxane

Industrial synthesis can begin from dimethyldichlorosilane and water by the following net reaction:



The polymerization reaction evolves [hydrochloric acid](#).



Reasons why Silicon is not used as the base of life are:

- Reactions of Silicon are much slower than reactions of Carbon.
- Bonds between Si and Si or between Si and H are not as stable as the bond between C and H.
- Molecules based on Si and H are not very stable in presence of water.

Comparison of Silicone Oil with Other Base Oils

	MINERAL OIL	PHOSPHATE ESTER	POLYGLYCOL	POLYESTER	DIESTER	PERFLUOROPOLYETHER	SILICONE	POLYALPHOLEFIN
Cost	L	VH	M	M	M	VH	H	M
Seal compatibility	AA	BA	A	BA	BA	AA	AA	AA
Compatible with mineral oil	-	BA	BA	A	A	BA	BA	E
Corrosion stability	E	AA	A	BA	BA	BA	A	E
Oxidation stability	BA	AA	AA	AA	A	E	E	AA
Viscosity range	AA	BA	A	BA	BA	A	A	A
Flash point	M	E	A	AA	A	E	E	AA
Pour point	A	AA	M	L	L	L	VL	L
Temperature range	BA	A	A	AA	A	E	E	AA

KEY	
E	EXCEPTIONAL
AA	ABOVE AVERAGE OR VERY GOOD
A	AVERAGE OR GOOD
BA	BELOW AVERAGE OR LESS THAN IDEAL
VL	VERY LOW
L	LOW
M	MEDIUM
H	HIGH
VH	VERY HIGH
NA	NOT AVAILABLE

Patent Competition Regarding PDMS 1947 (1951?)

Patented Dec. 2, 1947

2,431,878

UNITED STATES PATENT OFFICE

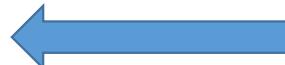
2,431,878

TREATING DIMETHYL SILICONE POLYMER WITH BORIC OXIDE

Rob Roy McGregor, Verona, and Earl Leathen Warrick, Pittsburgh, Pa., assignors to Corning Glass Works, Corning, N. Y., a corporation of New York

Treating Dimethyl Silicone with Boric Oxide

Rob Roy McGregor and
Earl Leathen Warrick



Patented Feb. 13, 1951

2,541,851

UNITED STATES PATENT OFFICE

2,541,851

PROCESS FOR MAKING PUTTYLIKE ELASTIC PLASTIC, SILOXANE DERIVATIVE COMPO- SITION CONTAINING ZINC HYDROXIDE

James G. E. Wright, Schenectady, N. Y., assignor
to General Electric Company, a corporation of
New York

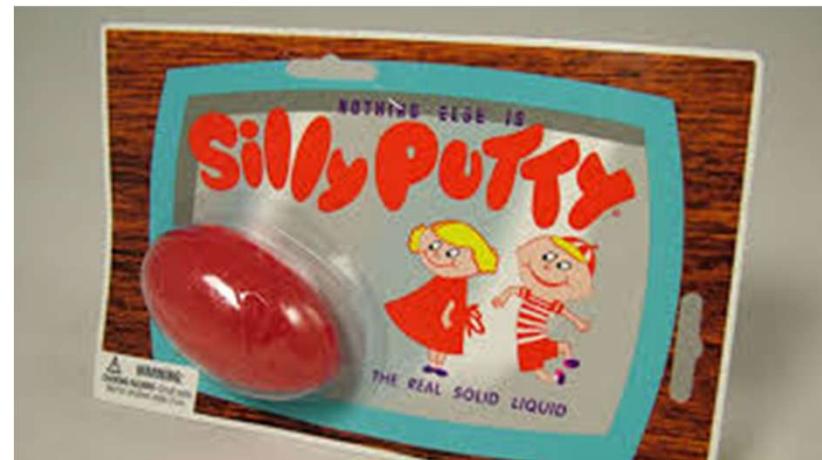
James G.E. Wright



Process for Making Putty-Like Plastic, Siloxane Derivative
Composition Containing Zinc Hydroxide

Silly Putty is Made from PDMS

Composition	Weight percentage
PDMS	65%
Silica	17%
Thixotrol	9%
Boric acid	4%
Glycerine	1%
Titanium dioxide	1%
Dimethyl cyclosiloxane	1%



Among a lot of other things, Silly Putty makes a great fire starter as it burns fairly easily and slowly, as well as gets white hot.

Hodgson developed and marketed Silly Putty. By the time of his death in 1976, Hodgson's net worth was around \$140 million.

Interestingly, Silly Putty dissolves in alcohol. Because of this, alcohol-based hand sanitizer is often the best way to get the putty out of hair or clothing.



Cross-linking of Polydimethylsiloxane to form an Elastomer

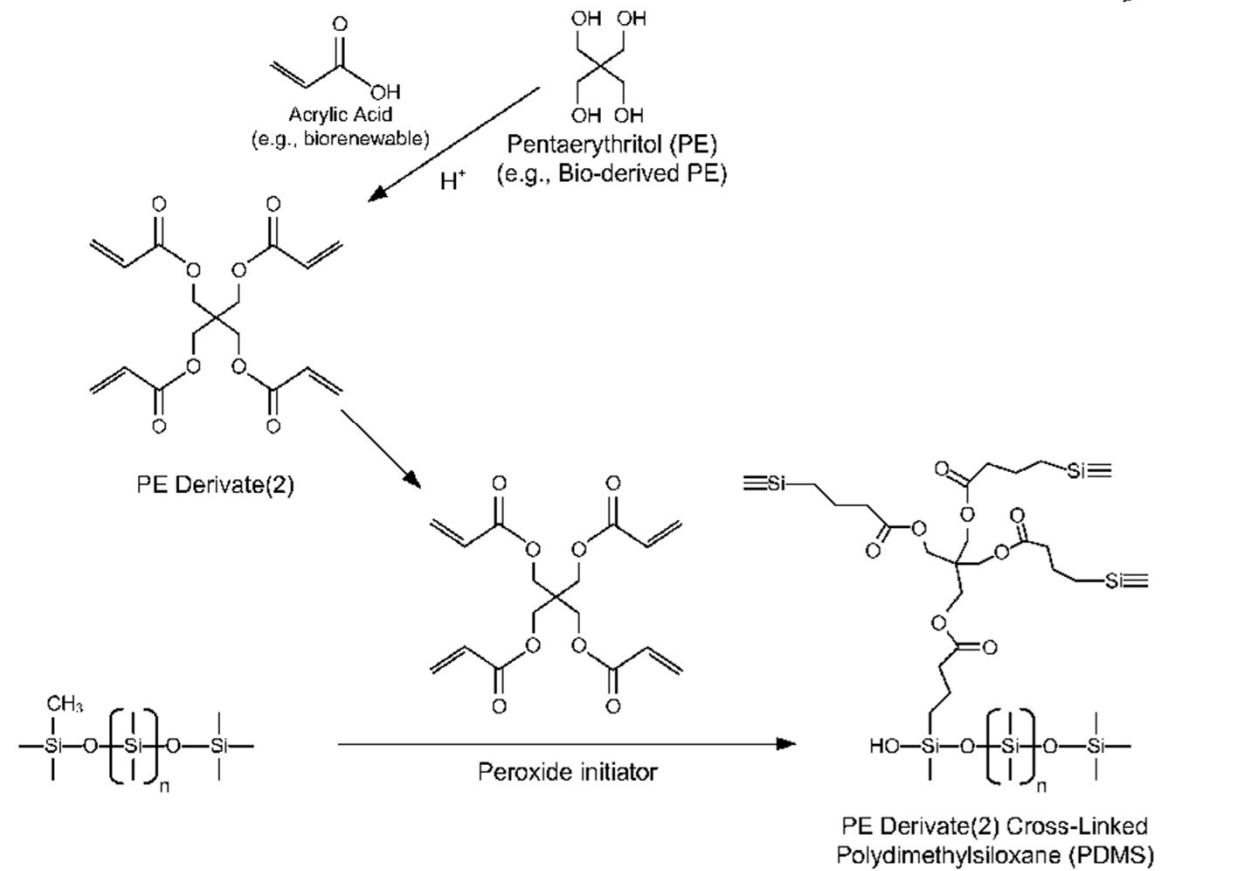
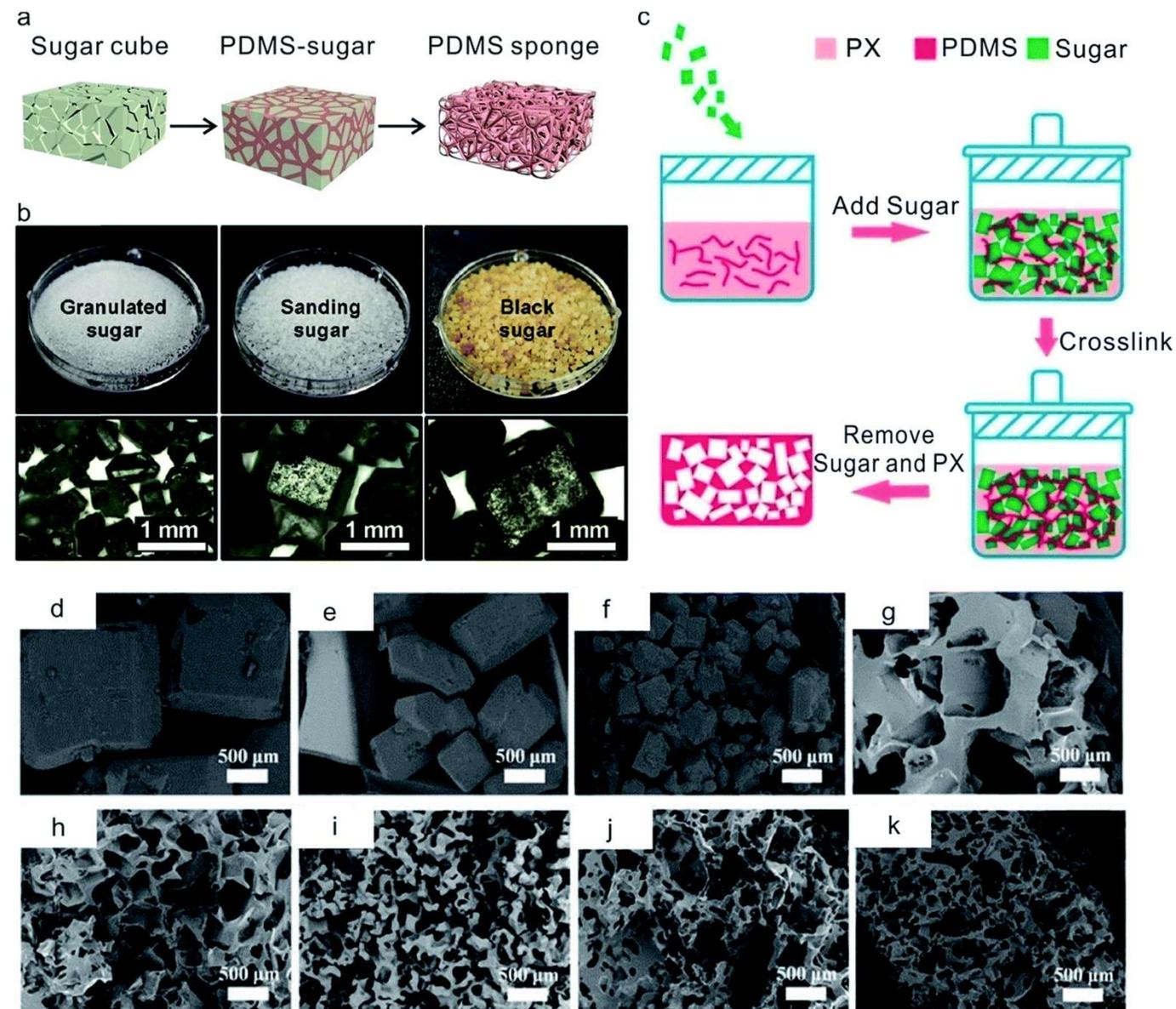
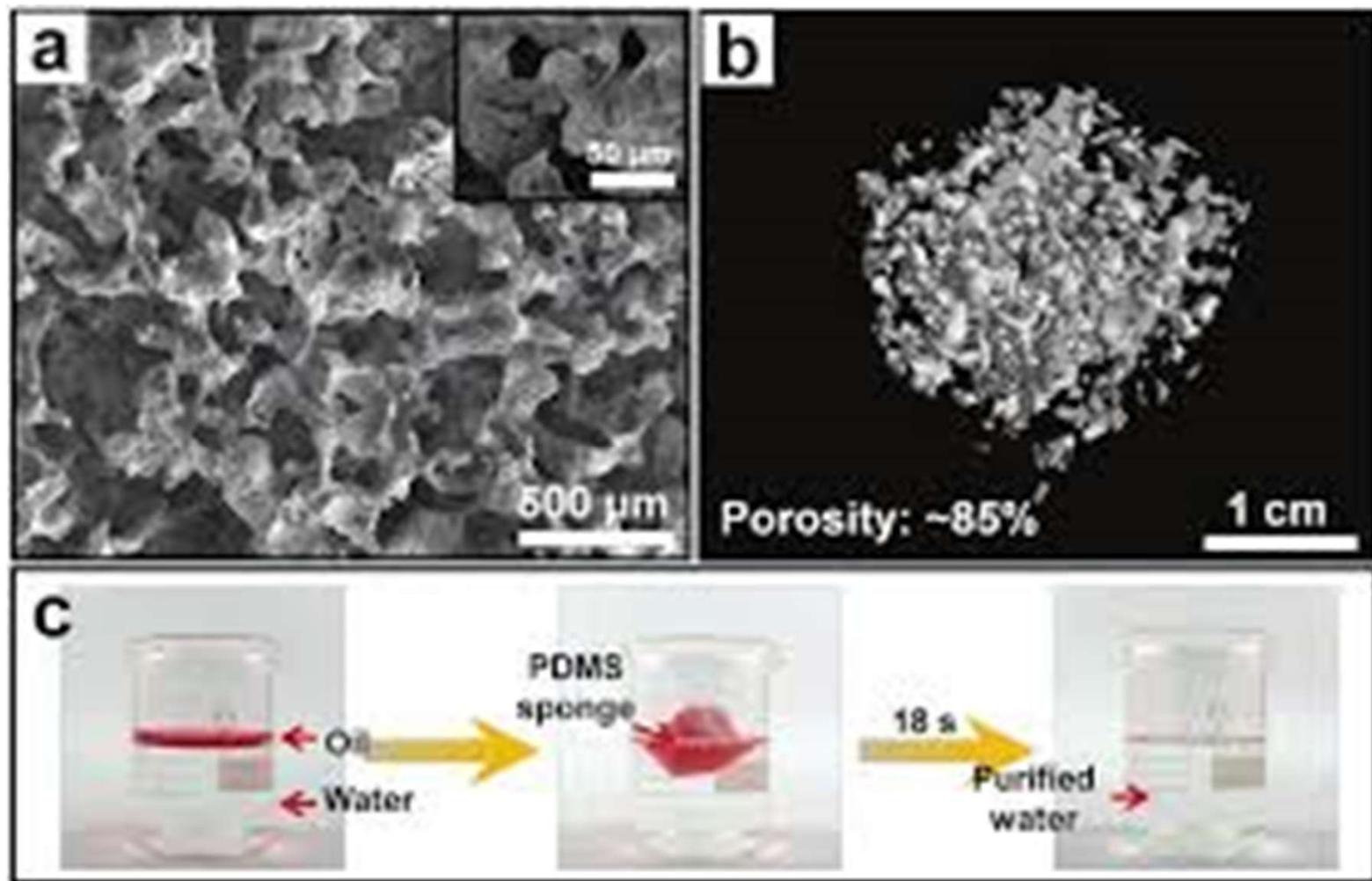


FIG. 4

Production of a PDMS Foam by using a Sugar Cube Template



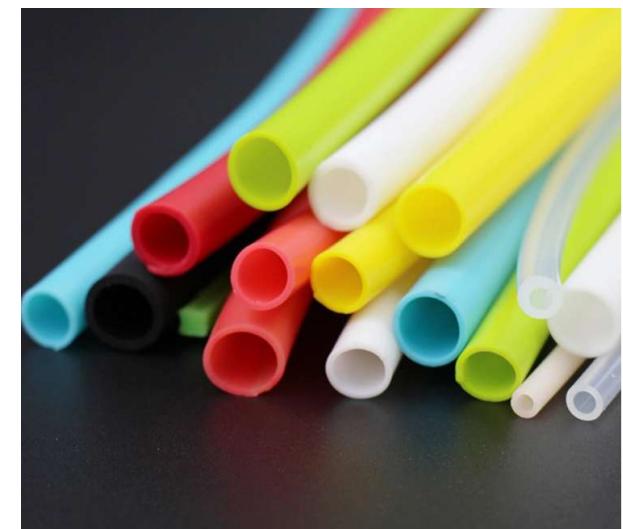
Oil Adsorption by a Crosslinked PDMS Sponge



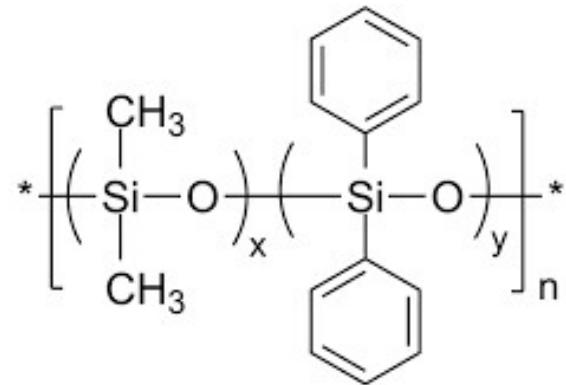
Properties of Silicone Rubber

40 Duro Red Silicone Rubber	Physical Properties
Color	Red
Durometer Hardness Shore A (± 5)	40 ($+/- 5$)
Service Temperature Limits (°F)	-80°F to 450°F
Tensile Strength - ASTM D412 (psi)	600 psi
Ultimate Elongation - ASTM D412 (%)	400%
Specific Gravity - ASTM D297 (g/cc)	1.25 g/cc
Available Widths (inches)	36" & 48"
Available Thicknesses (inches)	1/16" to 1"

Uses of Polydimethylsiloxane – Silicone Rubber



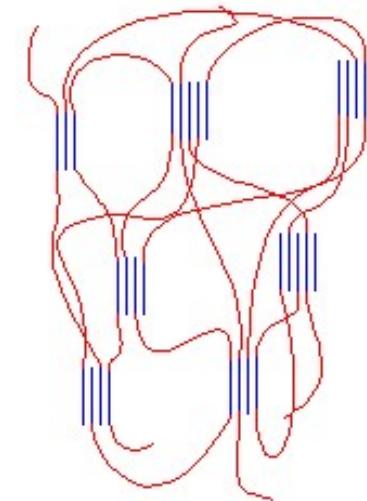
Tri Block Copolymer of Poly(diphenyl-co-dimethyl-co-diphenyl) Siloxane



Polydimethylsiloxane is an amorphous rubbery material.

Polydiphenylsiloxane is a semicrystalline polymer.

When polymerized the morphology of these tri-block copolymers will be similar to the domain morphology exhibited by styrene-butadiene-styrene tri-block copolymers.



Polydiphenylsiloxane domain morphology is semicrystalline.

Lecture 17: Continuation of Elastomers

Part 1: SBR (Cont'd)

Part 2: Polyisobutylene

Part 3: Polydimethylsiloxane

Questions?



Dr. Andy Olah, amo5@case.edu, C: 216-272-0505

"I just asked myself if I was crazy and we all said 'No'"

<https://www.bbc.com/future/article/20210308-rubber-the-wonder-material-we-are-running-out-of>

EMAC 276

Lecture 10 : The Polyolefin Family

Polyethylene – PE: Part 2: LDPE and HDPE

Polypropylene - PP

Poly(1-butene) – Polybutylene – PB

Andy Olah, Ph.D.

February 12, 2025

EMAC 276 - Homework Assignment #2

Due: Friday, February 14, 2025

Dr. Olah

During our classes we identified several common polymers that when initially discovered were described as “value-less”, “impossible to process”, “a useless mass”, etc. We also identified several methods (“tricks”) that were subsequently utilized to develop these polymers into successful products; many which are still with us today.

Your exercise is to select one polymer (either from our in-class discussion or from outside our class discussion) and describe 1) the polymer and the initial performance deficiency, 2) the action taken to overcome this deficiency, and, 3) the ensuing product(s) developed from this modification.

If you choose to use an “in class” example your maximum score will be 10.

If you choose to use an “outside the class” example your maximum score will be 12. (i.e., final score +2)

Your answer shall be short comprising between one-half to one page.

Your answer is shall be structured accordingly:

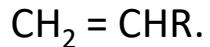
Paragraph #1: Identify and describe the polymer and it's initial deficiency **(3 Points)**

Paragraph #2: Identify the modification or “trick” which was utilized to overcome this deficiency. **(5 Points)**

Paragraph #3: Identify the commercial product or products resulting from this modification. **(2 Points)**

What is a “Olefin” Type Polymer?

Vinyl polymers are the most common type of polymers derived from “vinyl-type” monomers having the general structure:



Where,

polystyrene – R = C₆H₅

polyvinyl chloride – R = Cl

polyvinyl acetate – R = O₂CCH₃

polyacrylonitrile - R = CN

Not to be confused with poly(vinyl chloride) (PVC) materials which have traditionally been identified as “Vinyls”; i.e., vinyl siding, vinyl records, etc.

Olefin polymers are a subgroup of vinyl monomers produced from alkenes having a C_nH_{2n} monomer structure:

polyethylene – R = H => CH₂ = CH₂; (n = 2) => C₂H₄

polypropylene – R = CH₃ => CH₂ = CH-CH₃; (n = 3) => C₃H₆

polybutylene – R = CH₂-CH₃ => CH₂ = CH-CH₂-CH₃; (n=4) => C₄H₈

GLASSY TRANSITIONS IN SEMICRYSTALLINE POLYMERS

RAYMOND F. BOYER

*The Dow Chemical Company, Midland, Michigan 48640**

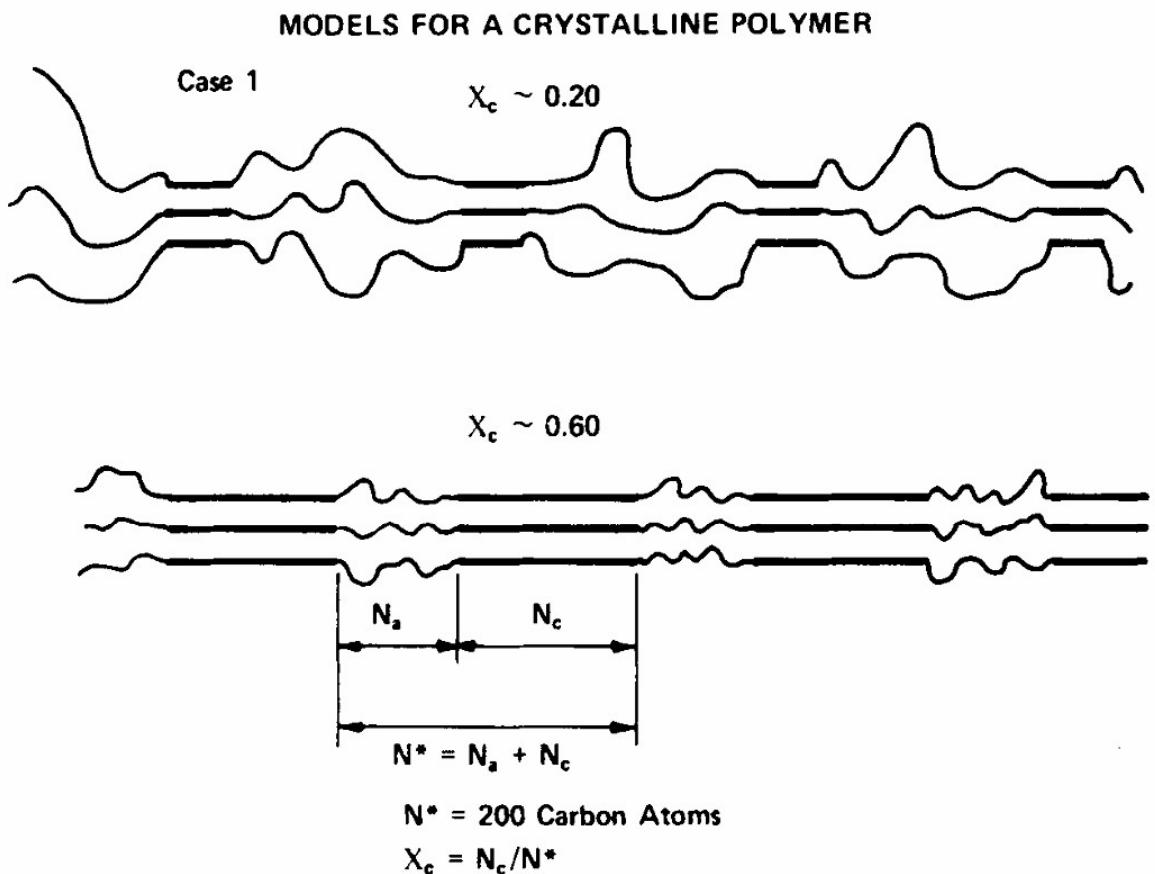


FIG. 13. Fringed micelle model used for calculating effect of crystallinity, x_c , on the intensity of T_g and $T < T_g$ peaks. N_a and N_c are the number of chain atoms in the amorphous and crystalline regions respectively. Very high mol wt is assumed.

Critical Properties for the Differentiation of the Polyethylene Types

Density

Crystalline Region

Perfect 1.00 g/cm³

Unit Cell Calculation (orthorhombic) 0.996

Single Crystal Determination 0.972

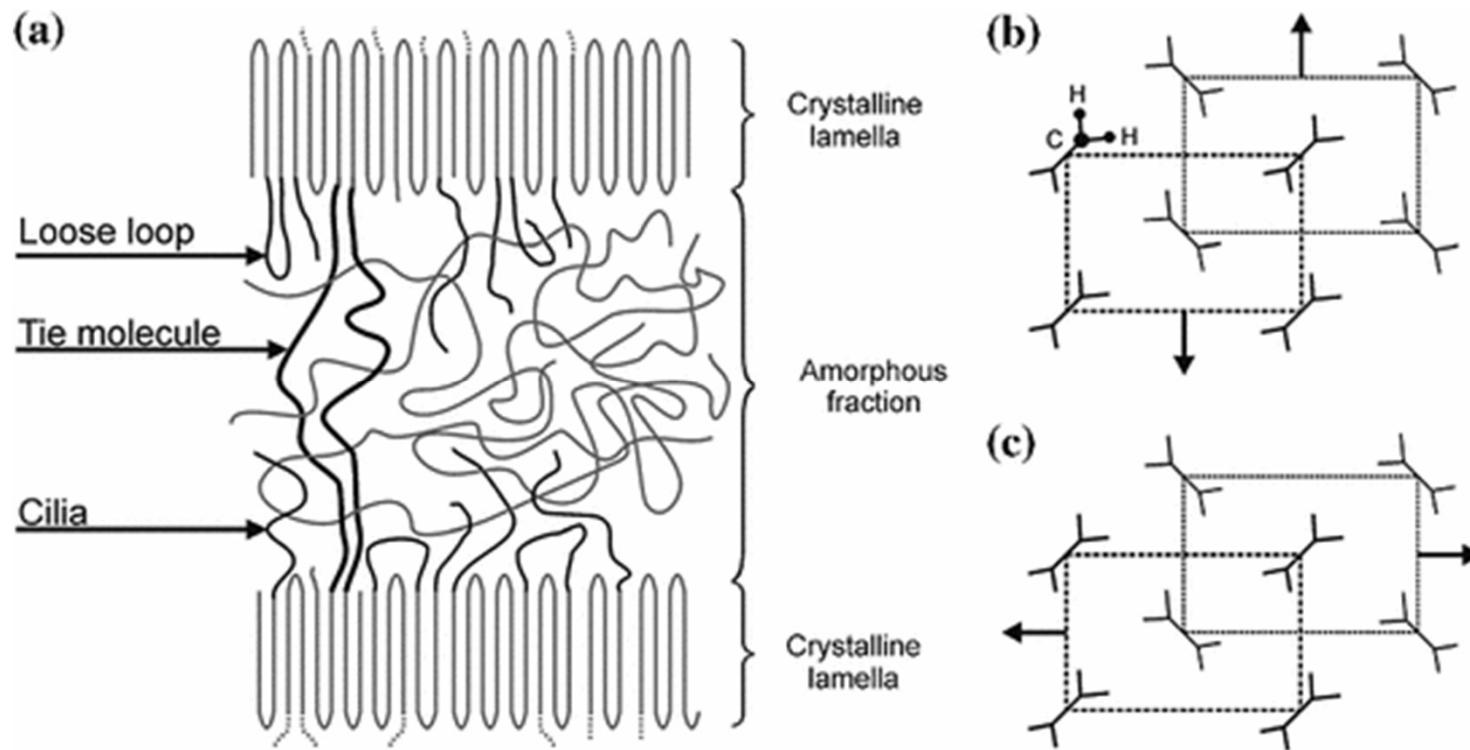
Amorphous Region 0.850 – 0.855

Transition Temperatures

Glass Transition Temperature **-78 C (195 K)**

Melt Transition Temperature (density dependent) 130-140 C

The Interlamellar and Interspherulitic Regions are the Amorphous Regions of Polyethylene



Boyer proposed that there exists two glass transition temperatures for polyethylene.

Glass Temperatures of Polyethylene

Raymond F. Boyer

The Dow Chemical Company, Midland, Michigan 48640. Received July 3, 1972

Macromolecules, 6, 288 – 299 (1973)

J. Poly., Sci., Symposium No. 50, 189 – 242 (1975)

"Linear and branched polyethylenes, especially in the Range of 50 – 75% crystallinity,, exhibit three amorphous Phase transitions or relaxation phenomena at the following temperature regions: 145 ± 10 K (-128 ± 10 C), 195 ± 10 K (-78 ± 10 C) and 240 ± 20 K (-33 ± 20 C)."

"Each of these regions has one or more characteristics of a true glass transition, i.e., an abrupt increase in the Coefficient of thermal expansion, and an abrupt increase in the specific heat; a dynamic mechanical loss peak Whose magnitude increases with amorphous content; . . ."

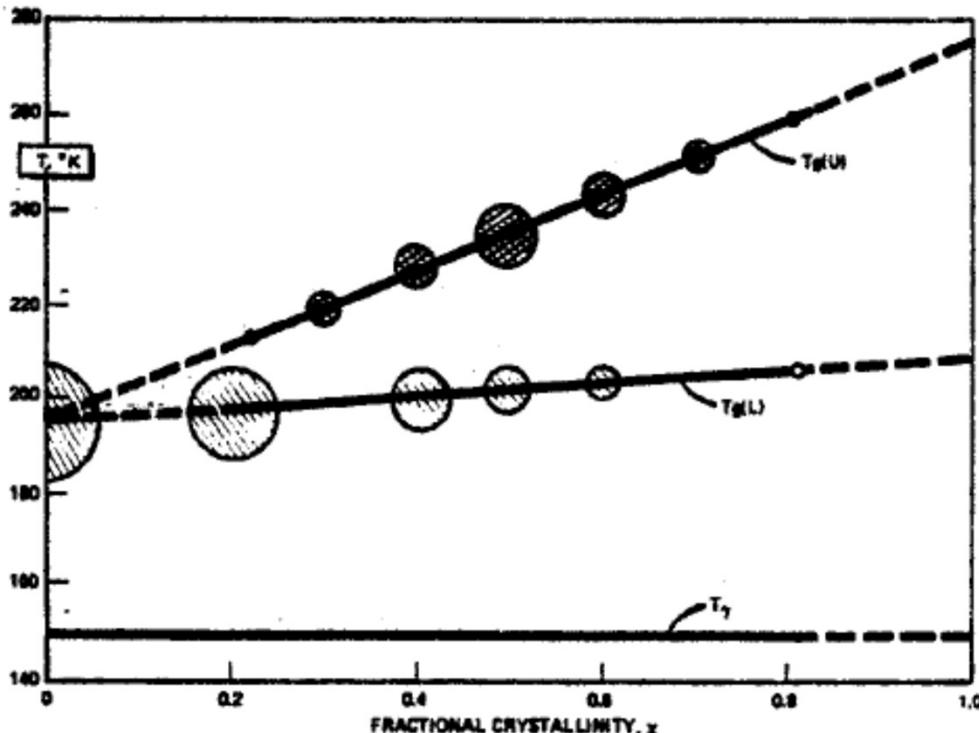


Figure 1. The double glass transition, $T_g(L)$ and $T_g(U)$, and the T_γ amorphous relaxation in linear polyethylene. The size of the circles indicate the intensity of the two glass transitions. Intensity of the T_γ transition increases continuously to the left. We associate $T_g(L)$ with cilia and polymer chains rejected by crystallites; and $T_g(U)$ with loose loops and/or tie molecules. This plot has been estimated by us from the thermal expansion data of Stehling and Mandelkern.²

Proposed Origin of $T_g(L)$ and $T_g(U)$

(4) Partially crystalline polyethylenes exhibit two glass transitions: a $T_g(L)$ around 195 K (-78 C) and a $T_g(U)$ around 240 K (-33 C) but both increase linearly with crystallinity. (5) These are ascribed to the existence of two types of amorphous material. For example, $T_g(L)$ may be associated with cilia and $T_g(U)$ may arise from loose loops and or tie molecules.

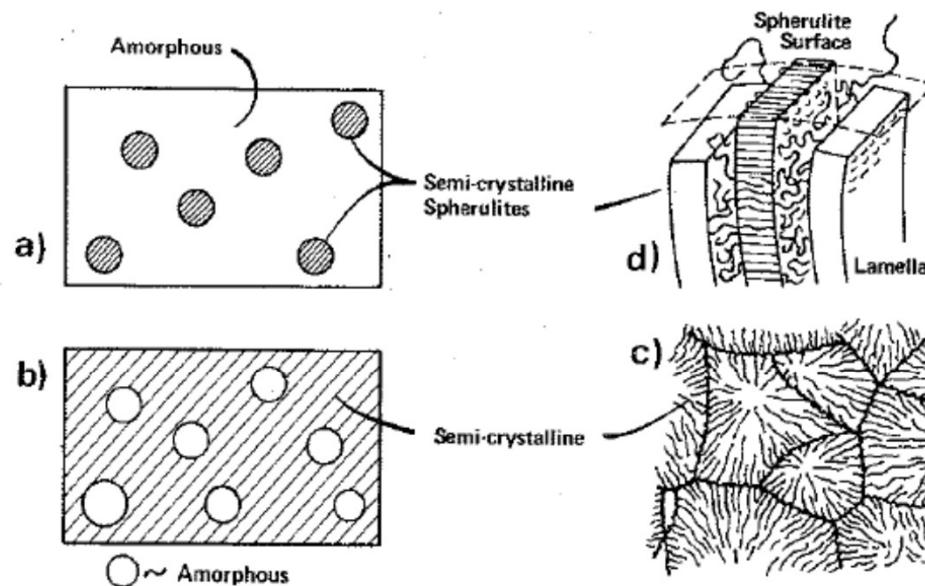


FIG. 9. Schematic morphology for the existence of a double glass transition. (a) isolated spherulites in continuous amorphous phase of $T_g = T_g(L)$; (b) rejected amorphous material of $T_g(L)$ at high x_c , actually appearing in grain boundaries as at (c); (d) Takayanagi model [34] showing interlamellar disorganized, or amorphous, material which may give rise to $T_g(U)$.

GLASSY TRANSITIONS IN SEMICRYSTALLINE POLYMERS

RAYMOND F. BOYER

*The Dow Chemical Company, Midland, Michigan 48640**

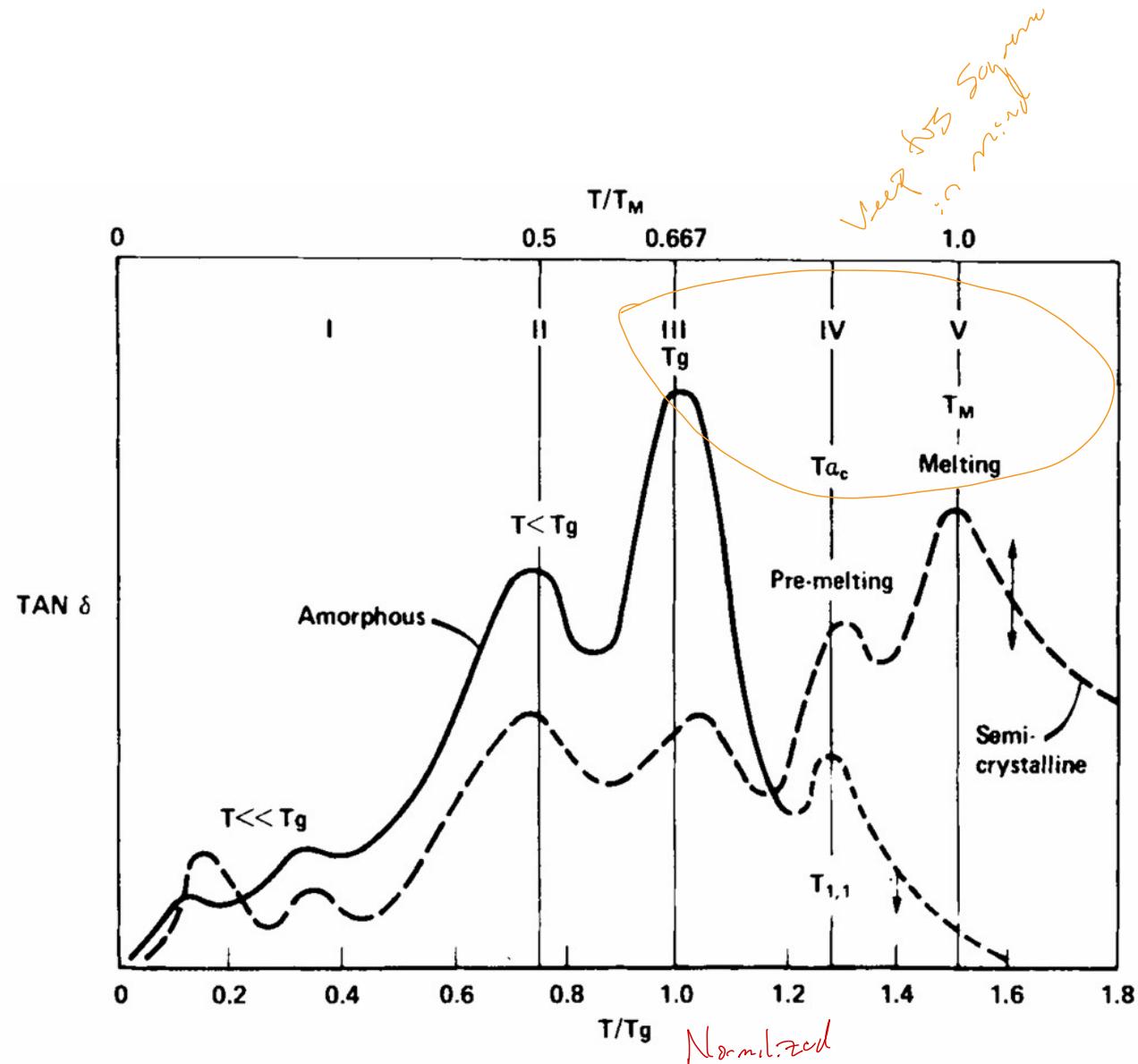
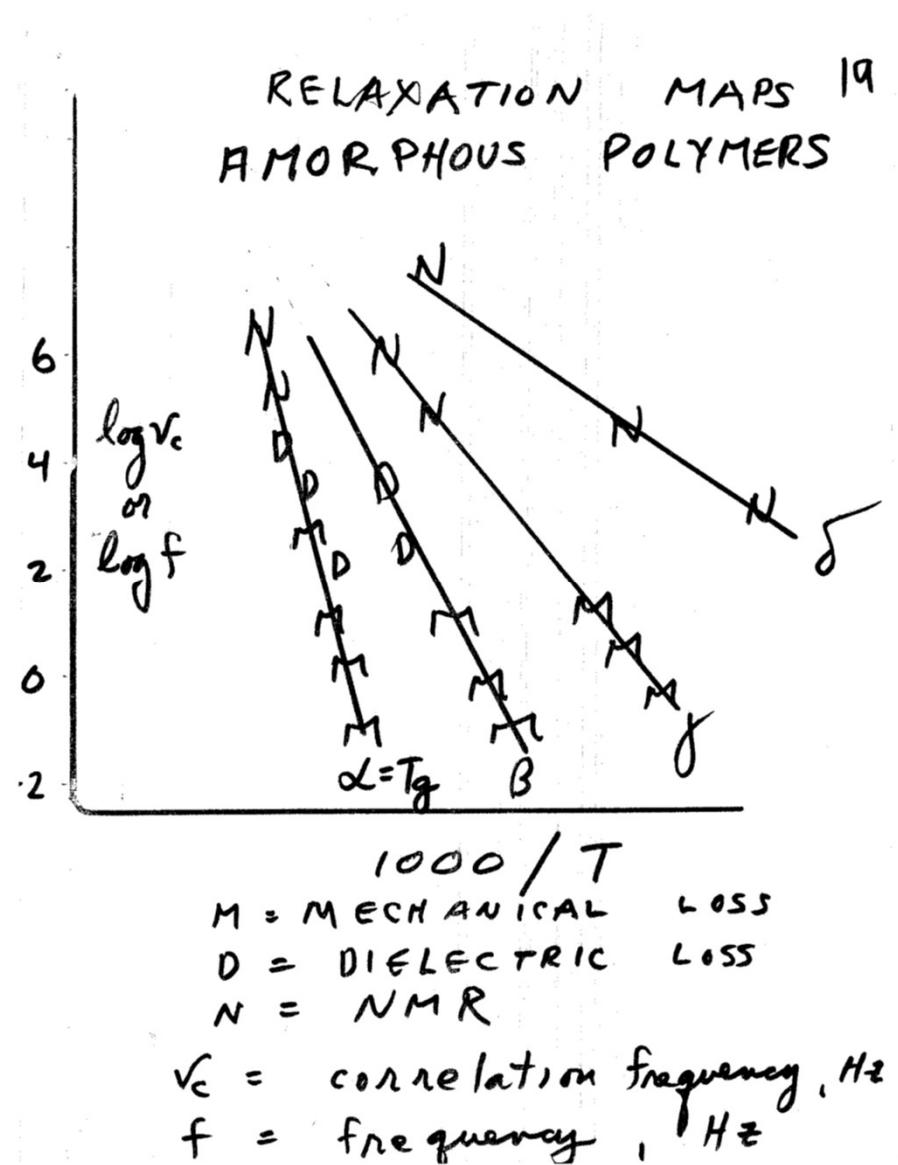


FIG. 6. Schematic "typical" mechanical relaxation spectra for atactic and bulk crystallized semicrystalline polymers. Roman numerals represent the several typical regions of activity. The designations associated with the several loss peaks are those used throughout this paper.

Image of Ray Boyer and Ray Boyer's class notes.



Plastics Hall of Fame Inductee



What is the Gamma Thermal Transition in Polyethylene

The gamma transition (T_g) in polyethylene refers to a low-temperature relaxation process involving localized movements of the CH₂ groups within the polymer chains, particularly in the amorphous and crystalline phases. It's essentially a type of molecular motion that occurs at relatively low temperatures, before the material transitions to a more flexible state.

- **Localized Movements:** The gamma transition involves small-scale movements of the CH₂ groups, which are the repeating units in the polyethylene chain. These movements can occur within both the amorphous (disordered) and crystalline (ordered) regions of the polymer.
- **Glass Transition and Relaxation:** The gamma transition region can also be considered part of the glass transition process, where the material transitions from a rigid, glassy state to a more rubbery, elastic state. In this context, the gamma transition reflects the onset of localized molecular motions that contribute to the overall change in material behavior.
- **Influence of Structure:** The structure of polyethylene, particularly the degree of crystallinity and the presence of defects, can influence the gamma transition. For example, differences in the structure of low-density and high-density polyethylene can affect the specific characteristics of the gamma transition in the crystalline phase.
- **Relevance to Mechanical Properties:** The gamma transition can impact the mechanical properties of polyethylene at lower temperatures. The ability of the CH₂ groups to undergo localized movements can influence the material's flexibility and toughness in the low-temperature range. In essence, the gamma transition in polyethylene represents a fundamental molecular motion that contributes to the material's overall behavior, especially at low temperatures, and can be viewed as a precursor to the larger-scale transitions that influence its mechanical properties.

What is the Beta Thermal Transition in Polyethylene

The beta (β) transition in polyethylene (PE) refers to a relaxation process that occurs in the temperature range of roughly -75°C to 0°C, and is associated with molecular motions in the amorphous regions of the polymer, particularly in the interlamellar regions between crystalline lamellae.

- **Nature of the Transition:** It's a solid-state transition, often considered a part of the broader glass transition phenomenon in amorphous polymers.
- **Molecular Mechanism:** The β -transition is believed to involve localized movements of chain segments, particularly in the amorphous regions between crystalline structures. These movements are related to the glass transition of polyethylene, where the polymer transitions from a rigid, glassy state to a more flexible, rubbery state.
- **Impact on Properties:** This transition can influence the mechanical and electrical properties of polyethylene at low temperatures. For example, the β -transition can affect the dielectric breakdown strength of LDPE (low-density polyethylene) at low temperatures.
- **Observed Effects:** The β -transition can be observed as a change in mechanical properties, such as an increase in loss modulus and tan delta in dynamic mechanical analysis (DMA) experiments, as well as changes in dielectric properties.
- **Controversy:** While the β -transition is well-established, the exact mechanism and the specific molecular motions involved are still a subject of some debate and research.

What is the Glass Transition in Polyethylene

The glass transition temperature (T_g) of polyethylene is the temperature at which the polymer changes from a rigid state to a rubbery state. The exact T_g depends on the type of polyethylene.

- **Low-density polyethylene (LDPE):** The T_g of LDPE is around -100°C . Below this temperature, LDPE is hard and rigid, and above it, it is rubbery.
- **High-density polyethylene (HDPE):** The T_g of HDPE is typically between -100°C and -130°C . Below this temperature, HDPE is hard and rigid.
- **Ultra-high molecular weight polyethylene (UHMWPE):** The T_g of UHMWPE is -80°C .

The T_g of a polymer is related to its thermal properties. The exact T_g depends on the structure of the polymer. For example, a small change in the structure of a polymer can result in a big change in its T_g .

The T_g of a polymer can be determined using differential scanning calorimetry (DSC) or dilatometry.

What is the Alpha Transition in Polyethylene

The alpha (α) thermal transition in polyethylene, also referred to as the α -relaxation or **the glass transition of the crystalline phase**, is a relaxation process associated with the segmental mobility of chain units within the crystalline regions of the polymer.

- **Segmental Mobility:** The α -transition involves the movement of relatively short segments of the polyethylene chains within the crystalline domains. This movement can be described as the rotation and/or translation of these chain segments along the chain axis.

- **Crystalline Regions:** While polyethylene is a semi-crystalline polymer, meaning it has both crystalline and amorphous regions, the α -transition specifically relates to the crystalline regions.

- **Importance:** This transition is significant because it influences the mechanical properties of polyethylene and plays a role in its behavior during processing and use.

- **Temperature Range:** The α -transition typically occurs at temperatures above the glass transition temperature (T_g) of the amorphous phase and below the melting point (T_m) of the crystalline phase. It's generally observed in the range of 303 to 393 K (30 to 120°C).

- **Factors Affecting α -transition:** The intensity and temperature of the α -transition can be affected by various factors like branching, copolymerization, and the presence of other chemical modifications in the polyethylene chain. In essence, the α -transition reflects the onset of chain mobility within the crystalline regions of polyethylene, influencing its mechanical and thermal properties.

GLASSY TRANSITIONS IN SEMICRYSTALLINE
POLYMERS

RAYMOND F. BOYER

*The Dow Chemical Company, Midland, Michigan 48640**

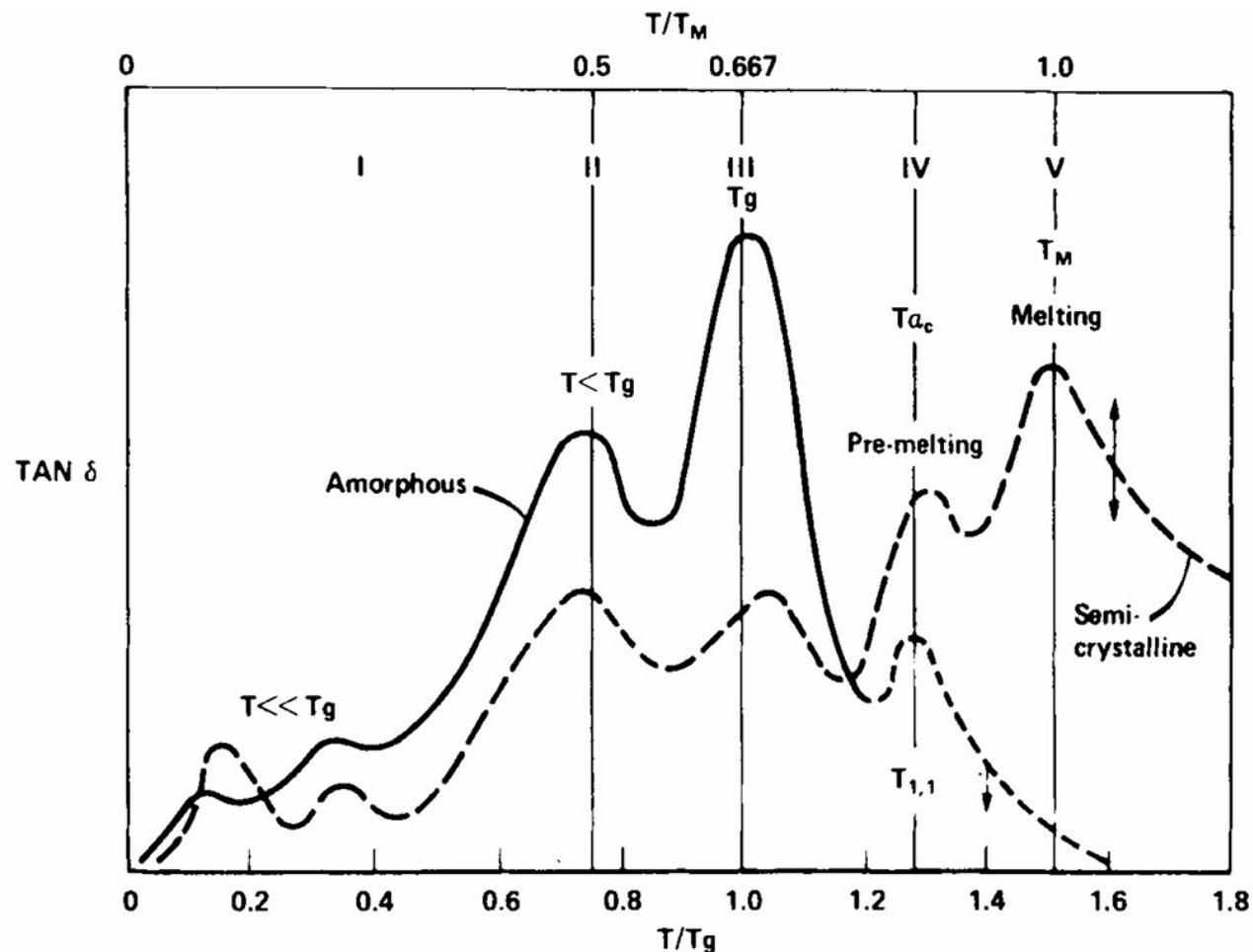


FIG. 6. Schematic "typical" mechanical relaxation spectra for atactic and bulk crystallized semicrystalline polymers. Roman numerals represent the several typical regions of activity. The designations associated with the several loss peaks are those used throughout this paper.

Amorphous linear polyethylene

POLYMER, 1979, Vol 20, July 903

J. Breedon Jones*, S. Barenberg† and P. H. Geil

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, USA

(Received 2 June 1978; revised 11 October 1978)

One of the results of the lack of amorphous polyethylene samples has been a long standing controversy over the location of the glass temperature (T_g) of PE. For details the reader is referred to several review articles by Boyer¹⁻⁴. The basic difficulty is that convincing experimental evidence, from several techniques, exists for T_g to be at any of three temperature ranges 145 ± 10 , 195 ± 10 and 240 ± 20 K. Boyer has attempted to resolve the problems by suggesting that 145K is the γ -transition where motions of segments 4–5 carbon atoms long begin, 195K is a lower T_g [$T_g(L)$] where motion of long chain segments unconstrained by crystallites occurs, and 240K is $T_g(U)$, where long segment motion occurs in chains held in tension or otherwise constrained by the lamellae.

Amorphous linear polyethylene

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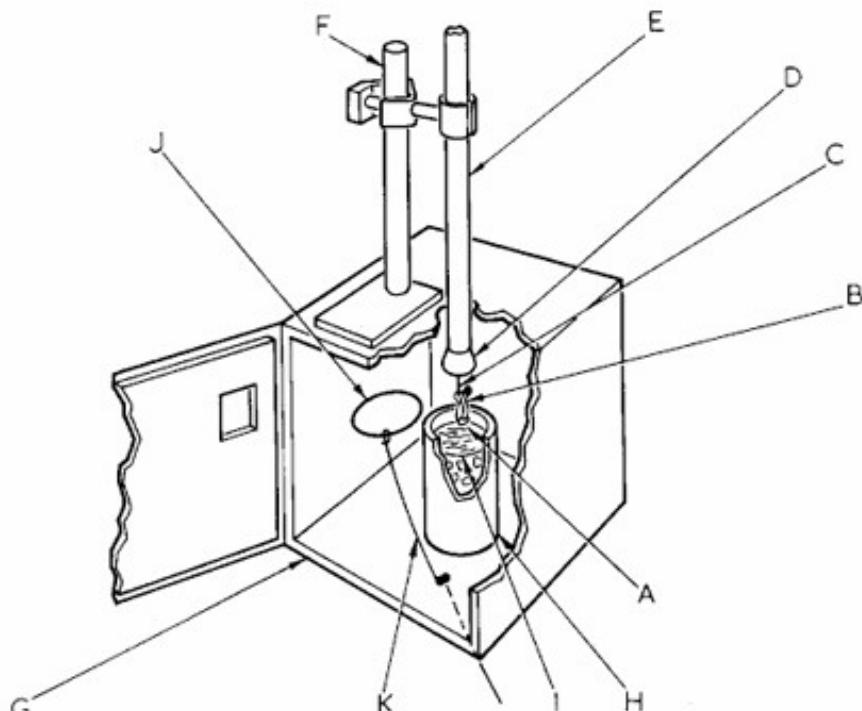


Figure 1 Nitrogen quench apparatus. A, Sample; B, clip; C, wire; D, cork; E, B-B gun; F, ring stand; G, furnace; H, dewar; I, quenchant; J, dewar cover; and K, cover wire

Nitrogen quench method

A schematic diagram of the quench apparatus is shown in *Figure 1*. The sample on its grid (A) was suspended vertically by a small steel alligator clip (B) attached to a 3–4 in. copper wire (C), the end of which was inserted into the large end of a cork (D). The cork was properly sized to fit into the end of the barrel of a Daisy Model 1105-BB gun (E) which had been sawed off 1.5 cm above the maximum extension of the plunger. The gun was clamped vertically to a ringstand (F) on the top of the furnace (G) in such a manner that the barrel extended through a hole in the top of the furnace. The height of the gun along the ringstand determined how far the sample hung above the tall Dewar (H) contained the quenchant. About one inch from the sample to the top of the Dewar seemed to be a satisfactory distance.

Amorphous linear polyethylene

POLYMER, 1979, Vol 20, July 903

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(Received 2 June 1978; revised 11 October 1978)

The first step of the quench procedure was to insert the cork bearing the wire and sample into the cocked BB gun so that the sample would be propelled straight down onto the quenchant. Alignment was critical for a fast quench. The sample was allowed to melt at 180°C for 5–10 min while the quenchant was prepared. The Dewar, filled with the nitrogen mixture to within 1 cm of the top, was placed quickly in the furnace directly under the sample. The cover was then set in place and the furnace was again closed. When the temperature in the furnace reached about 155K, the cover on the Dewar was removed. Care was taken to minimize vibrations of the gun that might keep the cork from going straight to the bottom of the Dewar. The cork permitted easy removal of the sample. The sample was kept inside a small beaker of liquid nitrogen during subsequent handling to keep it from warming.

Amorphous linear polyethylene

POLYMER, 1979, Vol 20, July 903

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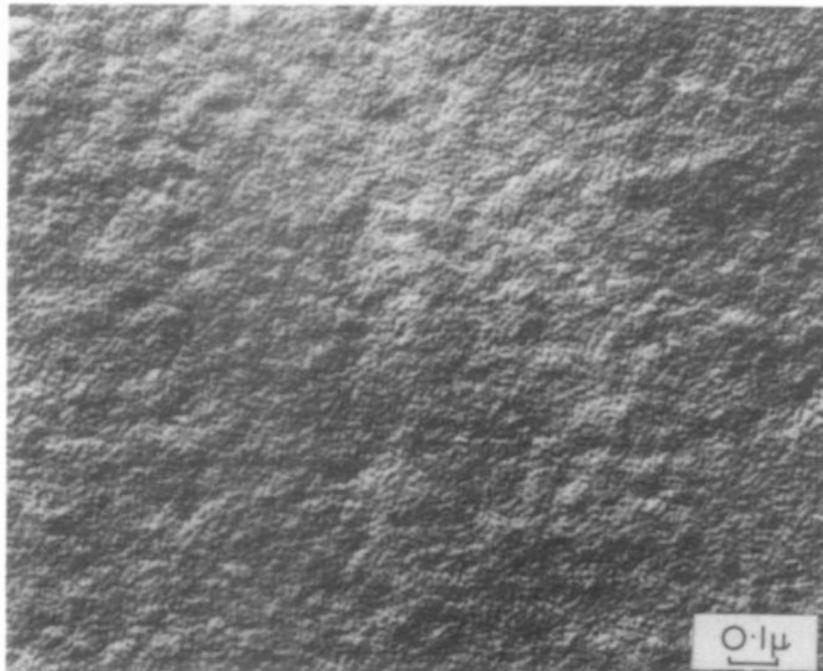


Figure 8 Nitrogen-quenched LPE film that gave predominantly amorphous diffraction when cold. Sample was kept cold before and during insertion and observation in the EM. Upon warming it was entirely crystalline. Pt/C shadowed after warming

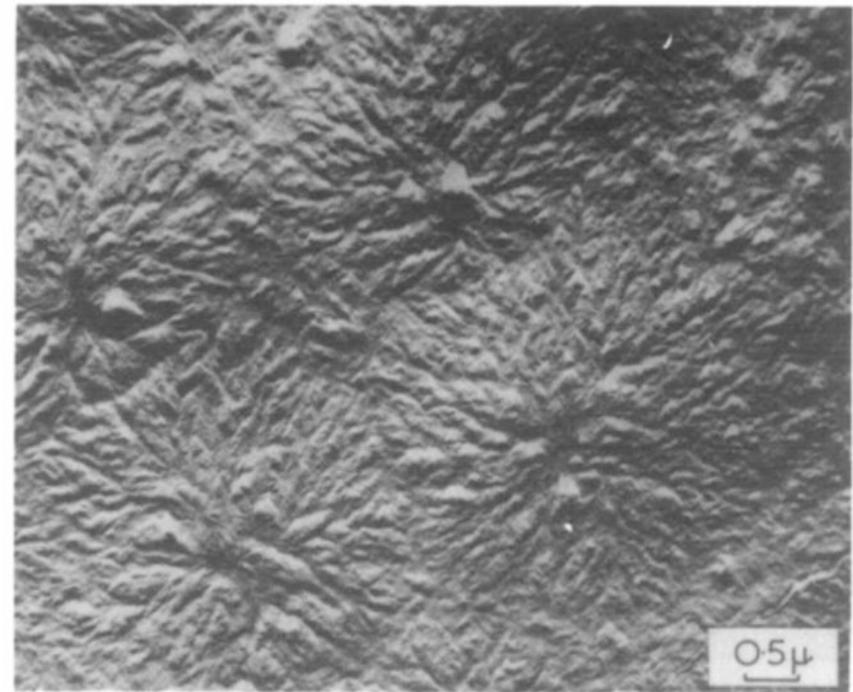


Figure 7 Spherulites in badly nitrogen-quenched LPE film. Sample was kept cold before and during Pt/C shadowing

Amorphous linear polyethylene

POLYMER, 1979, Vol 20, July 903

J. Breedon Jones*, S. Barenberg† and P. H. Geil

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, USA

(Received 2 June 1978; revised 11 October 1978)

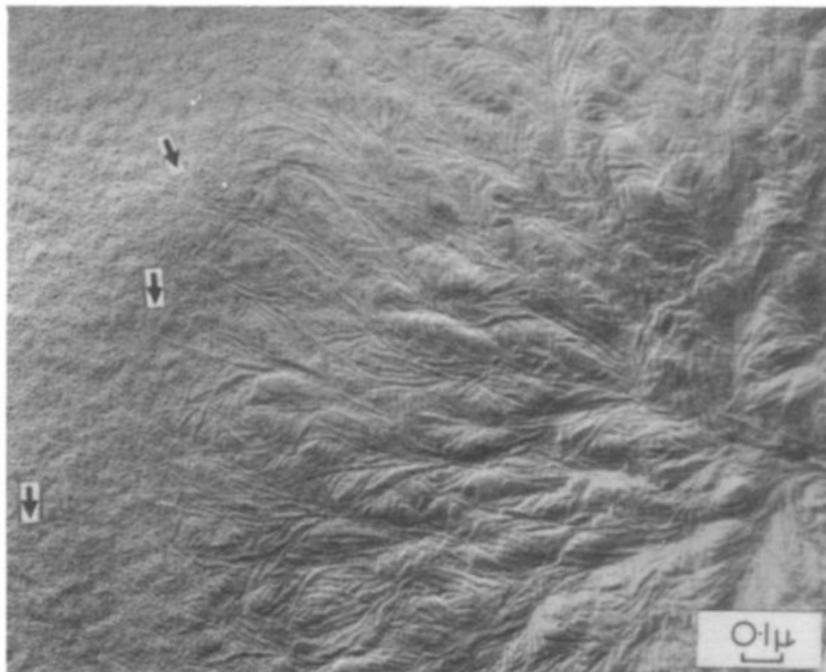


Figure 9 Boundary between crystalline and presumably amorphous areas of nitrogen-quenched LPE film. Arrows mark lamellae in which the nodules do not seem to have coalesced completely. Pt/C shadowed after warming

Amorphous linear polyethylene

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(Received 2 June 1978; revised 11 October 1978)

POLYMER, 1979, Vol 20, July 903

Conclusion

160K and 180K. Above 180K the amorphous portions of the spectrum are gradually converted to crystalline bands, suggesting that the true T_g lies around 180K.

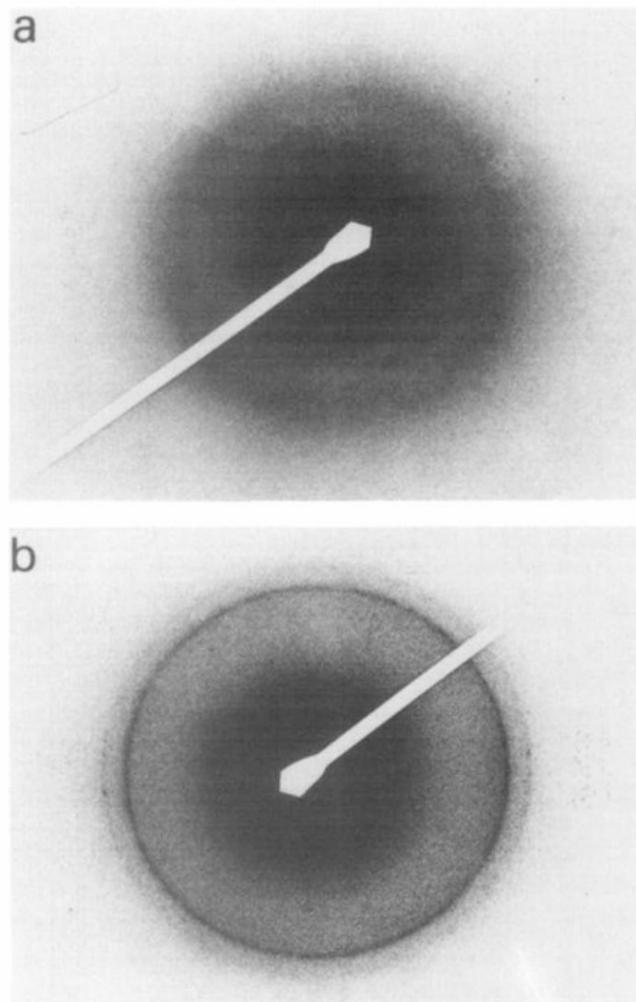


Figure 16 (a) Electron diffraction pattern of nitrogen-quenched LPE film kept cold before and during insertion and observation in EM. Carbon substrate. (b) Diffraction pattern from same film after warming to room temperature

Critical Properties for the Differentiation of the Polyethylene Types

Density

Crystalline Region

Perfect 1.00 g/cm³

Unit Cell Calculation (orthorhombic) 0.996

Single Crystal Determination 0.972

Amorphous Region 0.850 – 0.855

Transition Temperatures

Glass Transition Temperature -78 C (195 K)

Melt Transition Temperature (density dependent) 130-140 C

The Most Common Classification of Polyethylene is by Density

Table 1. Classification of polyethylenes by density

<i>Resin family</i>	<i>Lower density limit g/cc</i>	<i>Higher density limit g/cc</i>
High Density Polyethylene (HDPE)	0.941	0.975
Medium Density Polyethylene (MDP)	0.928	0.941
Linear Low Density Polyethylene(LLDPE/LDPE)	0.915	0.928
Very Low Density Polyethylene (VLDPE)	0.900	0.915
Elastomers/Plastomers	0.865	0.900

These Variations of Polyethylene Lead to a Diversity of Products

Linear Versions:

High density polyethylene (HDPE)

Ultra-high molecular weight polyethylene (UHMWPE)

Branched Versions:

Low-density polyethylene (LDPE)

Linear low density polyethylene (LLDE)

Medium-density polyethylene (MDPE)

Very-low-density polyethylene (VLDPE)

High-molecular-weight polyethylene (HMWPE)

Ultra-low-molecular-weight polyethylene (ULMWPE)

Chlorinated polyethylene (CPE)

Bimodal and Trimodal Polyethylene

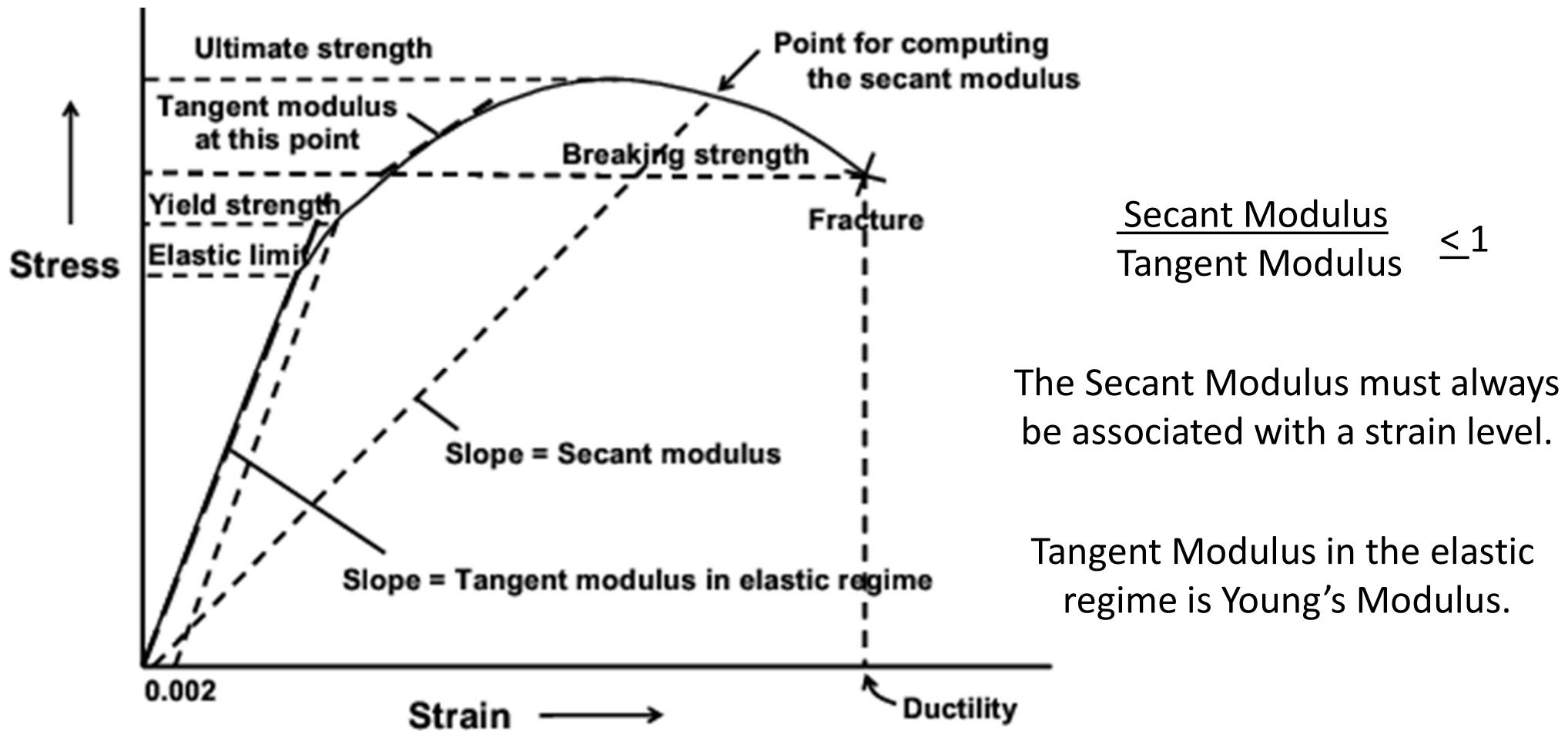
Cross-linked polyethylene (PEX): four forms (PEX-a, PEX-b . . etc)

Simplest of Monomer Structures Can Lead to a Large Diversity of Polymer Structures.

Three fundamental features of polyethylene leading to the diversity of structures and in turn performance are:

- a. Short chain and long chain branching.
- b. Co-monomer content and distribution.
- c. Molecular weight and molecular weight distribution.

Tensile Properties of Plastics is a Fingerprint of the Mechanical Performance



Molecular weight Dependence on Polyethylene Properties

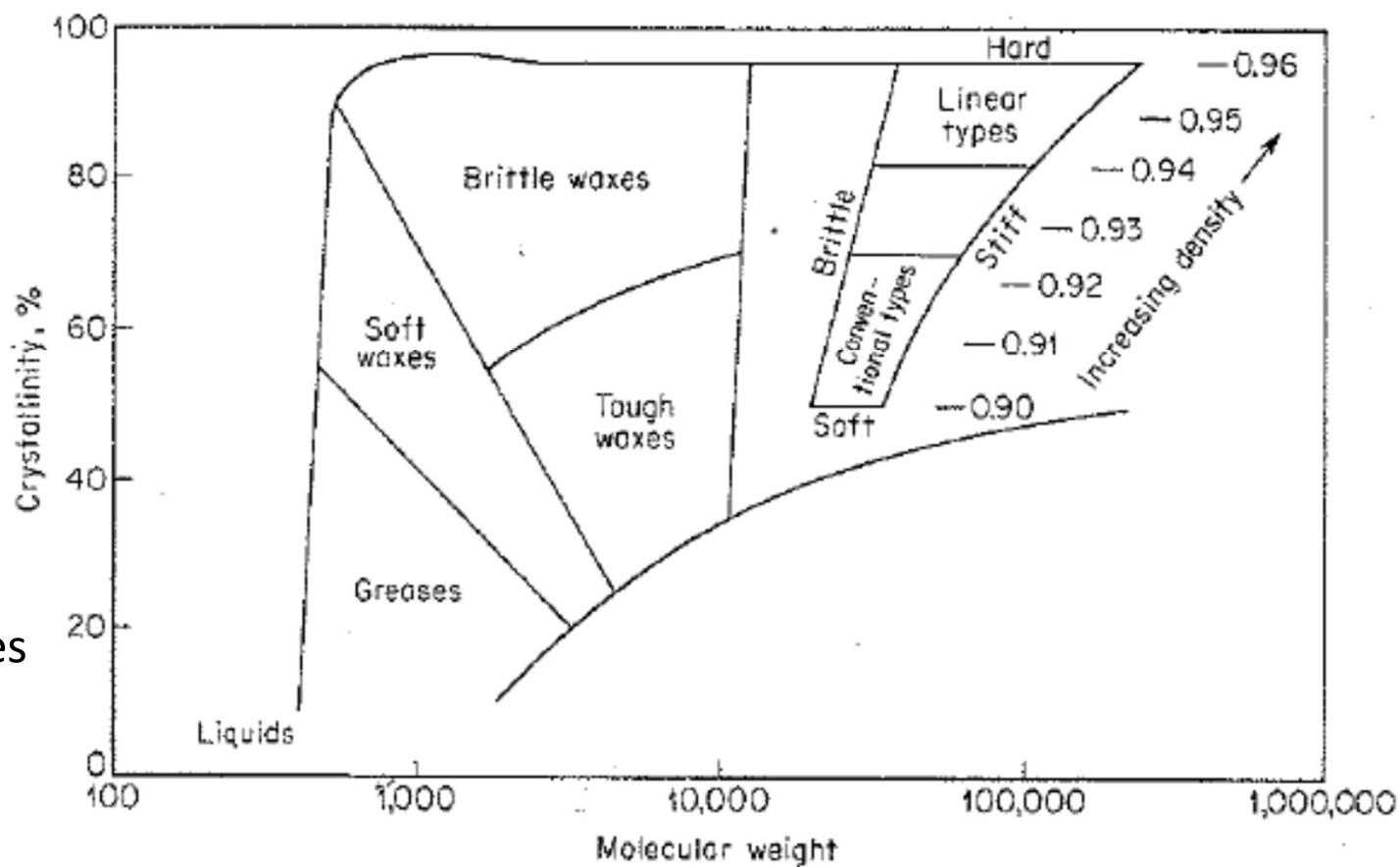


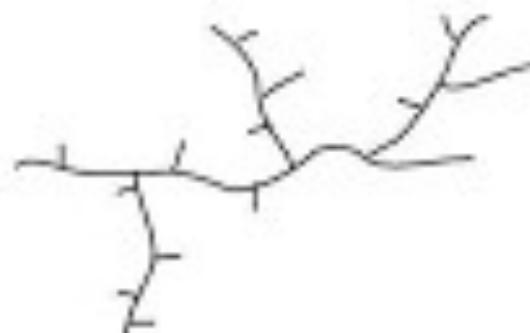
FIGURE 13-1

Relationships between crystallinity, molecular weight, and mechanical properties of polyethylene [3]. (After Kratz and Lyle, *Encyclopedia of Chemical Technology*, First Suppl., Interscience, 1957.)

The Variance of Most Polyethylene Products is Based on Branching



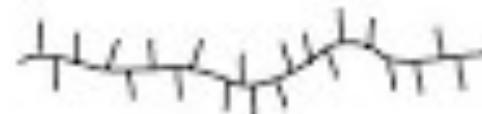
High-Density Polyethylene (HDPE)
 $X_c \sim 55\text{-}77\%$ $T_m \sim 125\text{-}132^\circ\text{C}$



Low-Density Polyethylene (LDPE)
 $X_c \sim 30\text{-}54\%$ $T_m \sim 98\text{-}115^\circ\text{C}$



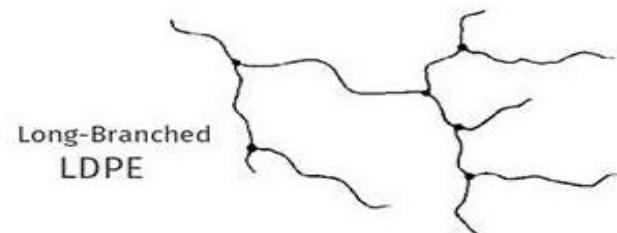
Linear Low-Density Polyethylene (LLDPE)
Branching density ~ 25-100 C atoms
 $X_c \sim 22\text{-}55\%$ $T_m \sim 100\text{-}125^\circ\text{C}$



Very Low-Density Polyethylene (VLDPE)
Branching density ~ 7-25 C atoms
 $X_c \sim 0\text{-}22\%$ $T_m \sim 60\text{-}100^\circ\text{C}$

Low Density Polyethylene (LDPE)

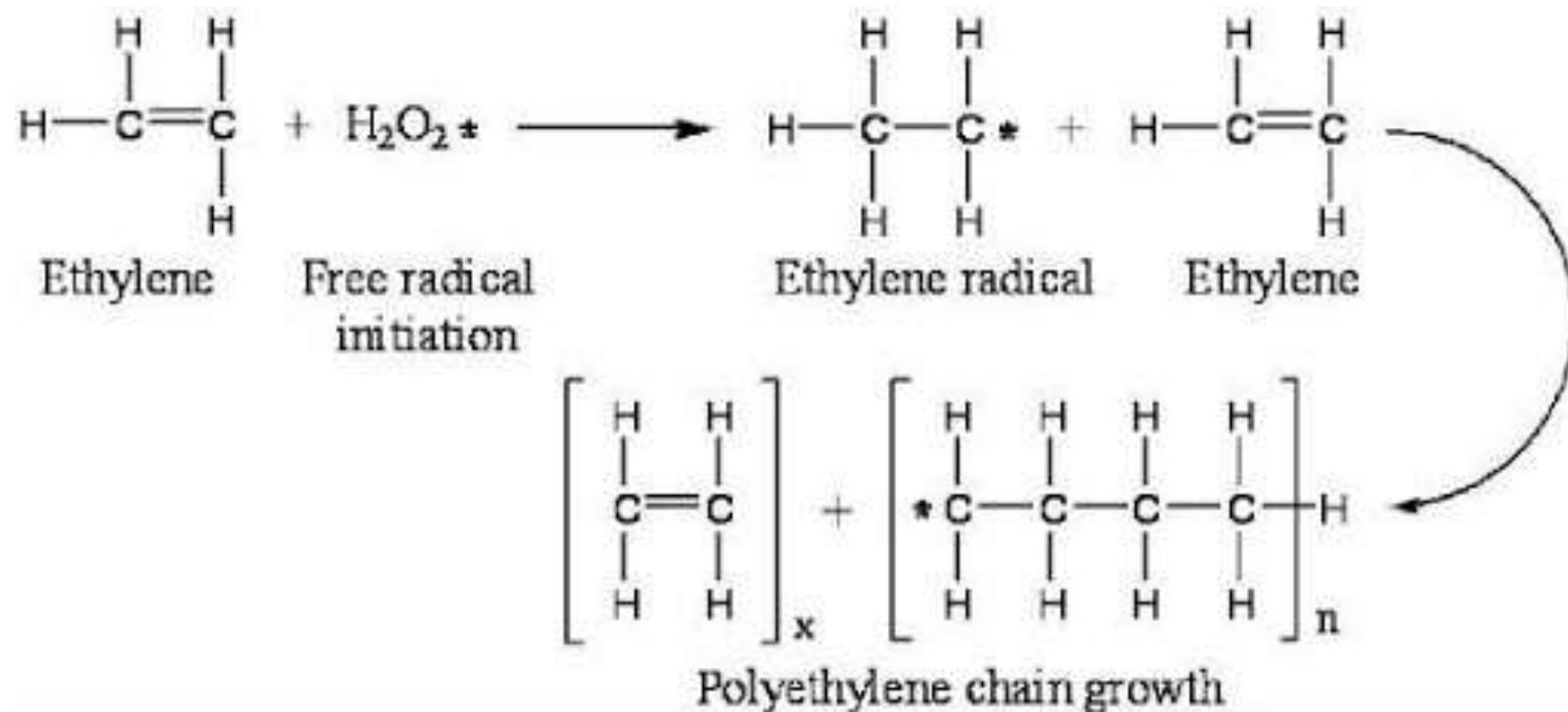
- LDPE was the first polyethylene commercially produced.
- It is the only one made utilizing free radical chemistry under high temperatures and pressures.
- Its unique structure contains long chain branching which makes it highly desirable in the manufacture of thin films either by itself or blends with other types of polyethylene.
- Its long chain branching is a consequence of the high pressure process where intermolecular hydrogen abstraction by a growing chain end from another polyethylene is the source of this highly desirable properties especially in melt processing.



Low Density Polyethylene (LDPE)

- The presence of long chain branches has a significant impact on the rheology of low density polyethylene.
- The presence of long chain branches increases the shear thinning of the polymer, meaning at high shear rates the polymer has lower viscosity than expected while at low shear rates the polymer has higher viscosity than expected.
- The low viscosity at high shear rates also helps to reduce the energy required to process the resin.

Free Radical Polymerization of LDPE



Process Schematic for Producing Low Density Polyethylene

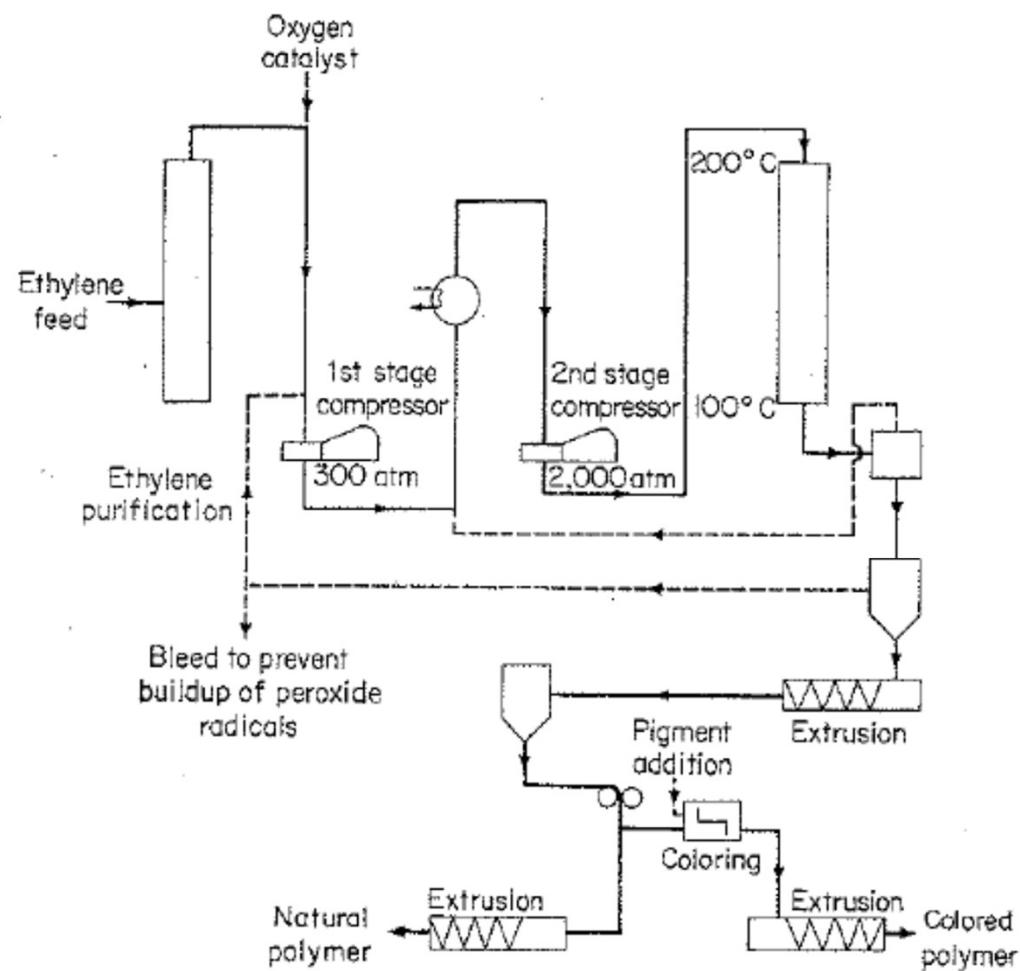


FIGURE 13-2
Simplified flow scheme for the high-pressure polymerization of ethylene [4].

Properties of Low Density Polyethylene

- LDPE Melting Point: 105 – 115 C
- Density of LDPE: 0.910 – 0.940 g/cm³
- Chemical Resistance of LDPE
 - Good resistance to alcohols, dilute alkalis and acids
 - Limited resistance to aliphatic and aromatic hydrocarbons, mineral oils, oxidizing agents and halogenated hydrocarbons
- Operating temperature up to 80 C continuously and 95 C for short periods
- Low cost polymer with good processability
- High impact strength at low temperatures, good weatherability
- Excellent electrical insulating properties
- Very low water absorption.
- FDA compliant
- Transparent in thin film form

Disadvantages of Low Density Polyethylene

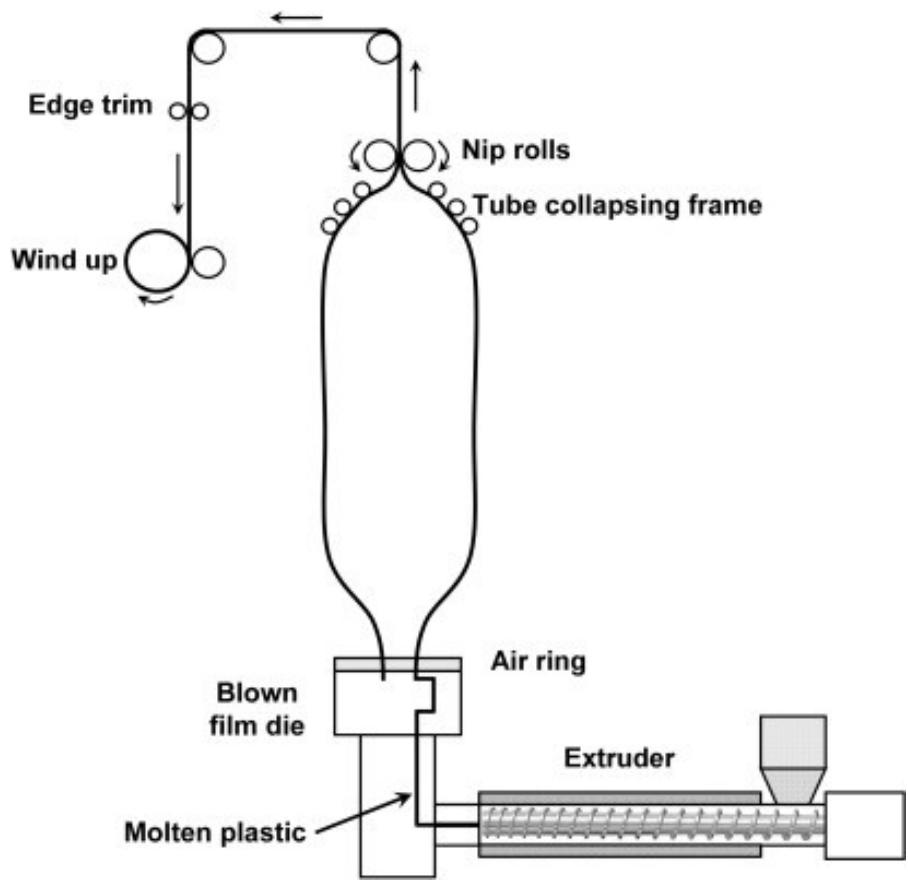
- Susceptible to stress cracking (ESC – Environmental Stress Cracking)
- Low strength, stiffness and maximum service temperature
- High gas permeability, particularly carbon dioxide
- Poor UV resistance
- High flammability
- Impossible to apply high frequency welding and joining

Applications for Low Density Polyethylene

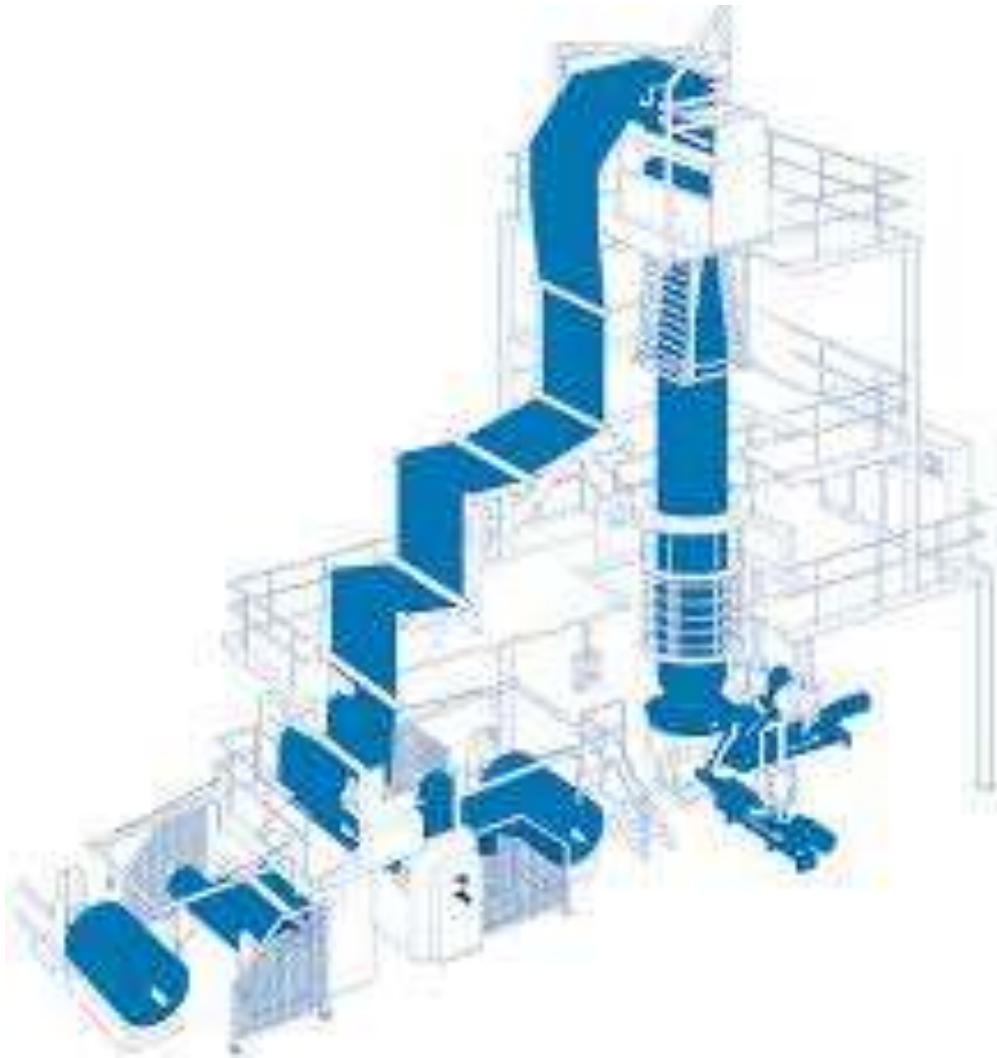
The most popular application of LDPE is the production of plastic bags. Due to the Low cost and flexibility, LDPE is used in the packaging industry for pharmaceutical And squeeze bottles, caps and closures, tamper evident, liners, trash bags, Films for food packaging (frozen, dry goods, etc.) and laminations.

Low Density Polyethylene is also used to manufacture water pipes and hoses For the pipe and fitting industry due to its flexibility and low water absorption.

One End-Use for LDPE is PE Bags by the Blown Film Process



The Blown Film Process for Low Density Polyethylene



Other End-Use Products Made from LDPE

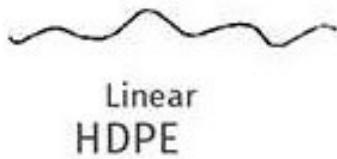


LDPE



High Density Polyethylene (HDPE)

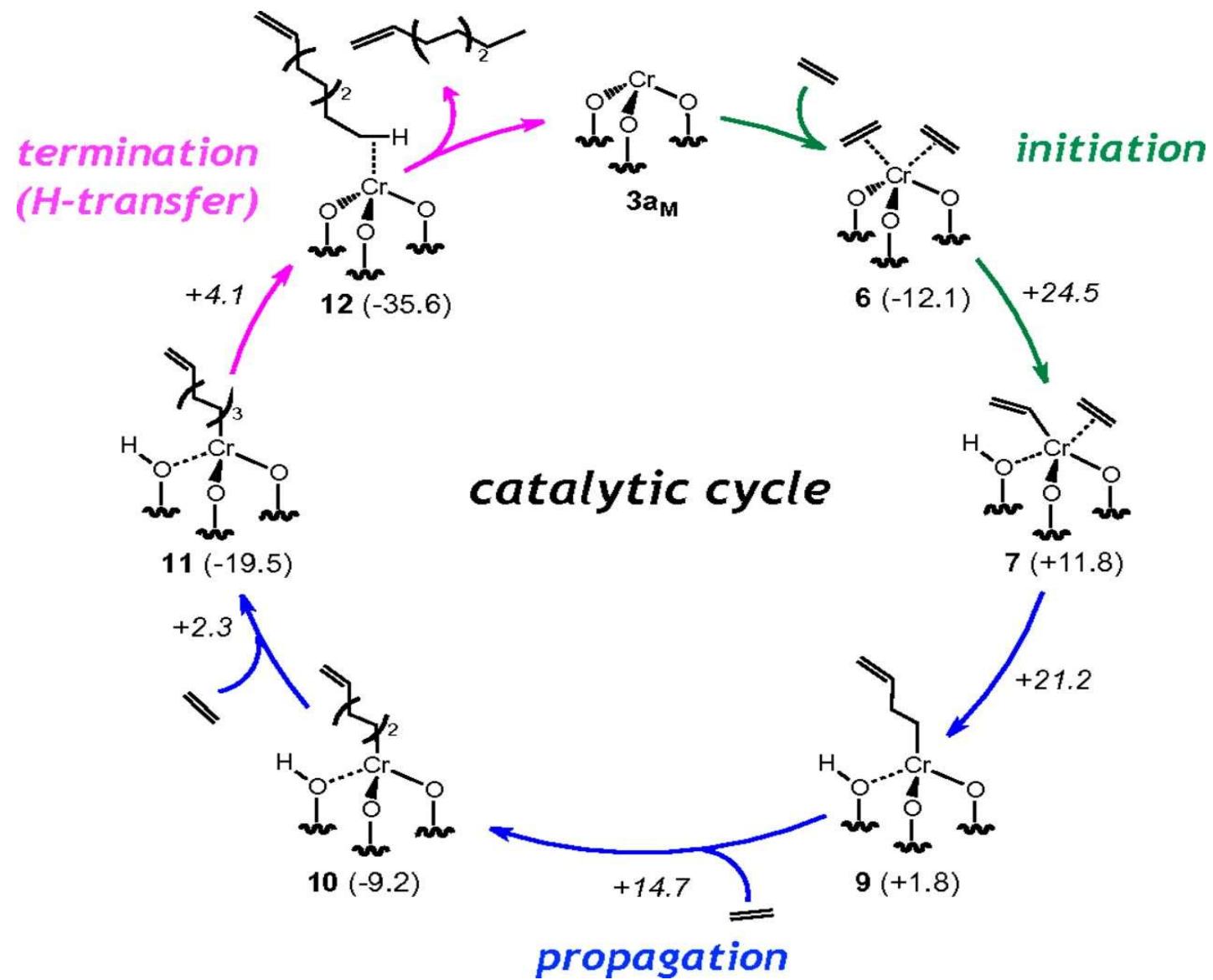
Unlike low density polyethylene (LDPE) which utilizes free radical chemistry, high density polyethylene (HDPE) is produced through coordination chemistry catalysis.



There are three basis coordination chemistry catalyst used to produce HDPE:

1. Chromium Catalyst for Slurry and Gas Phase Process – developed in the early 1950's by Robert Banks and J. P. Hagen at Phillips Petroleum. Initially used chromium trioxide. Required lower pressures (< 1000 psi) and lower temperatures (80 – 110 C).

Phillips Petroleum
Chromium Catalysis
for the Polymerization
Of Polyethylene



High Density Polyethylene (HDPE)

There are three basis coordination chemistry catalyst used to produce HDPE:

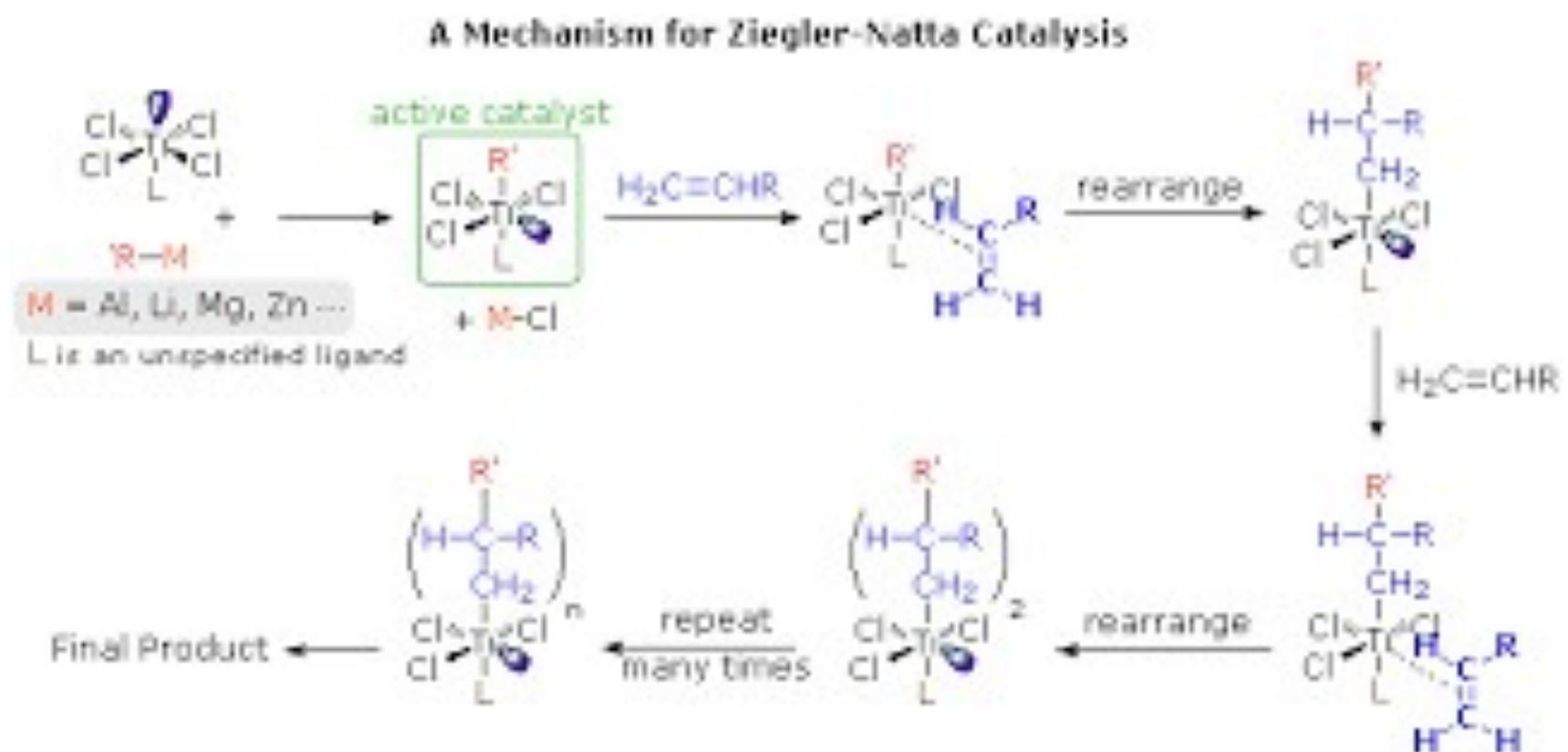
2. Ziegler – Natta Polymerization and the Gas Phase Process

This process was initially developed by Karl Ziegler at the Max Plank Institute in Mulheim, Germany and later refined by Giulio Natta , at the Institute of Industrial Chemistry In Milan, Italy. Natta used the titanium tetrachloride discovered by Ziegler and enhanced it with an aluminum alkyl.

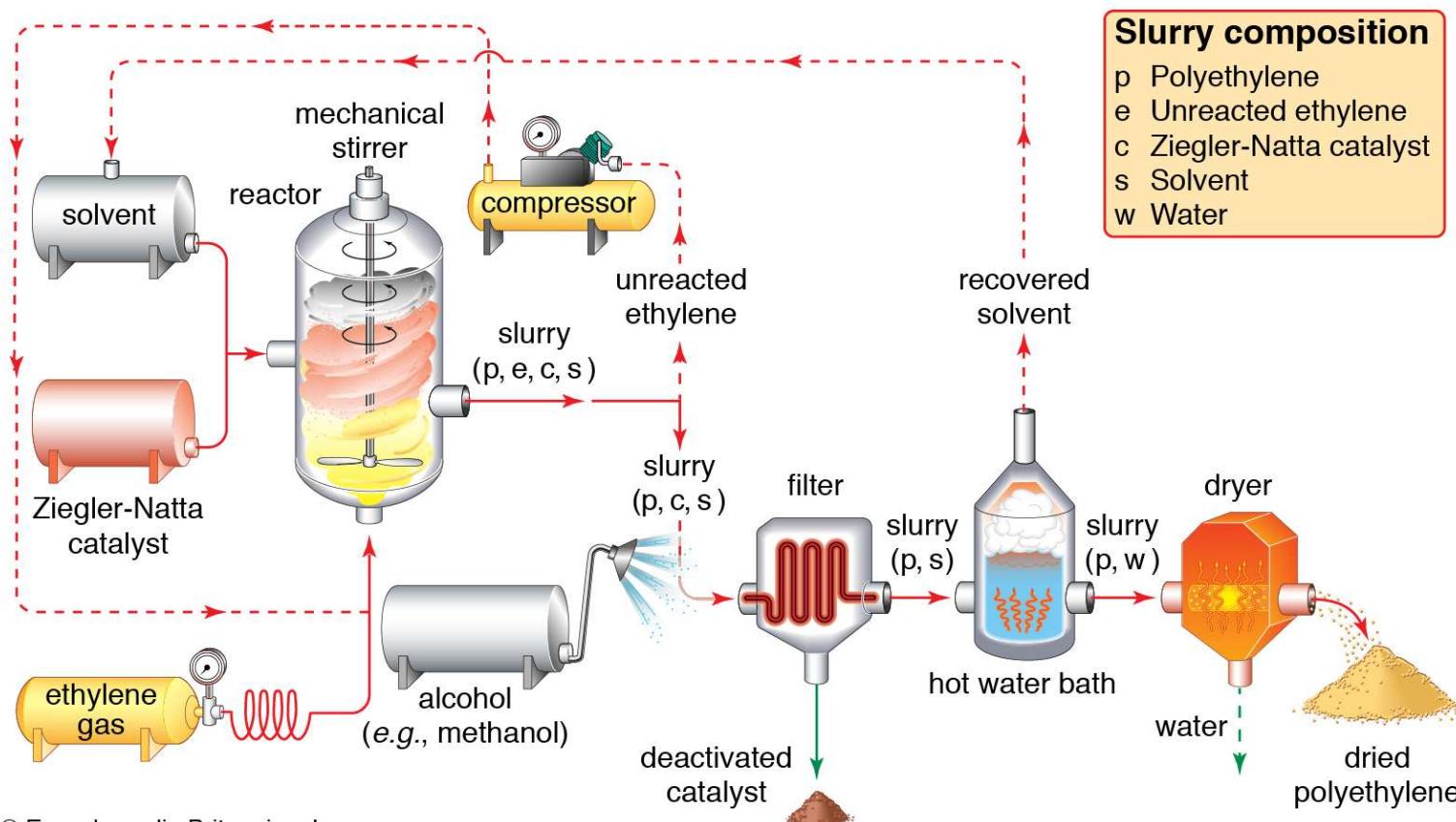
Initial Z-N catalysts were not supported and the active site activity would become limited.

In 1970 supported Z-N catalysts were developed to enhance the catalyst activity: $Mg Cl_2$

Ziegler – Natta Polymerization Mechanism



Ziegler-Natta Polymerization Process for HDPE

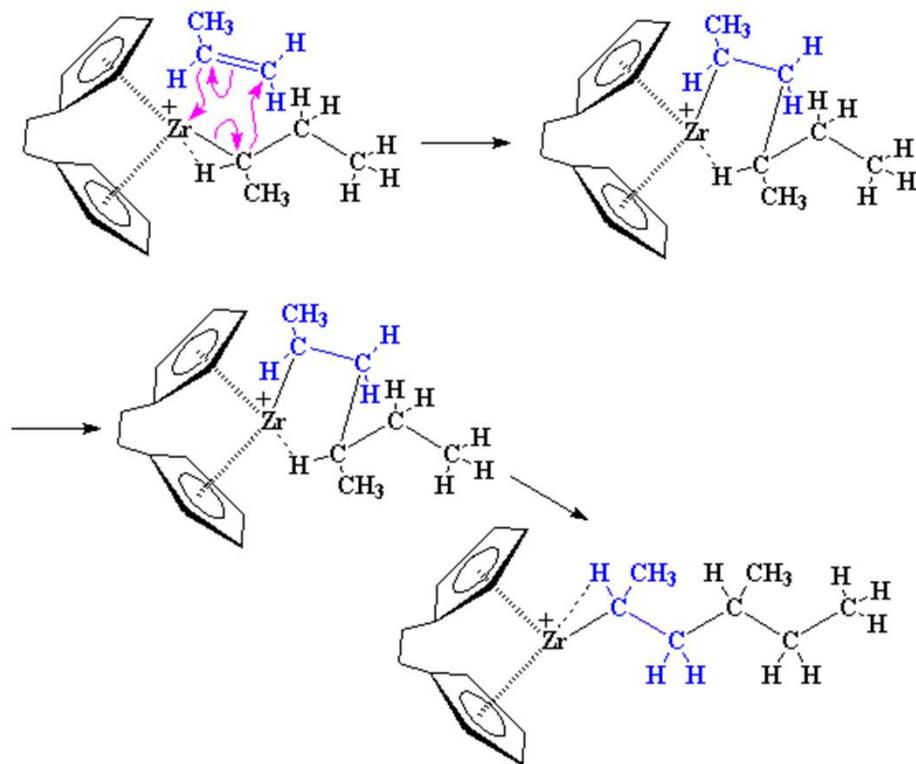


High Density Polyethylene (HDPE)

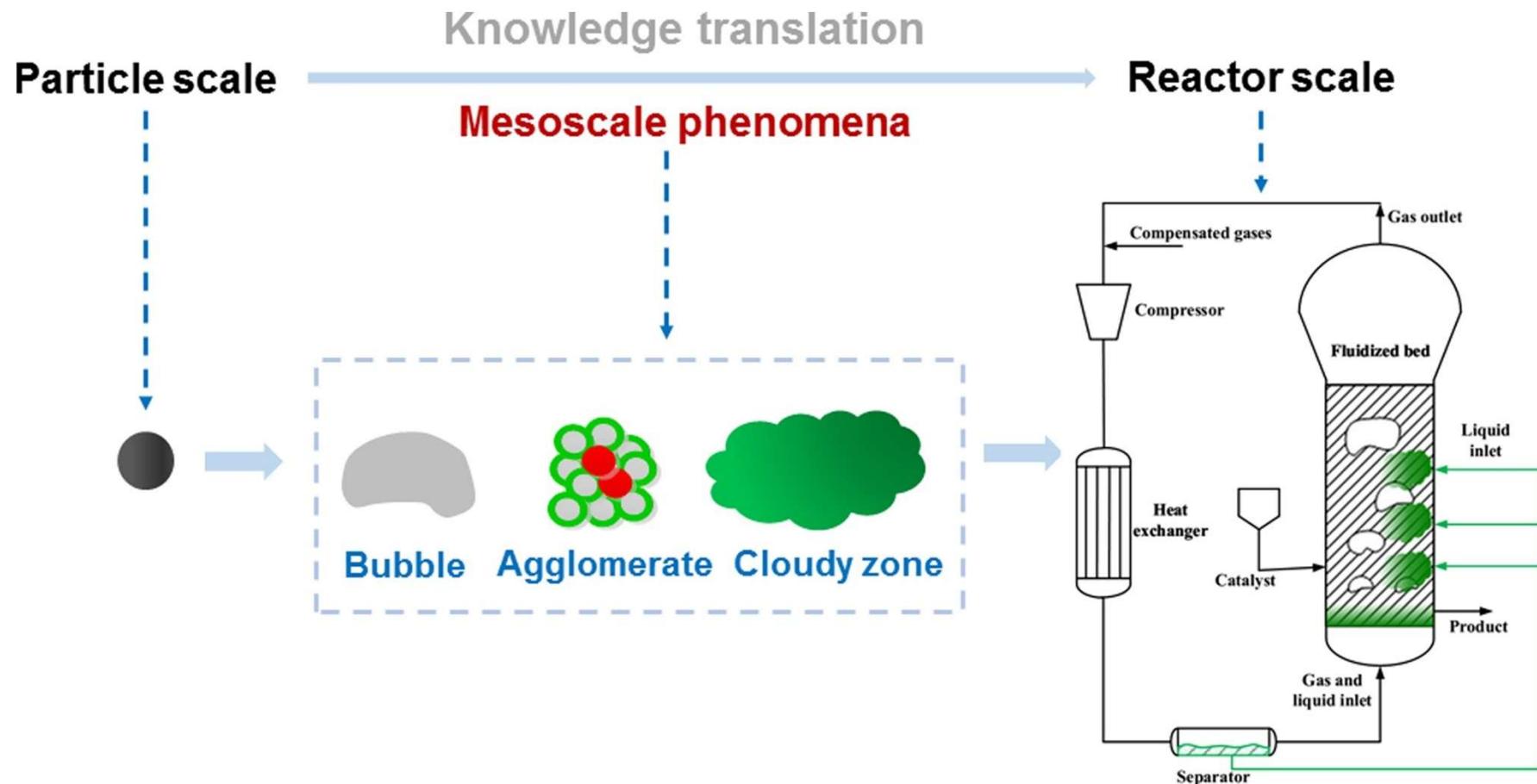
There are three basis coordination chemistry catalyst used to produce HDPE:

3. Metallocene Catalysts - The newest type of PE catalysts having much higher control on the molecular parameters. First discovered in 1976 by Walter Kaminsky and Hansjorg Sinn in Germany. The process can be either slurry or gas phase. This catalyst system has only one active center which results in having the copolymer molecular composition always the same. Very high yields are produced by this catalysis system: millions of grams of polymer per gram of catalyst.

Metallocene Polymerization Mechanism



Metallocene Polymerization Process for HDPE



High Density Polyethylene (HDPE)



High Density Polyethylene

The chemical structure of high density polyethylene (HDPE) lends itself to greater toughness – roughly twice the tear and puncture strength and better chemical resistance than low density polyethylene (LDPE) and linear low density polyethylene (LLDPE). On the downside, HDPE film is less flexible and less clear than its LDPE and LLDPE cousins.

courtesy of LADDAWN

Properties of High Density Polyethylene

- HDPE Melting Point: 120 – 140 C
- Density of LDPE: 0.93 – 0.97 g/cm³
- Chemical Resistance of LDPE
 - Excellent resistance to most solvents
 - Very good resistance to alcohols, dilute alkalis and acids
 - Moderate resistance to oils and greases
 - Poor resistance to aliphatic and aromatic hydrocarbons, mineral oils, oxidizing agents and halogenated hydrocarbons
- Operating temperature from – 50 to 60 C
- Relatively stiff material with useful temperature capabilities
- Higher tensile strength compared to other forms of polyethylene
- Good low temperature resistance
- Excellent electrical insulating properties
- Very low water absorption.
- FDA compliant

Disadvantages of High Density Polyethylene

- Susceptible to stress cracking (ESC – Environmental Stress Cracking)
- Low strength, stiffness
- High gas permeability, particularly carbon dioxide
- Poor UV resistance; can be modified with carbon black
- High flammability
- Impossible to apply high frequency welding and joining

Applications for High Density Polyethylene

1. Packaging Applications – High density polyethylene is used in several packaging applications including crates, trays, bottles for milk and fruit juices, drums, and industrial bulk containers.
2. Consumer goods – Low cost and easy processability make HDPE a material of choice in several household/ consumer goods like garbage containers, housewares, ice boxes and toys.
3. Fibers and Textiles – Due to its high tensile strength, HDPE is widely used in ropes, fishing and sport nets, nets for agricultural use, and industrial and decorative fabrics.

Other applications include pipe and fittings (gas, water, sewage, drainage), wire and cable coating, steel pipe coating and automobile fuel tanks.

Performance Comparison LDPE and HDPE

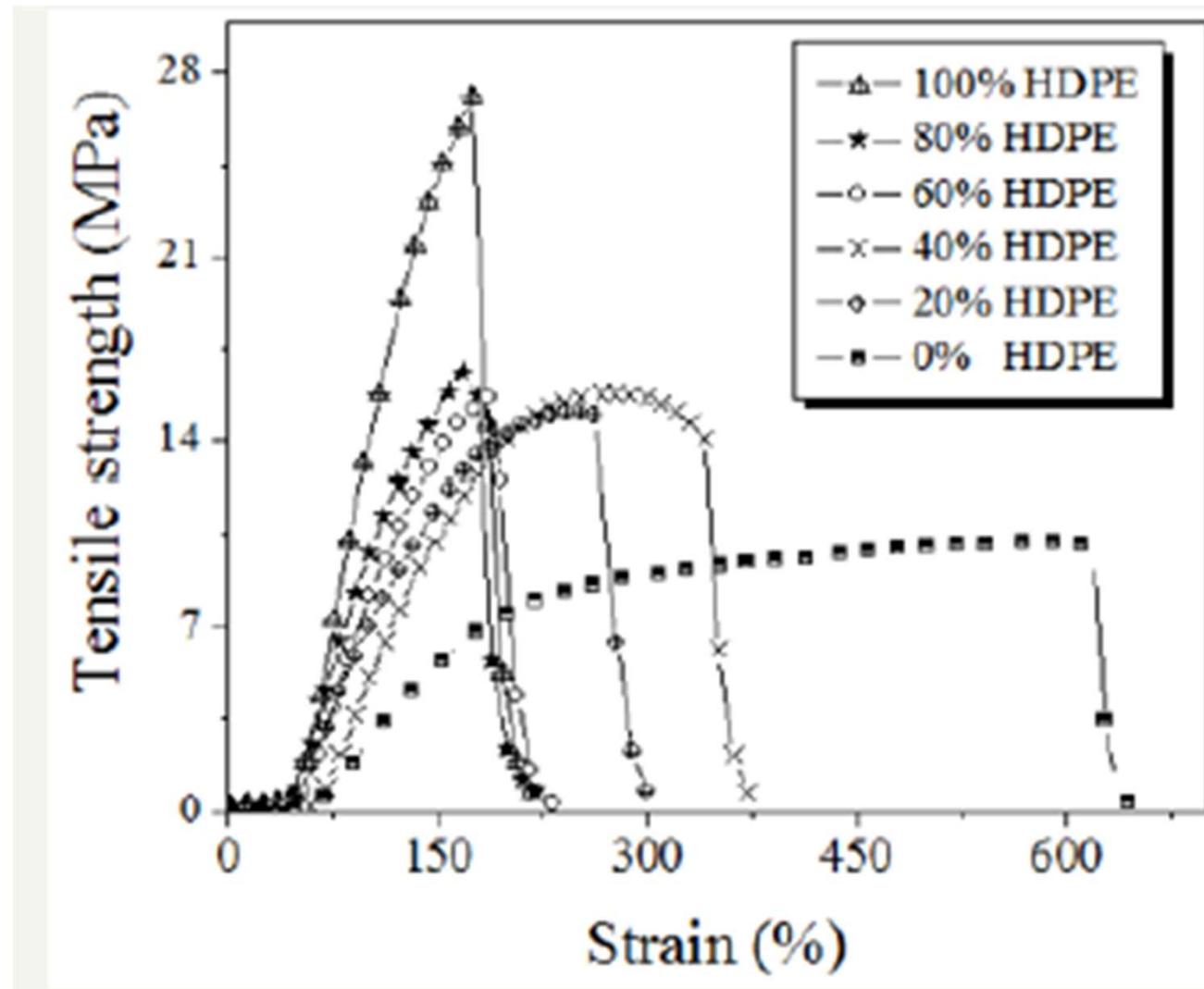
Material	Density (kg/m ³)	Tensile modulus (GN/m ²)	Shear modulus (GN/m ²)	Poisson's ratio
Polyethylene- High Density (HDPE)	955	1.05	0.39	0.34
Polyethylene- Low Density (LDPE)	920	0.32	0.11	0.45

Performance Comparison LDPE and HDPE

Properties	LLDPE*	LDPE*	HDPE*	HDPE-pc
Density (g/cm ³)	0.910 - 0.925	0.915 - 0.935	0.941 - 0.967	-
Melting (0C)	121 - 125	106 - 112	130 - 133	130
Stress (MPa)	14 - 21	7 - 17	18	20
Elongation (%)	200 - 1200	100 - 700	20 - 100	12
Impact resistance (J/m)	-	0.67 - 21	27 - 160	42
Elastic modulus (MPa)	100 - 200	102 - 240	960 - 1000	453

*According to references 17 and 18.

Tensile Performance Change when Modifying HDPE with LDPE



Lesson 10: Polyolefin – PE 2

Questions?



Dr. Andy Olah, amo5@case.edu, O: 216-368-0606, C: 216-272-0505

“Having plans sounds like a good idea until you have to put on clothes and leave the house.”

EMAC 276

Lecture 11 : The Polyolefin Family

Polyethylene – PE: Part 3: PE Short Chain Copolymers

Polypropylene - PP

Poly(1-butene) – Polybutylene – PB

Andy Olah, Ph.D.

February 14, 2025

EMAC 276 - Homework Assignment #2

Due: TODAY!, February 14, 2025

Dr. Olah

During our classes we identified several common polymers that when initially discovered were described as “value-less”, “impossible to process”, “a useless mass”, etc. We also identified several methods (“tricks”) that were subsequently utilized to develop these polymers into successful products; many which are still with us today.

Your exercise is to select one polymer (either from our in-class discussion or from outside our class discussion) and describe 1) the polymer and the initial performance deficiency, 2) the action taken to overcome this deficiency, and, 3) the ensuing product(s) developed from this modification.

If you choose to use an “in class” example your maximum score will be 10.

If you choose to use an “outside the class” example your maximum score will be 12. (i.e., final score +2)

Your answer shall be short comprising between one-half to one page.

Your answer is shall be structured accordingly:

Paragraph #1: Identify and describe the polymer and it's initial deficiency **(3 Points)**

Paragraph #2: Identify the modification or “trick” which was utilized to overcome this deficiency. **(5 Points)**

Paragraph #3: Identify the commercial product or products resulting from this modification. **(2 Points)**

These Variations of Polyethylene Lead to a Diversity of Products

Linear Versions:

High density polyethylene (HDPE)

Ultra-high molecular weight polyethylene (UHMWPE)

Branched Versions:

Low-density polyethylene (LDPE)

Linear low density polyethylene (LLDE)

Medium-density polyethylene (MDPE)

Very-low-density polyethylene (VLDPE)

High-molecular-weight polyethylene (HMWPE)

Ultra-low-molecular-weight polyethylene (ULMWPE)

Chlorinated polyethylene (CPE)

Bimodal and Trimodal Polyethylene

Cross-linked polyethylene (PEX): four forms (PEX-a, PEX-b . . etc)

Simplest of Molecular Structures Can Lead to a Large Diversity of Structures.

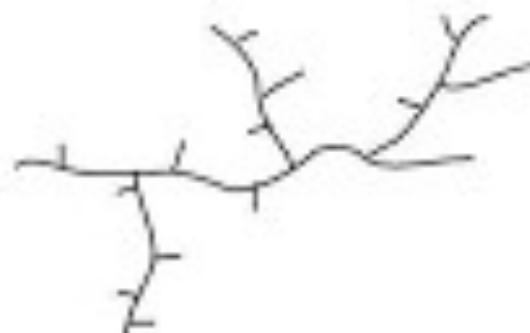
Three fundamental features of polyethylene leading to the diversity of structures and in turn performance are:

- a. **Short chain** and long chain branching.
- b. **Co-monomer content and distribution.**
- c. Molecular weight and molecular weight distribution.

The Variance of Most Polyethylene Products is Based on Branching



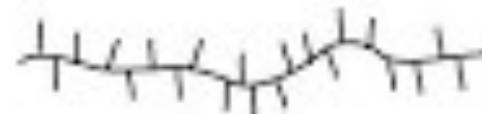
High-Density Polyethylene (HDPE)
 $X_c \sim 55\text{-}77\%$ $T_m \sim 125\text{-}132^\circ\text{C}$



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 $X_c \sim 30\text{-}54\%$ $T_m \sim 98\text{-}115^\circ\text{C}$



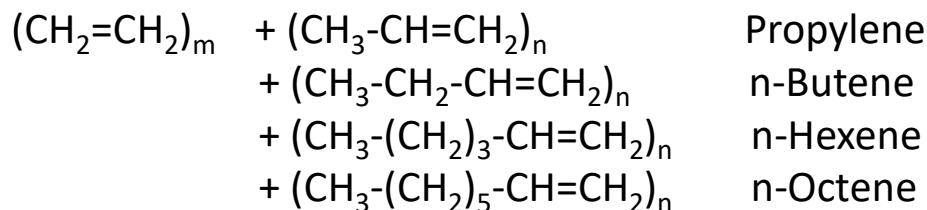
Linear Low-Density Polyethylene (LLDPE)
Branching density ~ 25-100 C atoms
 $X_c \sim 22\text{-}55\%$ $T_m \sim 100\text{-}125^\circ\text{C}$



Very Low-Density Polyethylene (VLDPE)
Branching density ~ 7-25 C atoms
 $X_c \sim 0\text{-}22\%$ $T_m \sim 60\text{-}100^\circ\text{C}$

The Comonomers used with PE Determine the Short Chain Branch Structure

□ Copolymers of Polyethylene : m>>n



□ Heterogeneous Catalysts for the Synthesis of Polyethylene Copolymers:

- i. Ziegler – Natta Catalyst
- ii. Constrained Geometry Catalyst Technology (CGCT)
- iii. “Shuttle” Technology

Morphological Property Dependence of PE

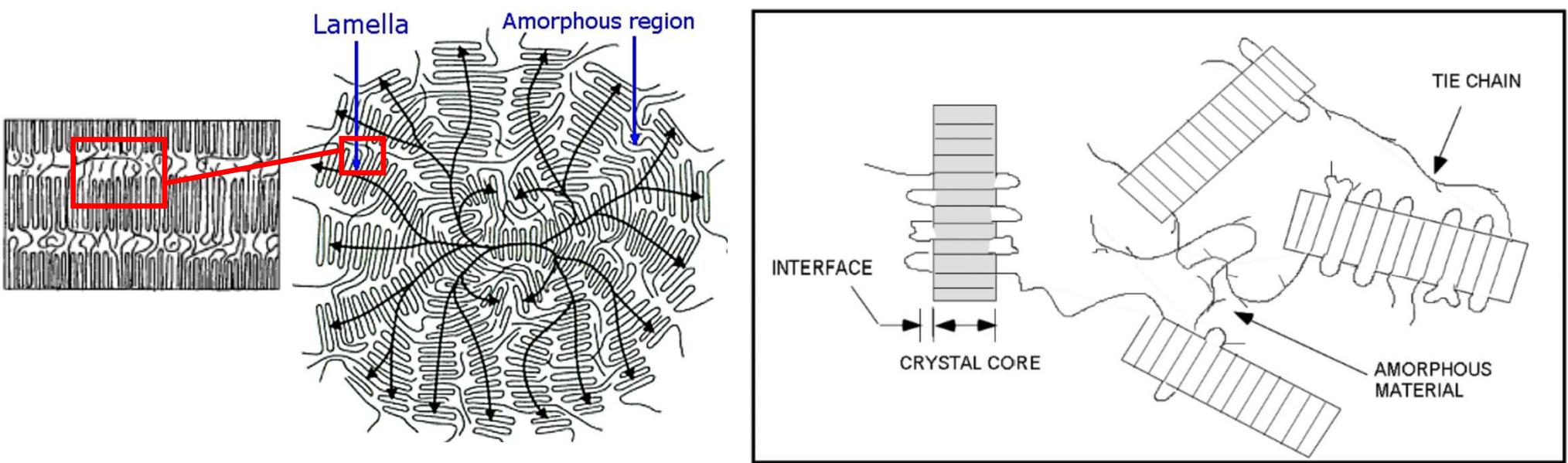


Figure 1. Graphical description of tie chains.

The critical morphological structure that determines most of the properties is the semicrystalline structure of polyethylene.

The molecular connectivity between the amorphous phase and the crystalline phase and the interconnected nature of the crystalline network defines most of the physical properties.

Octene Comonomer Provides the Highest Concentration of Tie Chains in Polyethylene

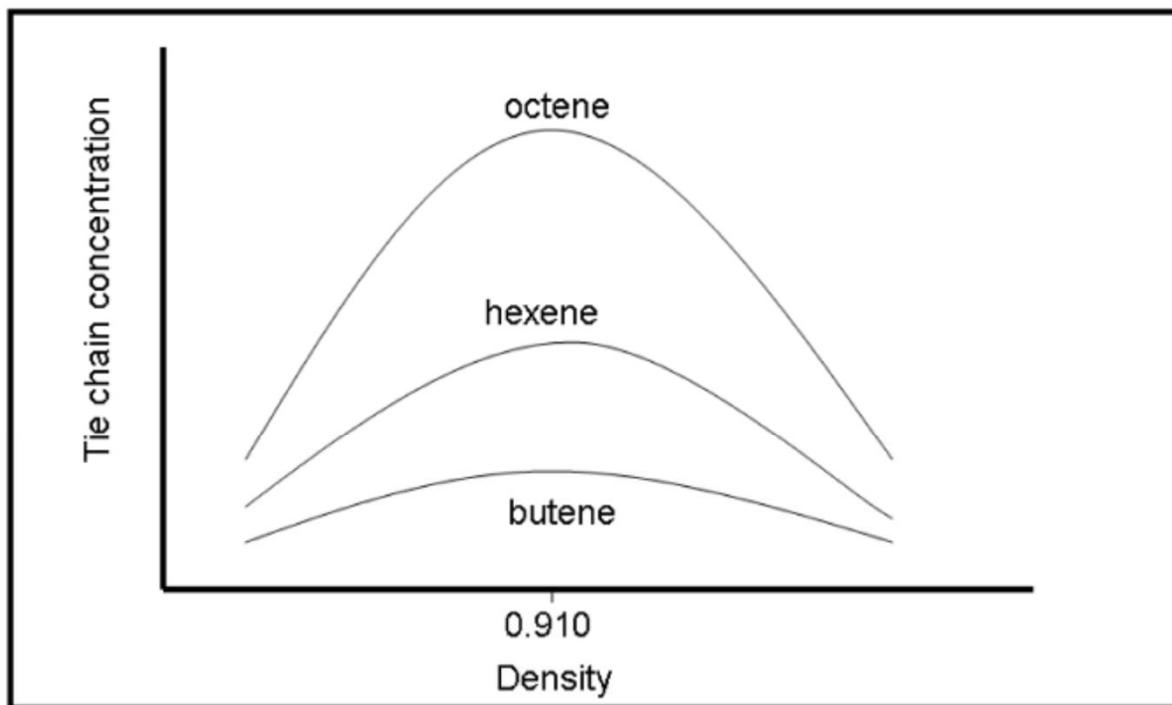
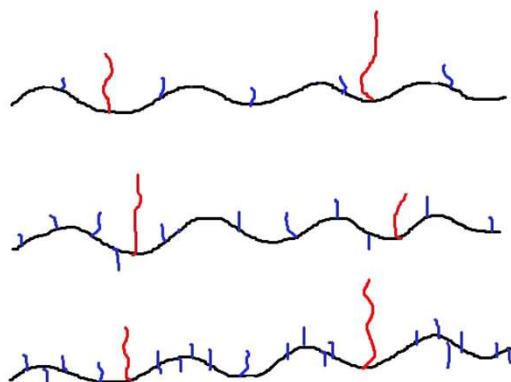


Figure 2. Tie chain concentration vs. density for common alpha olefin comonomers.

Heterogeneous Catalysts

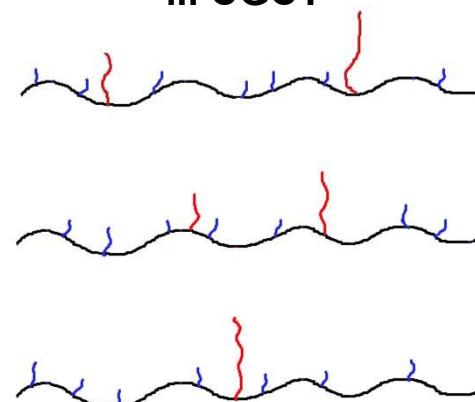
i. Ziegler – Natta Catalyst



The concentration of SCB is different in each macromolecular chain

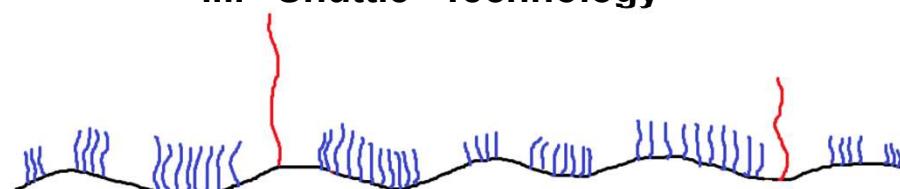
- Macromolecular Chains
- Short chain branch (random)
- Long chain branch (Ethylene)

ii. CGCT



The concentration of SCB is the same in each macromolecular chain

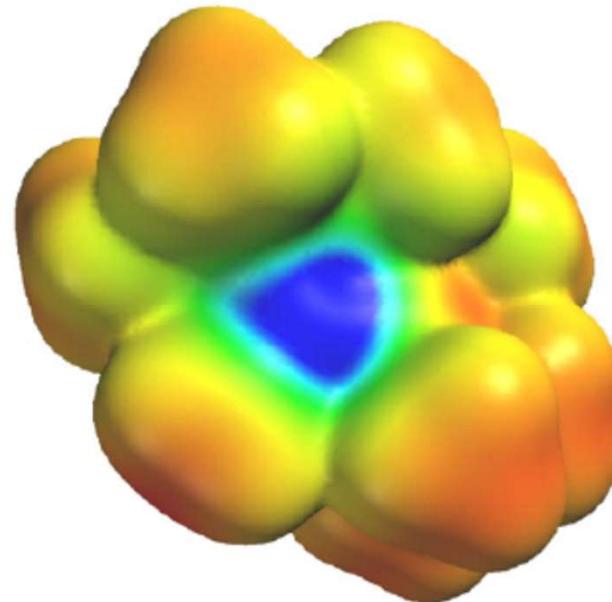
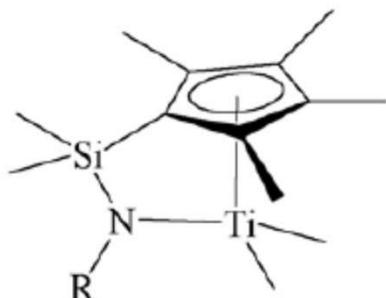
iii. “Shuttle” Technology



Blocks of SCBs with different length

Constrained Geometry Catalysis is a Metallocene Type of Catalyst

Constrained Geometry Catalysts



Example of CGC catalyst for high temperature solution polymerization of olefins having controlled levels of long-chain branching

Fig. 7. Constrained geometry catalysts (CGC) technology developed by Dow.

Benefits of CGCT for Polyethylene Copolymerization

Metallocene technology allows for the production of polyolefin copolymers with tailored molecular structures that can be modeled. The constrained geometry catalyst (CGC) technology in a solution process developed by The Dow Chemical Company in the early 90s, Trademarked INSITE® technology, has the most flexibility of the various technologies in its ability to control polymer structure design due to its simplicity of a one-phase system. This technology produces simple, homogeneous structures which can be characterized and modeled relating the structure to the physical properties.

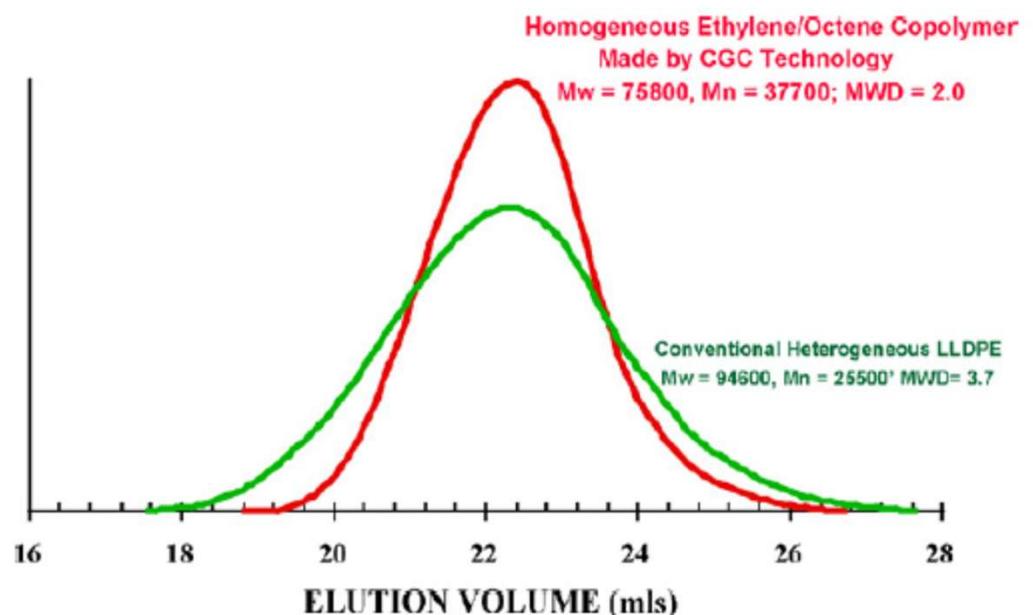
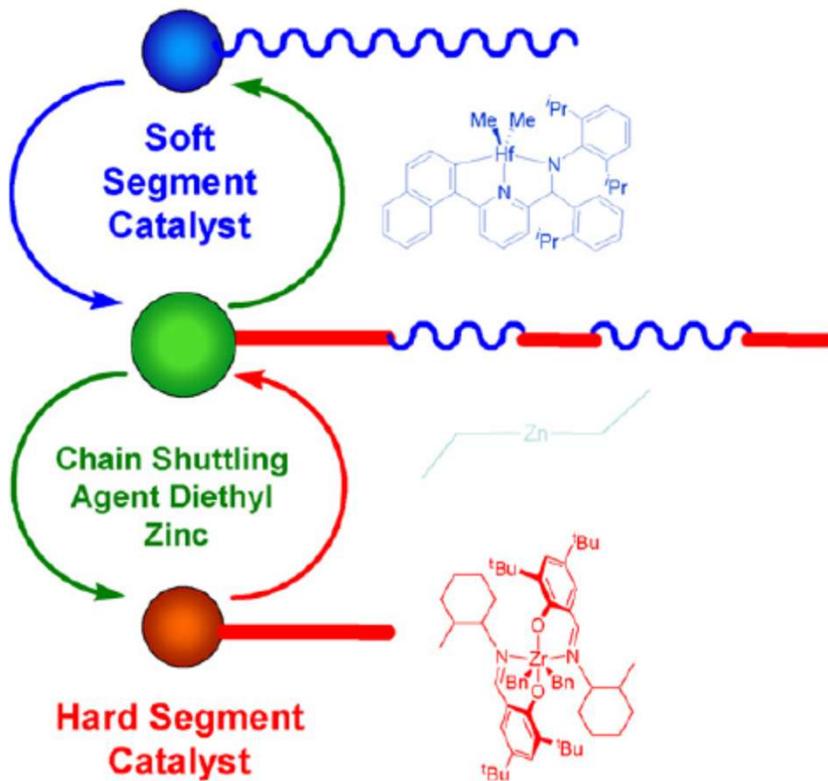


Fig. 11. GPC molecular weight distribution comparison of 2 ethylene-octene copolymers with density 0.920 g/cm^3 .

Chain Shuttling Polymerization of Ethylene - Octene

Catalytic Block Technology



Dow Chain Shuttling System

- Coupled, reversible chain transfer between 2 different catalysts in one reactor
- High catalyst efficiency
- Excellent control of average block lengths
- Excellent control of number of blocks per chain
- Compatible with a wide variety of low cost monomers (octene, butene, etc.)
- Made in Dow's solution process

Fig. 26. Chain shuttling technology for olefin block copolymers.

Classification of Homogeneous Ethylene-Octene Copolymers Based on Comonomer Content

S. BENSON,¹ J. MINICK,^{1*} A. MOET,^{1†} S. CHUM,² A. HILTNER,^{1‡} and E. BAER¹

¹Department of Macromolecular Science and Center for Applied Polymer Research, Case Western Reserve University, Cleveland, Ohio 44106; ²Polyolefins and Elastomers Research and Development, The Dow Chemical Company, Freeport, Texas 77541

Table I. Constrained Geometry Catalyst Technology (CGCT) Polymers

Polymer Designation	Pellet Density (g/cc)	Mole % Comonomer	I_2 (g/10 min)	I_{10}/I_2
CGCT96-H	0.9550	0	1.0	8.0
CGCT9180-O	0.9158	2.8	1.0	8.7
CGCT9099-O	0.9079	4.0	1.0	9.3
CGCT9016-O	0.9014	5.2	0.9	8.8
CGCT896-O	0.8968	6.2	0.9	11
CGCT8817-O	0.8879	8.2	0.9	8.7
CGCT8730-O	0.8781	10.7	1.1	6.7
CGCT8702-O	0.8724	12.3	0.8	8.1
CGCT8630-O	0.8682	13.6	0.5	n/a

Morphology Dependent Properties

Systematic copolymer composition with crystallinity, morphology and tensile stress-strain behavior have been obtained using copolymers prepared by Dow's INSITE constrained geometry catalyst (CGCT) and process technology.

A composition of about 7 % octane comonomer (approximately 30% crystallinity) marks a gradual transition in the solid state structure, characterized by a loss of spherulitic texture and a change in crystal morphology from chain folded lamellar to fringed micellar.

Morphology Dependent Properties

The transition occurs as random incorporation of increasing amounts of the non-crystallizable comonomer gradually reduces the length of the crystallizable ethylene sequences.

When the comonomer content is high enough the crystallizable sequences are not long enough to chain-fold into lamellar crystals.

In the absence of chain folding the crystallizable sequence length dictates the crystal thickness, the lateral dimensions are restricted by crowding at the crystal-amorphous interface.

STRUCTURAL MODEL FOR CGCT POLYMERS

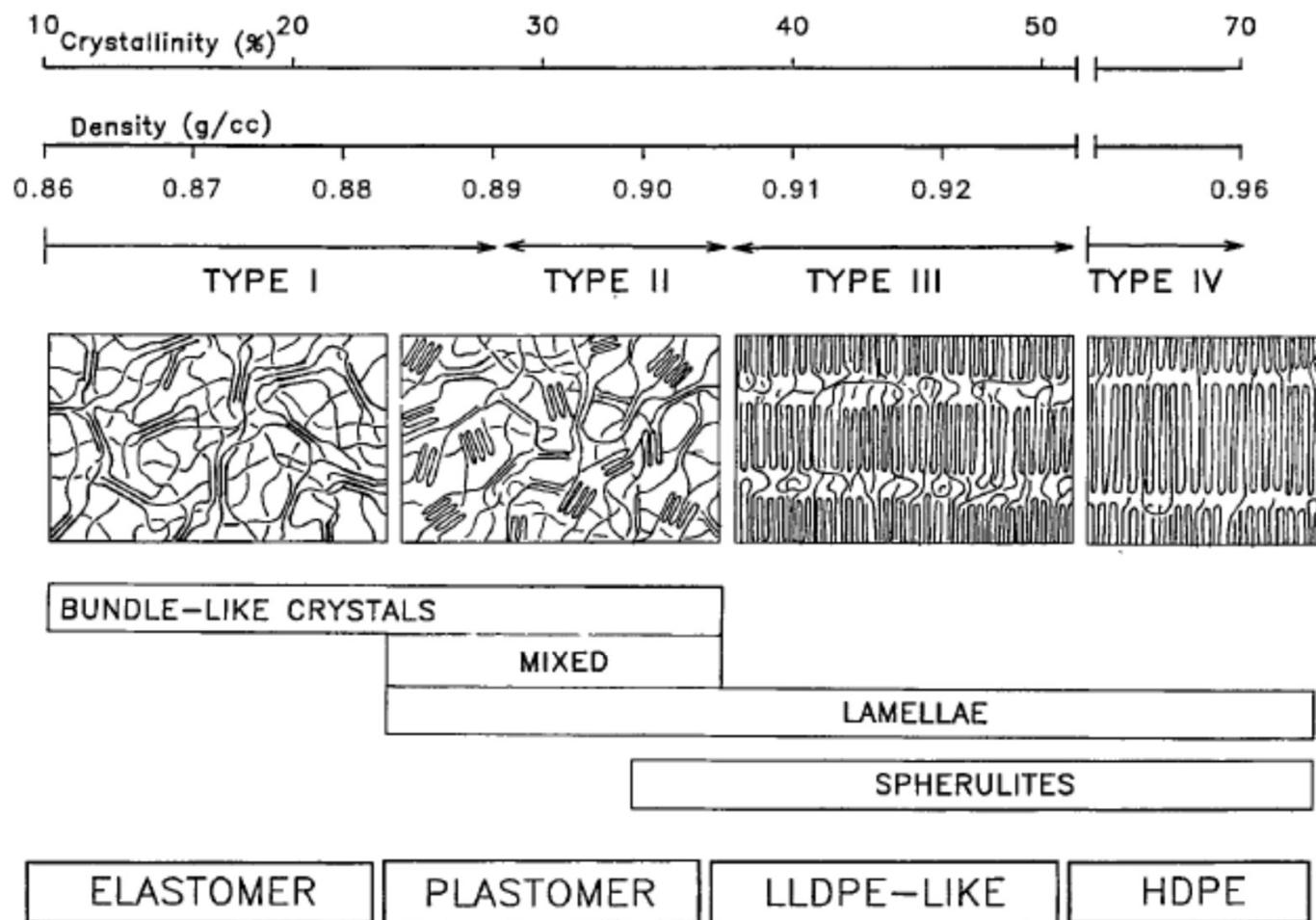


Figure 9. Schematic illustration of the four types of CGCT polymers. The terms elastomer and plastomer are taken from Hwang et al.⁷

What is a plastomer?

- A *plastomer* is a polymer material which combines qualities of elastomers and plastics, such as rubber-like properties with the processing ability of plastic. As such, the word *plastomer* is a combination of the words plastic and elastomer.
- Significant *plastomers* are ethylene-alpha olefin copolymers.

Mechanical Performance as a Function of Octene Comonomer Content

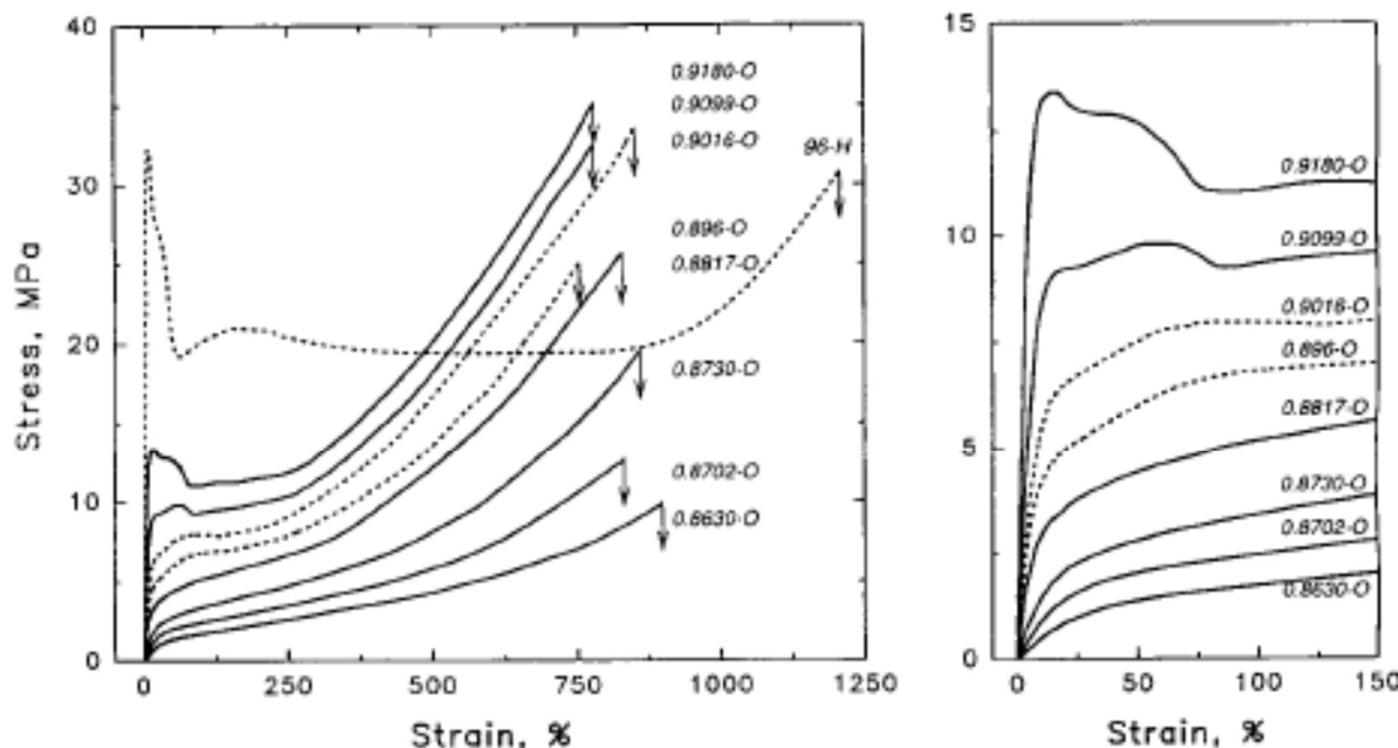


Figure 12. Engineering stress-strain curves of CGCT polymers cooled at $1^{\circ}\text{C}/\text{min}$ with the yield region of the copolymers enlarged. Results for type IV and type II polymers are given by dashed curves, those for type III and type I by solid curves.

Classification of Homogeneous Ethylene-Octene Copolymers Based on Comonomer Content

S. BENSON,¹ J. MINICK,^{1*} A. MOET,^{1†} S. CHUM,² A. HILTNER,^{1‡} and E. BAER¹

¹Department of Macromolecular Science and Center for Applied Polymer Research, Case Western Reserve University, Cleveland, Ohio 44106; ²Polyolefins and Elastomers Research and Development, The Dow Chemical Company, Freeport, Texas 77541

Table I. Constrained Geometry Catalyst Technology (CGCT) Polymers

Polymer Designation	Pellet Density (g/cc)	Mole % Comonomer	I_2 (g/10 min)	I_{10}/I_2
CGCT96-H	0.9550	0	1.0	8.0
CGCT9180-O	0.9158	2.8	1.0	8.7
CGCT9099-O	0.9079	4.0	1.0	9.3
CGCT9016-O	0.9014	5.2	0.9	8.8
CGCT896-O	0.8968	6.2	0.9	11
CGCT8817-O	0.8879	8.2	0.9	8.7
CGCT8730-O	0.8781	10.7	1.1	6.7
CGCT8702-O	0.8724	12.3	0.8	8.1
CGCT8630-O	0.8682	13.6	0.5	n/a

Mechanical Performance as a Function of Octene Comonomer Content

Table III. Tensile Properties of CGCT Polymers

Polymer	Cooling Condition	DSC Crystallinity (%)	Elastic Modulus (GPa)	Yield Stress (MPa)	Fracture Stress (MPa)	Fracture Strain (%)
CGCT96-H	1°C/min	77	1.5 ± 0.4	31.7 ± 0.6	25.6 ± 5.2	1088 ± 150
	quenched	62	0.8 ± 0.2	23.5 ± 0.6	36.9 ± 0.7	1332 ± 68
CGCT9180-O	1°C/min	46	0.4 ± 0.1	13.0 ± 0.4	34.6 ± 2.0	755 ± 30
	quenched	42	0.16 ± 0.02	9.8 ± 0.2	31.7 ± 3.6	712 ± 64
CGCT9016-O	1°C/min	33	0.12 ± 0.01	7.8 ± 0.1*	30.9 ± 0.2	761 ± 10
	quenched	31	0.055 ± 0.005	7.0*	27.8 ± 1.0	664 ± 28
CGCT8702-O	1°C/min	14	0.0065 ± 0.0007	—	12.4 ± 0.6	771 ± 16
	quenched	14	0.0070 ± 0.0004	—	12.5 ± 0.9	757 ± 15

* Plateau yield stress.

CGCT96-H = 0% Octene; CGCT9180-O = 2.8% Octene;
 CGCT9016 = 5.2% Octene; CGCT8702 = 12.3% Octene

Mechanical Performance between Quenched and Slow Cooled Poly(ethylene/octene) Copolymers

CGCT9180 = 2.8% Octene
CGCT8702 = 12.3% Octene

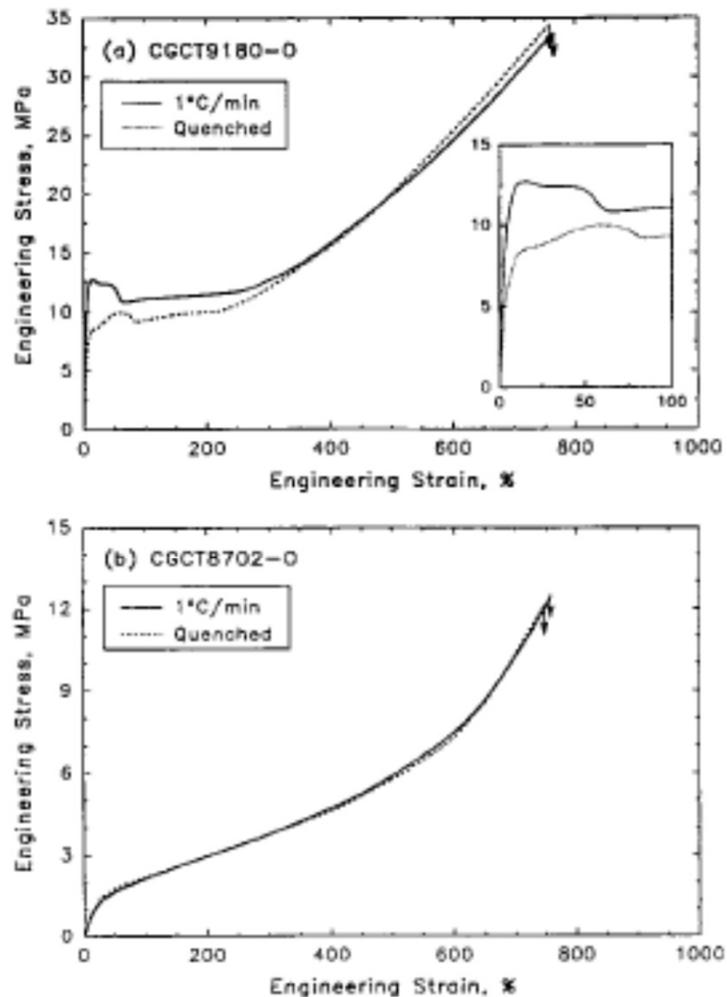


Figure 14. Effect of cooling rate on the engineering stress-strain curve: (a) CGCT9180-O; and (b) CGCT8702-O.

Correlation of Crystallinity from DSC and Density Measurements

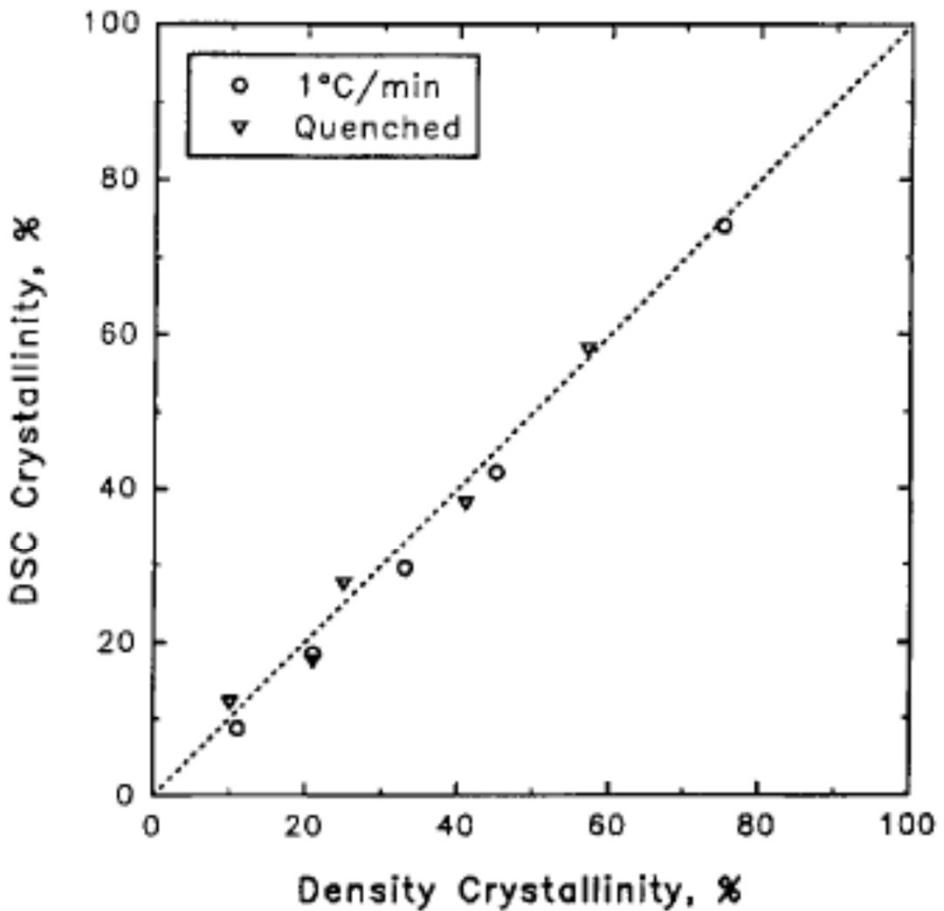
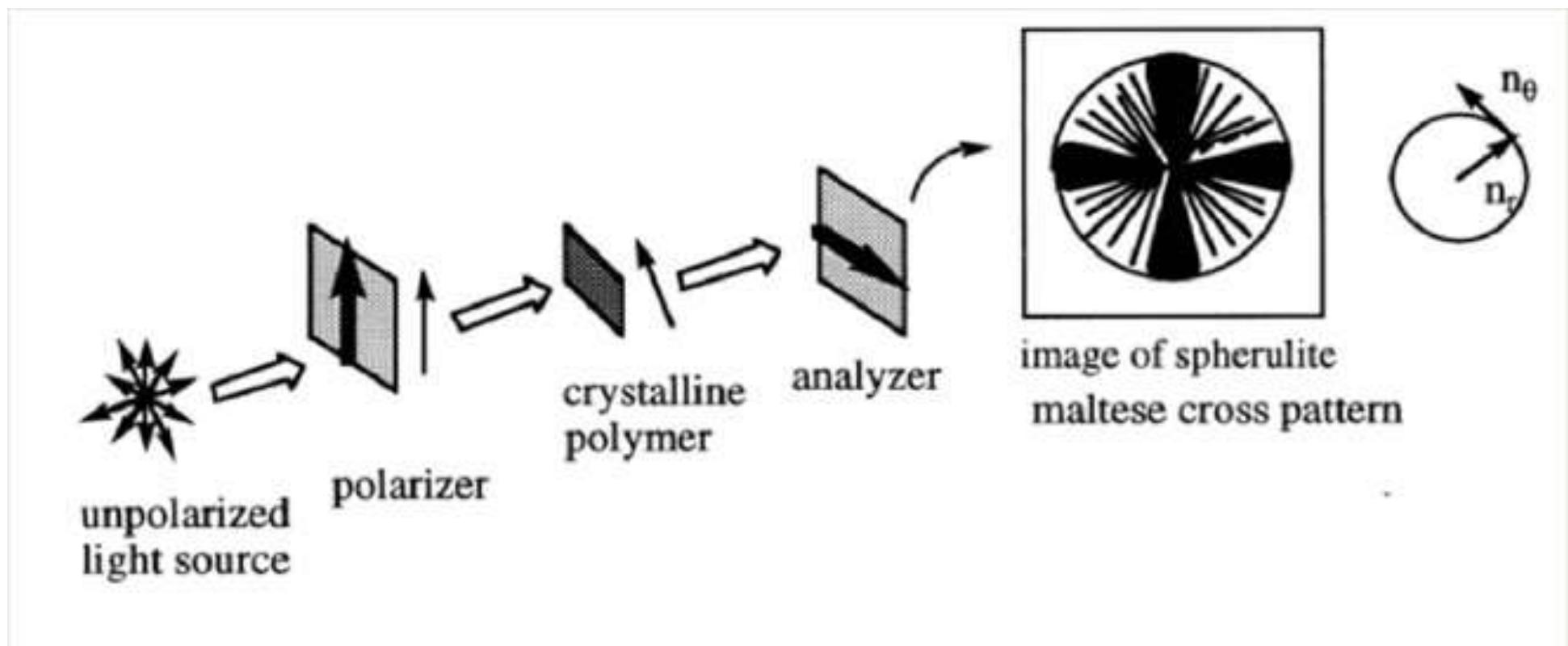
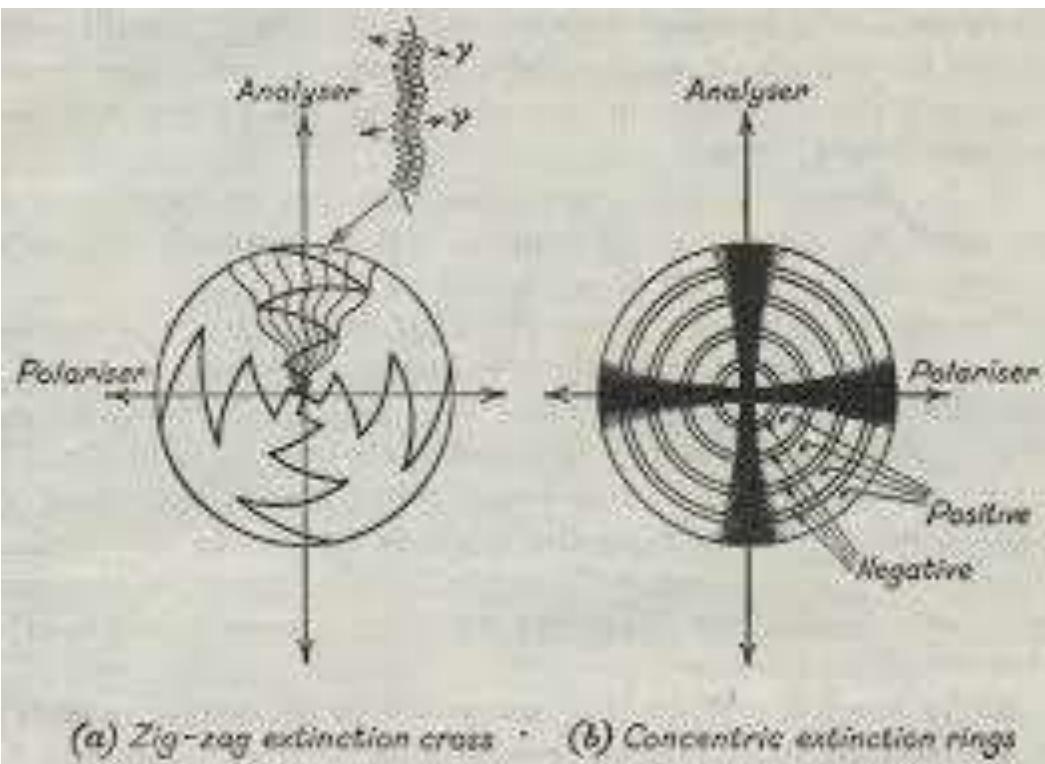
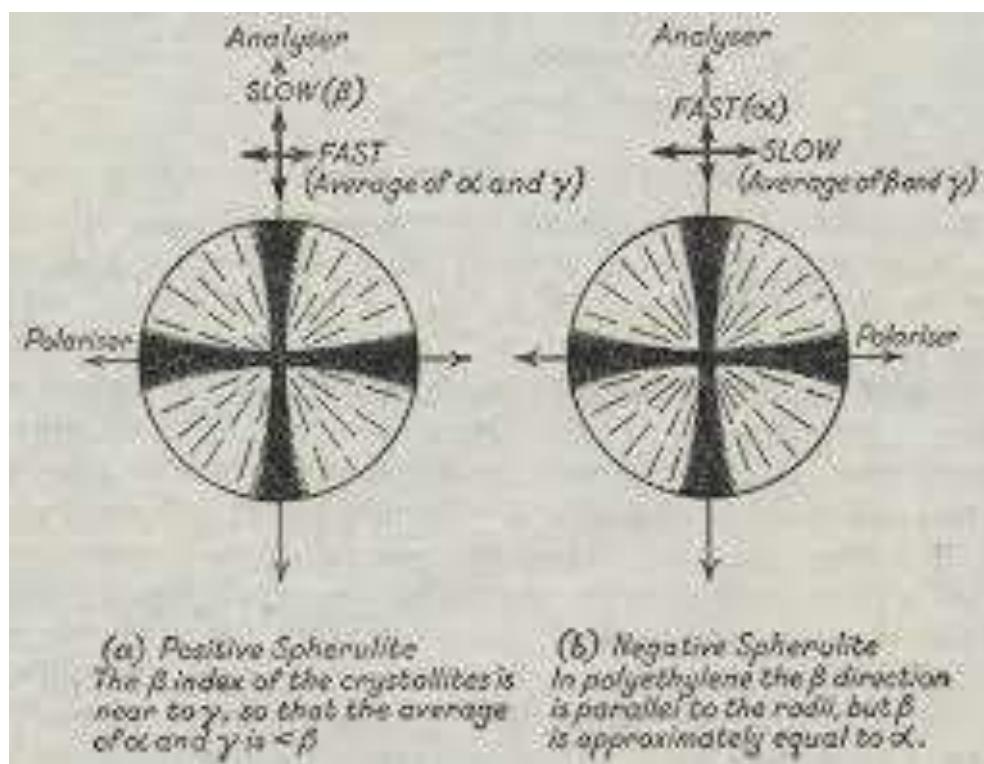


Figure 2. Plot of percent crystallinity from DSC versus percent crystallinity from density: (∇) quenched, and (\circ) cooled at $1^{\circ}\text{C}/\text{min}$.

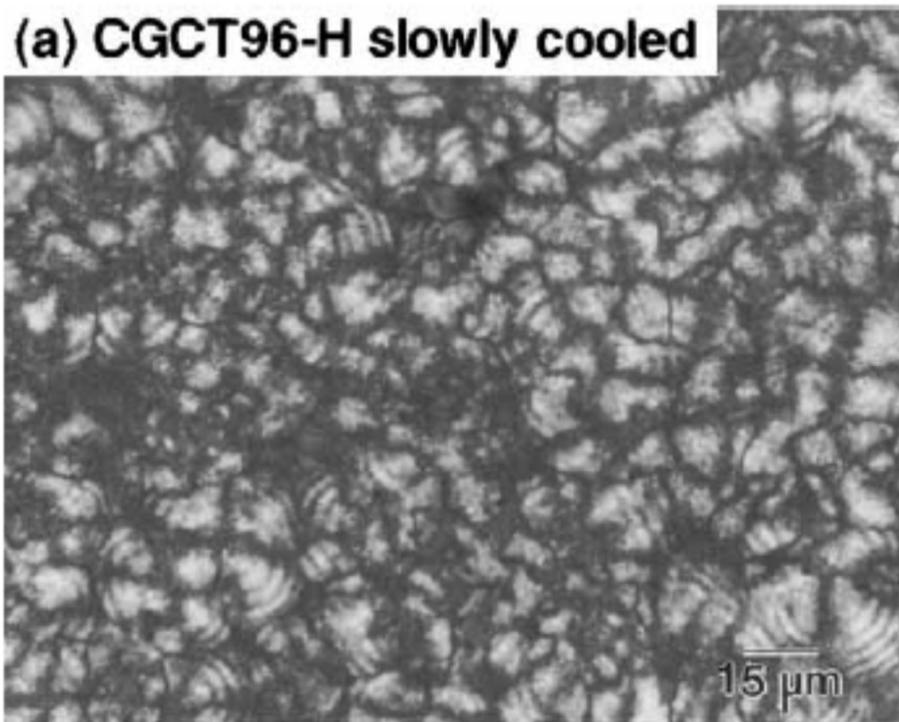
Observation of Spherulites via Polarized Light Microscopy



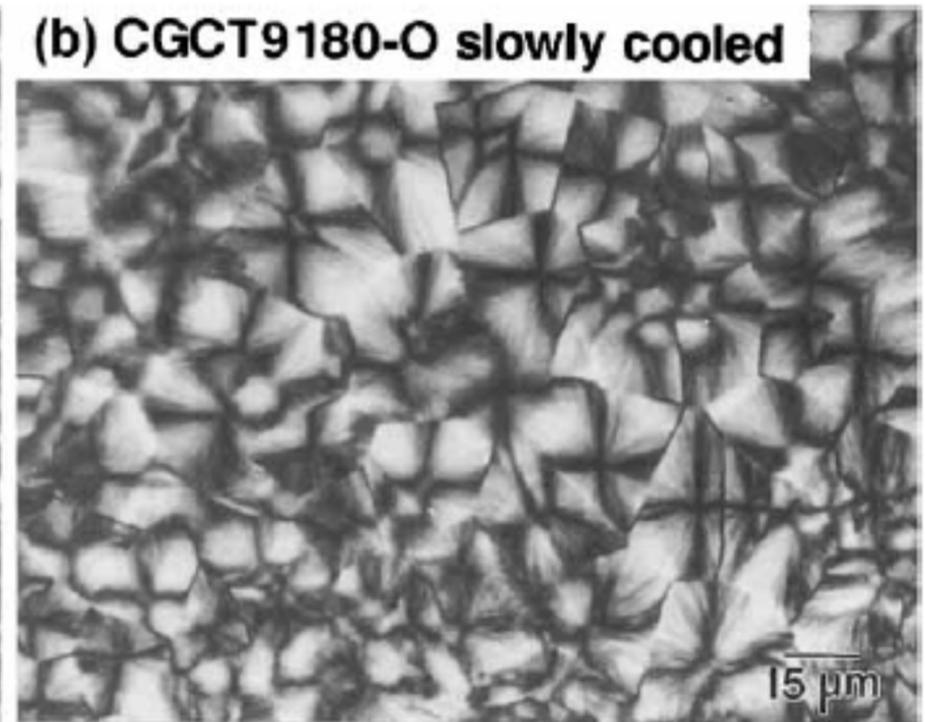
Observation of Spherulites via Polarized Light Microscopy



Spherulite Morphology Relative to Cooling Rate

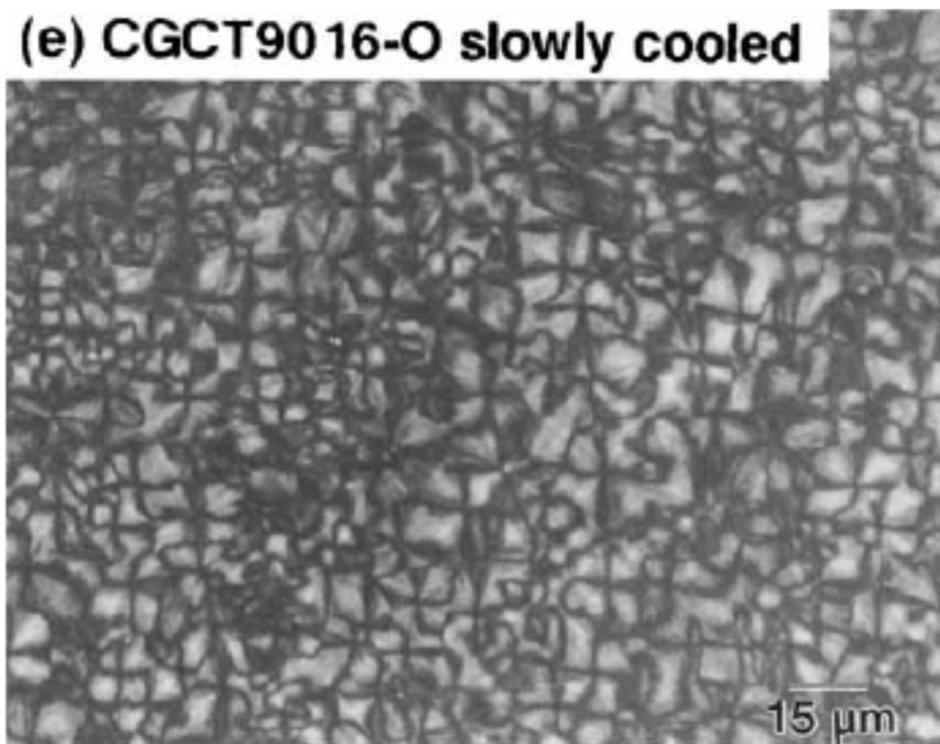


0% Octene Comonomer

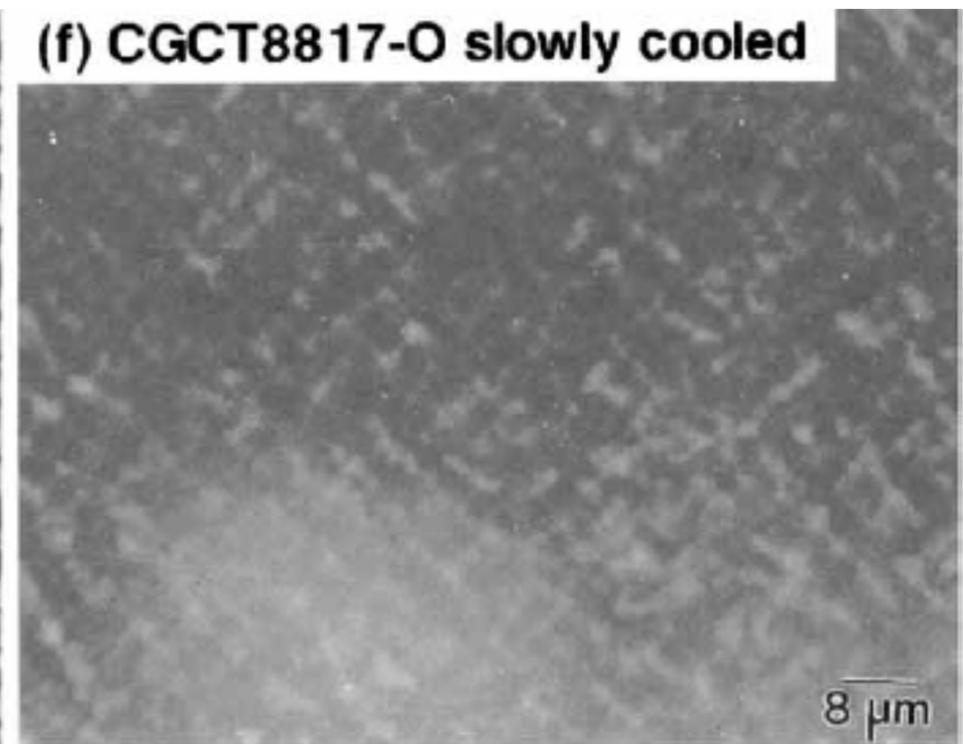


2.8% Octene Comonomer

Spherulite Morphology Relative to Cooling Rate



5.2% Octene Comonomer



8.2% Octene Comonomer

Deformation of Elastomeric Ethylene–Octene Copolymers

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*Department of Macromolecular Science and Center for Applied Polymer Research,
Case Western Reserve University, Cleveland, Ohio 44106, and Polyolefins and
Elastomers Research, The Dow Chemical Company, Freeport, Texas 77541*

Received November 15, 1996; Revised Manuscript Received February 5, 1997[®]

Table 1. Characteristics of Elastomeric CGCT Ethylene–Octene Copolymers

(a) Comonomer Content Variable						
polym desig	mol % comonomer	melt index (g/10 min)	density ^a (g/cm ³)	density crystallinity (%)	heat of melting ^b (J/g)	DSC crystallinity (%)
CGCT88	8.2	0.9	0.8883	23	55	19
CGCT87	12.3	0.8	0.8730	12	36	12
CGCT86	13.6	0.5	0.8679	9	27	9
(b) Molecular Weight Variable						
polym desig	M_w	M_n	melt index (g/10 min)	density ^a (g/cm ³)	density crystallinity (%)	heat of melting ^b (J/g)
CGCT87-57K	131700 ^c	56700 ^c	0.8	0.8730	12	36
CGCT87-37K	81700	37300	5	0.8757	14	36
CGCT87-32K	68600	32000	10	0.8747	14	37
CGCT87-26K	52300	26000	30	0.8751	14	32
CGCT87-20K	40200	19700	73	0.8763	15	41

Influence of Octene Comonomer Content on the Mechanical Performance

CGCT88 = 8.2% Octene; CGCT87= 12.3% Octene CGCT86 = 13.6% Octene

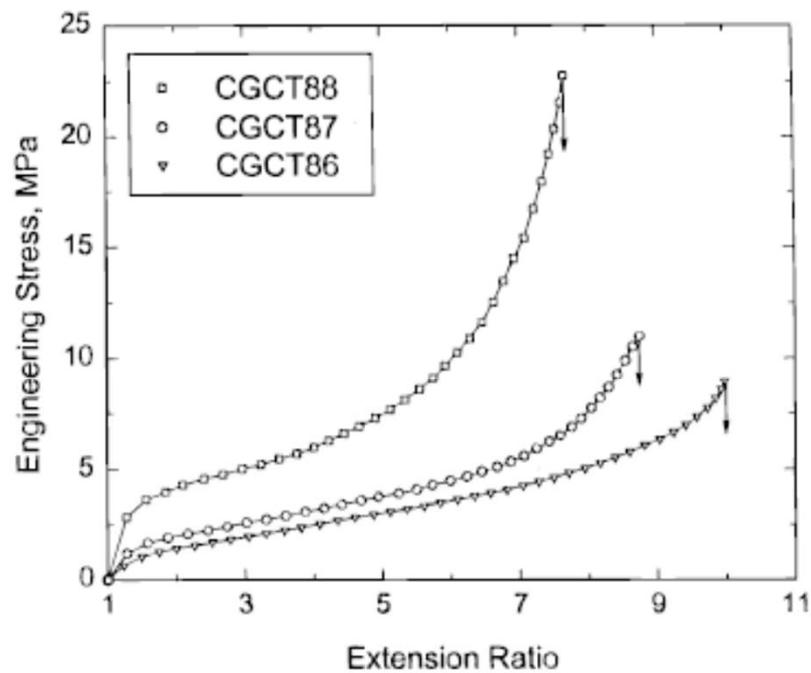


Figure 1. Stress-strain curves of three elastomeric CGCT copolymers at room temperature.

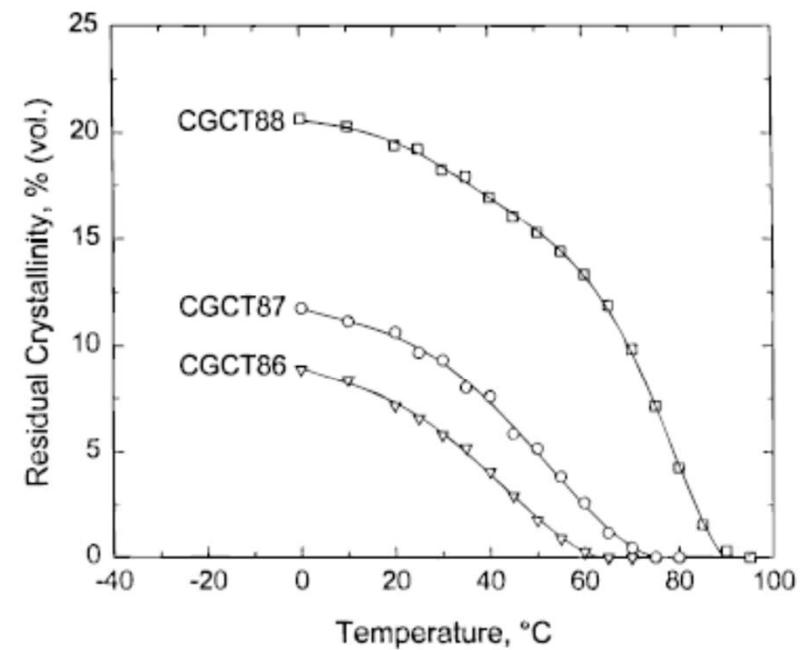
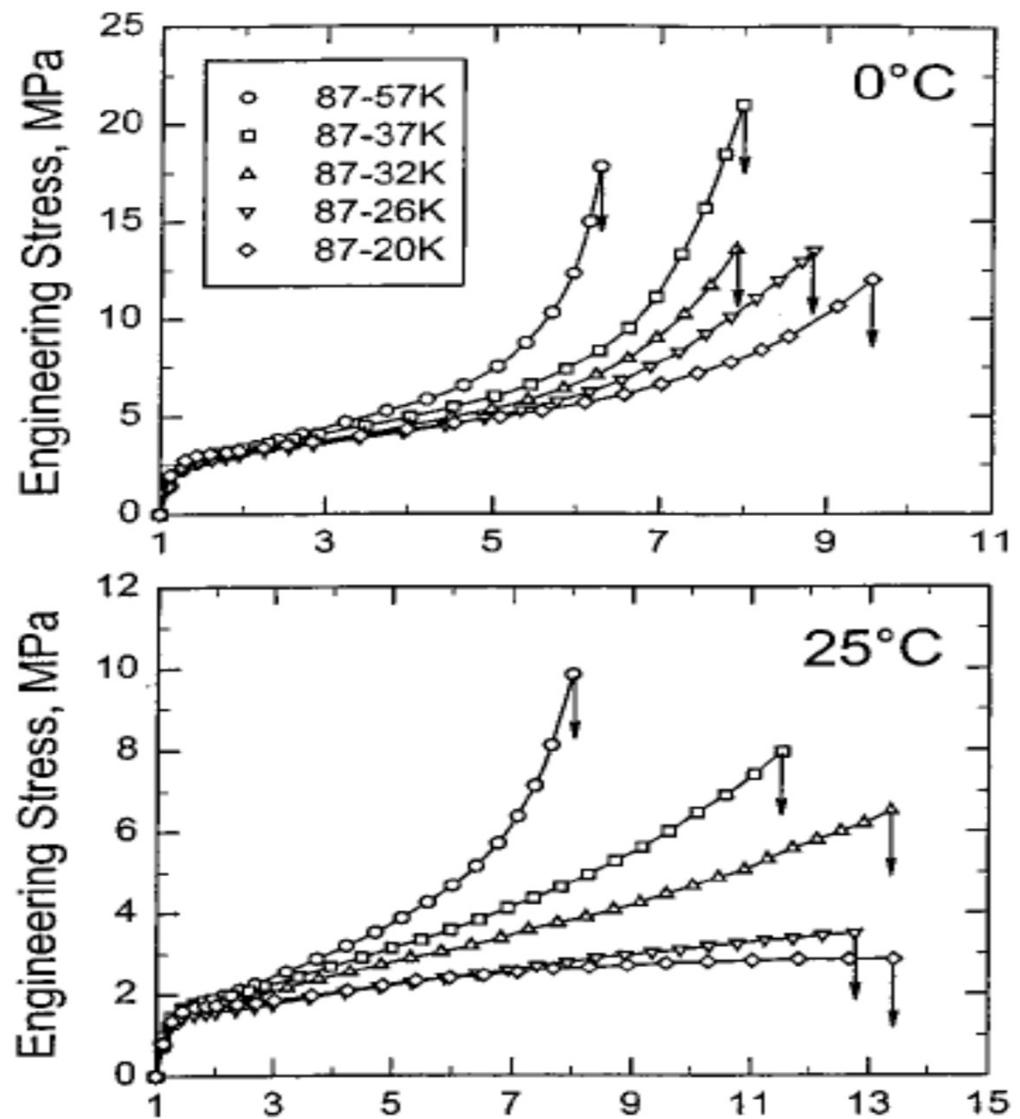


Figure 2. Volume crystallinity as a function of temperature in the melting range.

Influence of Molecular Weight on the Mechanical Performance of Ethylene-Octene Copolymers; 12.3% Octane.

Figure 11. Stress-strain curves of CGCT87 copolymers of various molecular weights: (a) at 0 °C; (b) at 25 °C; (c) at 40 °C.



Slip Link Model for Mechanical Performance

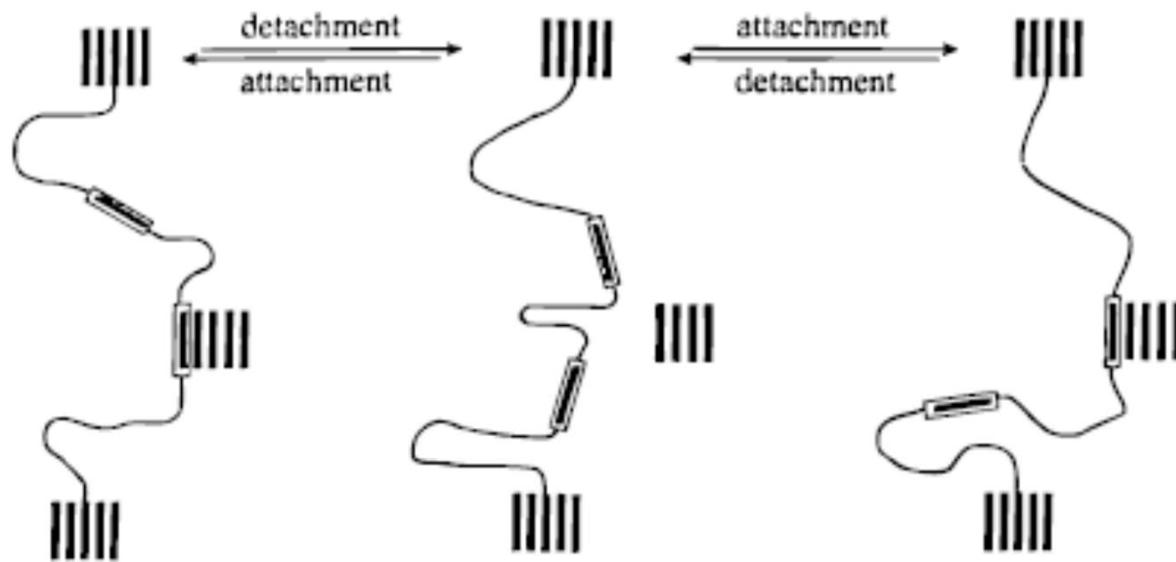


Figure 10. Schematic representation of detachment–attachment of crystallizable chain segments to produce a topological constraint equivalent to a slip-link.

Lesson 11: Polyolefin – PE 3: PE Short Chain Copolymers

Questions?



Dr. Andy Olah, amo5@case.edu, C: 216-272-0505

If life during Covid was a math word-problem :

*"You're going down a river at 2 MPH and your canoe loses a wheel,
how much pancake mix would you need to re-shingle your roof?"*

EMAC 276

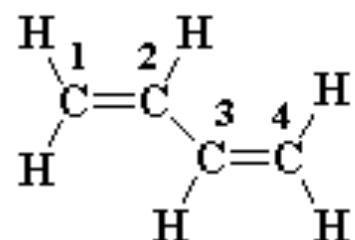
Lecture 15: Polydienes
from Natural Rubber to Synthetic Rubber
Part 1: Natural Rubber, Polyisoprene

Andy Olah, Ph.D.
February 24, 2025

What is a diene?

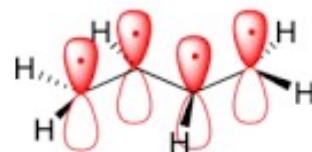
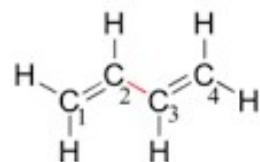
A diene is an unsaturated hydrocarbon containing two double bonds between carbon atoms.

Butadiene is the simplest diene:



Butadiene has two carbon-carbon double bonds, in the 1 and 3 positions, that is, starting at the carbon atoms numbered 1 and 3.

Dienes and Polydienes can Adopt Numerous Configurations

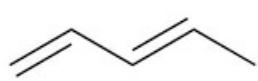


1,3-butadiene

The placement of the double bond.



Cumulated



Conjugated



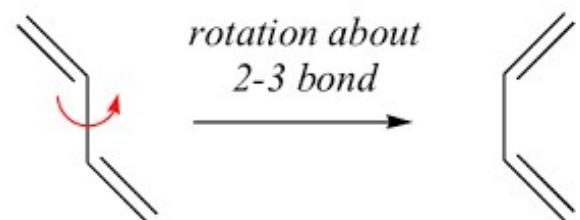
Isolated

Cumulated – pi bonds are adjacent.

Conjugated – pi bonds are separated by exactly ONE single bond.

Isolated – pi bonds are separated by any distance greater than ONE single bond.

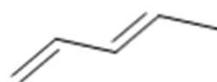
Rotation around the single bond.



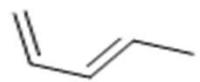
s-trans

Isolated

s-cis



s-trans

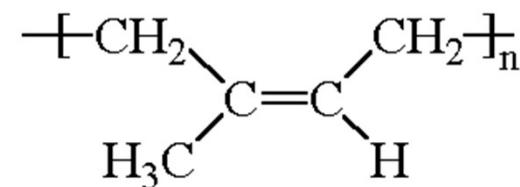


s-cis

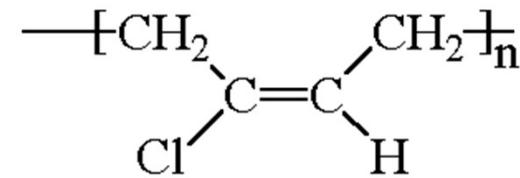
Monomer

Diene Based Polymers that We Will Consider

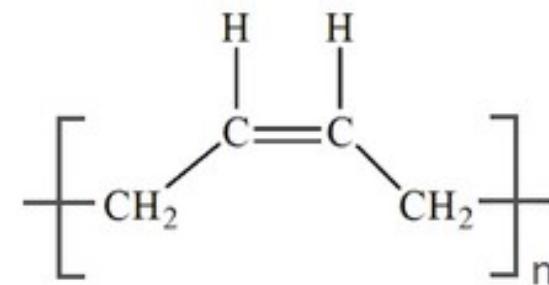
Polyisoprene



Polychloroprene (Neoprene)



Polybutadiene



Caotchouc is the Origin of Rubber

caou·tchouc/noun

'kou,CHōok,-,CHōo(k)/noun:
unvulcanized natural rubber.

Natural rubber, also called by other names of **India rubber, latex, Amazonian rubber, caucho** or **caoutchouc**, as initially produced, consists of polymers of the organic compound isoprene, with minor impurities of other organic compounds, plus water. Forms of polyisoprene that are used as natural rubbers are classified as elastomers.



Origin of “Rubber”: Material and Name

The first use of rubber was by the indigenous cultures of Mesoamerica. The earliest archeological evidence of the use of natural latex from the *Hevea* tree comes from the Olmec culture, (1200 BCE) in which rubber was first used for making balls for the Mesoamerican ballgame. Rubber was later used by the Maya and Aztec cultures.

1736 – Charles Marie de la Condamine 1751 introduced samples of rubber to the French, Academie Royale des Sciences.

1751 – He presented a paper on the properties of rubber.



Origin of “Rubber”: Material and Name

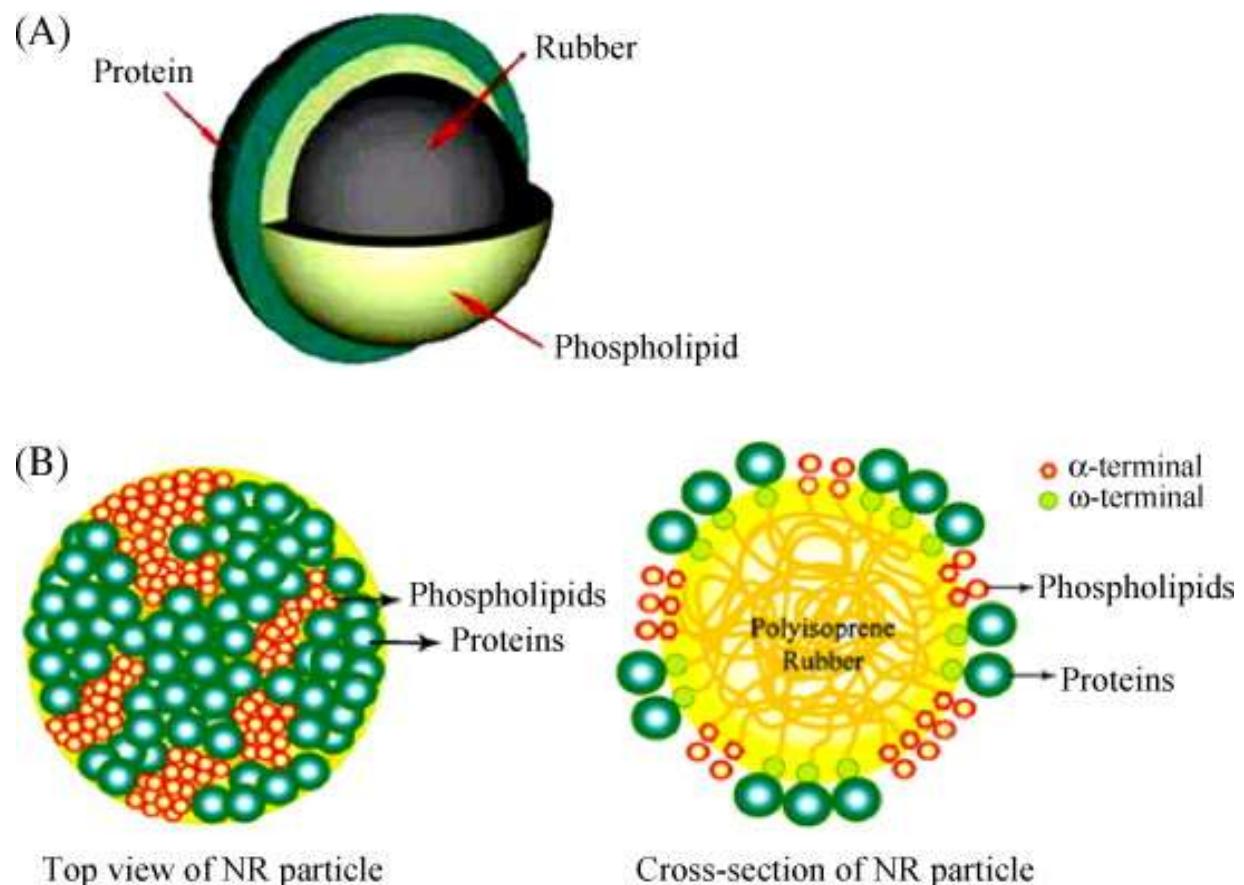
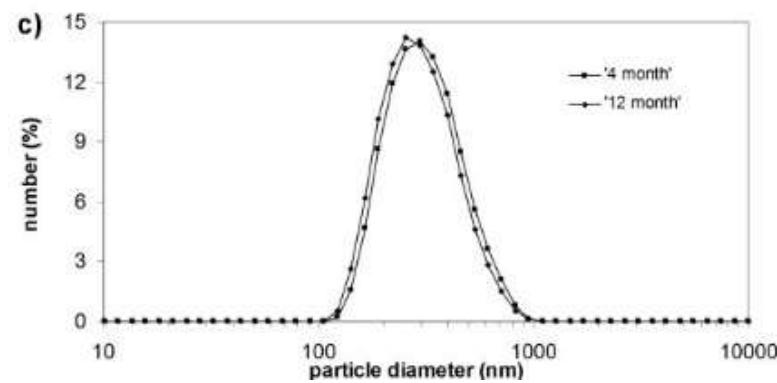
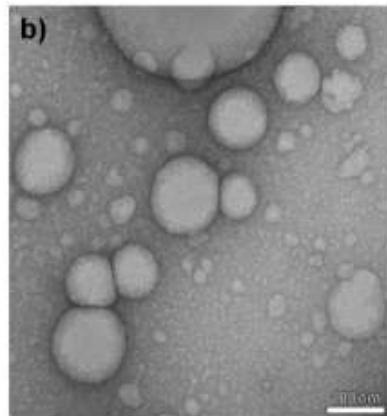
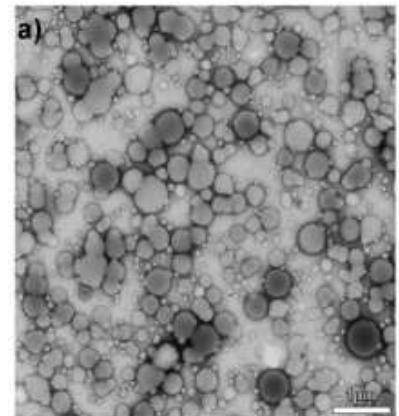
Ancient rubber was made from latex of the rubber tree (*Castilla elastica*), which is indigenous to the tropical areas of southern Mexico and Central America. The latex was made into rubber by mixing it with the juice of what was likely *Ipomoea alba* (a species of morning glory), a process which preceded Goodyear's vulcanization by several millennia. The resultant rubber would then be formed into rubber strips, which would be wound around a solid rubber core to build the ball.



Origin of the term “Rubber”

In England, Joseph Priestley, in 1770, observed that a piece of India gum (i.e., natural rubber) was extremely good for rubbing off pencil marks on paper, hence the name "rubber".

Composition of Rubber Latex and Natural Rubber



Composition of Rubber Latex and Natural Rubber

	<i>Latex^a</i>		<i>Dry rubber^c</i>
	<i>% w/v fresh latex^a</i>	<i>% w/w dry matter of latex^b</i>	<i>% w/w dry matter</i>
Rubber hydrocarbon	35.0	87.0	94.0
Proteins	1.5	3.7	2.2
Carbohydrates	1.5	3.7	0.4
Lipids	1.3	3.2	3.4
Organic solutes	0.5	1.1	0.1
Inorganic substances	0.5	1.2	0.2

Approximate values only (highly dependent on clone, season and physiological status of the tree).

^aaveraged from data published by Wititsuwannakul, 2001.¹⁰⁰

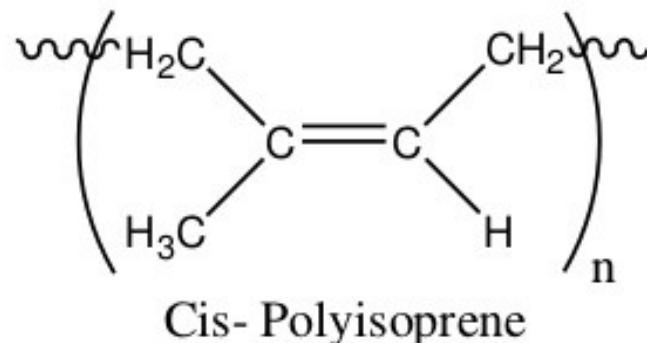
^bcalculated.

^cSainte-Beuve, 2006.¹¹⁵

Latex, colloidal suspension, either the milky white liquid emulsion found in the cells of certain flowering plants such as the rubber tree (*Hevea brasiliensis*) or any of various manufactured water emulsions consisting of synthetic rubber or plastic

Composition of Rubber Latex and Natural Rubber

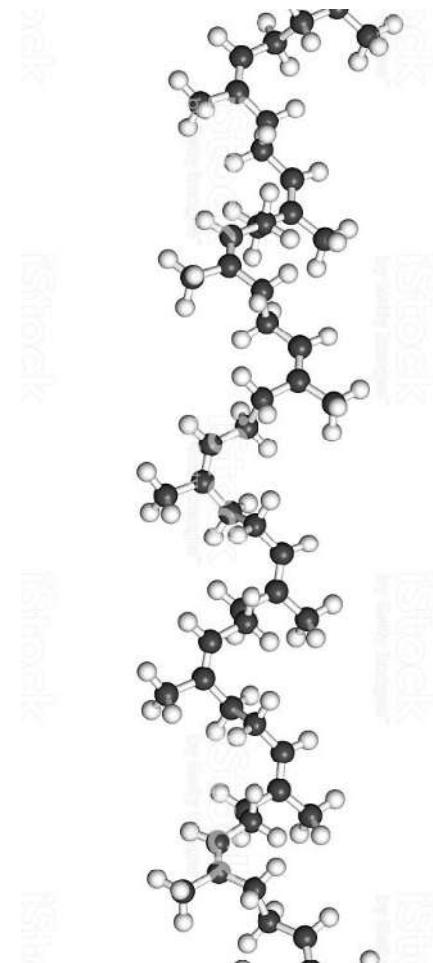
Polyisoprene (Natural Rubber)



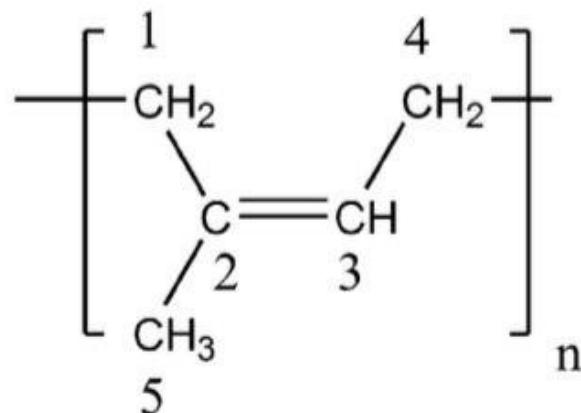
Natural Rubber contains 98% cis 1,4-Polyisoprene

Natural rubber is characterized to have

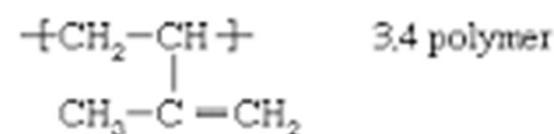
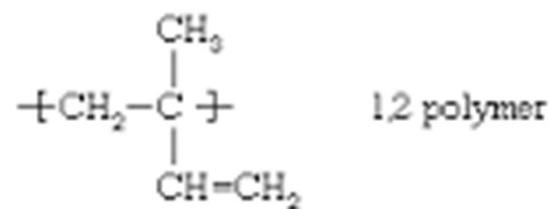
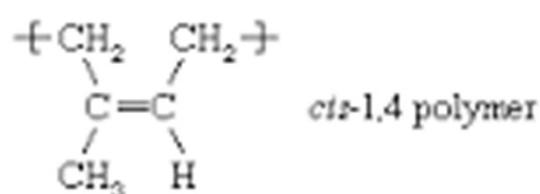
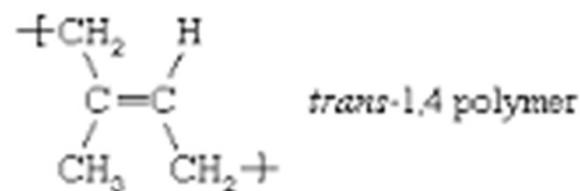
- Good elastic properties, amorphous in nature
- Good Resilience and damping behavior
- Mw ranging from 1 to 2.5×10^6 .
- But poor resistance to heat, oxygen and ozone due to presence of high no. of unsaturation.



Configurations of Polyisoprene

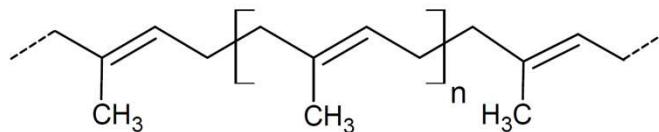


cis-1,4-polyisoprene

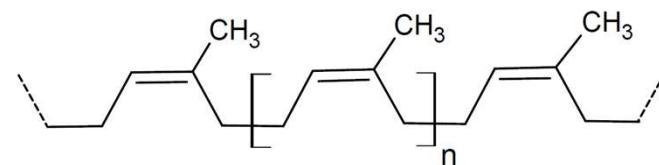


Two Configurations for 1,4-Polyisoprene

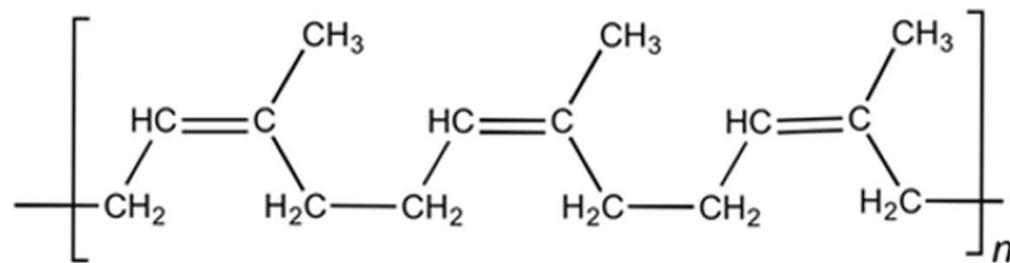
trans-1,4-Isoprene:



cis-1,4-Isoprene:



Natural Rubber is Poly-Isoprene in Cis configuration.



Composition of Rubber Latex and Natural Rubber



Dry natural rubber does not have good elastomeric properties.

The History of Charles Goodyear



In 1834 Charles Goodyear visited the Roxbury India Rubber Company In New York. The manager showed Goodyear a warehouse where Shelves held heaps of misshapen blobs, their folds stuck together. Goodyear began his work to make this material suitable for industrial Use. Moving from New York, to Massachusetts, to Philadelphia and to Connecticut Goodyear continued his experiments working primarily In his kitchen.

In 1839 while working at the Eagle India Rubber Company Goodyear accidentally combined on a hot stove natural rubber and sulfur. The resulting mixture didn't melt and flow as does natural rubber but kept it's shape, hardening further when additional heat was applied.

Charles Goodyear patented the process in 1844 after establishing the Naugatuck India-Rubber Company. He named the discovery vulcanization, after Vulcan, the Roman god of fire.

Goodyear's Vulcanization Patent

UNITED STATES PATENT OFFICE.

CHARLES GOODYEAR, OF NEW YORK, N.Y.

IMPROVEMENT IN INDIA-RUBBER FABRICS.

Specification forming part of Letters Patent No. 3,633, dated June 15, 1844.

U.S. Patent No. 3633; Issued June 15, 1844

Charles Goodyear died in 1860 at age 59, \$200,000 in debt. The Goodyear Tire and Rubber Co., was founded in Akron, Ohio, in 1898, and was named in his honor.

- Charles Goodyear never lived in Akron, Ohio.
- Charles Goodyear did not start the Goodyear Tire and Rubber Company

I do claim—

1. The combining of the said gum with sulphur and with white lead, so as to form a triple compound, either in the proportions herein named or in any other within such limits as will produce a like result; and I will here remark that although I have obtained the best results from the carbonate of lead, other salts of lead or the oxides of that metal may be substituted therefor, and will produce a good effect. I therefore under this head claim the employment of either of the oxides or salts of lead in the place of the white lead in the above-named compound.

2. The formation of a fabric of the india-rubber by interposing layers of cotton-batting between those of the gum, in the manner and for the purpose above described.

3. In combination with the foregoing, the process of exposing the india-rubber fabric to the action of a high degree of heat, such as is herein specified, by means of which my improved compound is effectually changed in its properties so as to protect it from decomposition or deterioration by the action of those agents which have heretofore been found to produce that effect upon india-rubber goods.

CHARLES GOODYEAR.

Interesting Patent found During the Goodyear Search

Nathaniel Hayward, U.S. Patent No. 1090, Issued: February 24, 1839

UNITED STATES PATENT OFFICE.

NATHANIEL HAYWARD, OF WOBURN, ASSIGNOR TO CHARLES GOODYEAR,
OF BOSTON, MASSACHUSETTS.

IMPROVEMENT IN THE MODE OF PREPARING CAOUTCHOUC WITH SULPHUR FOR THE MANUFACTURE OF
VARIOUS ARTICLES.

Specification forming part of Letters Patent No. 1,090, dated February 24, 1839.

What I claim as my invention, and desire to secure by Letters Patent, is—

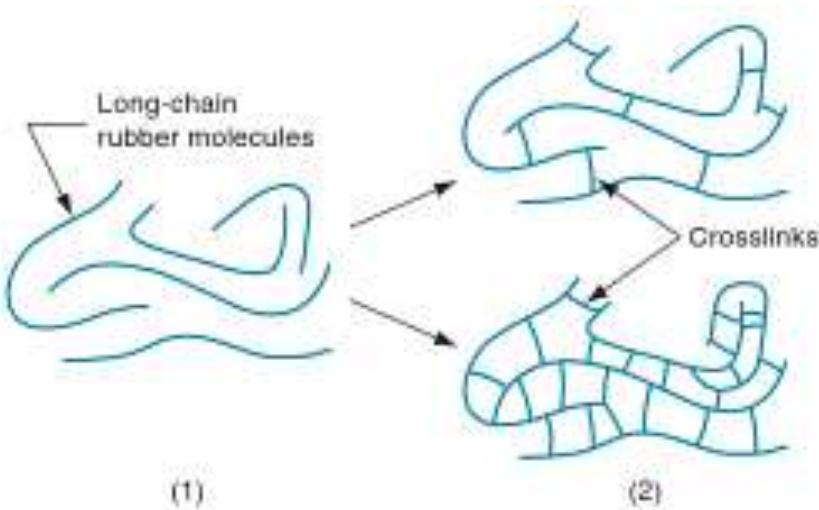
The combining of sulphur with gum-elastic, either in solution or in substance, either in the modes above pointed out or in any other which is substantially the same, and which will produce a like effect.

In witness whereof I, the said NATHANIEL HAYWARD, have hereunto set my hand this 23d day of November, A. D. 1838.

NATHANIEL HAYWARD.

IMPROVEMENT IN THE MODE OF PREPARING CAOUTCHOUC WITH SULPHUR
FOR THE MANUFACTURE OF VARIOUS ARTICLES

What Happens Molecularly During Vulcanization?



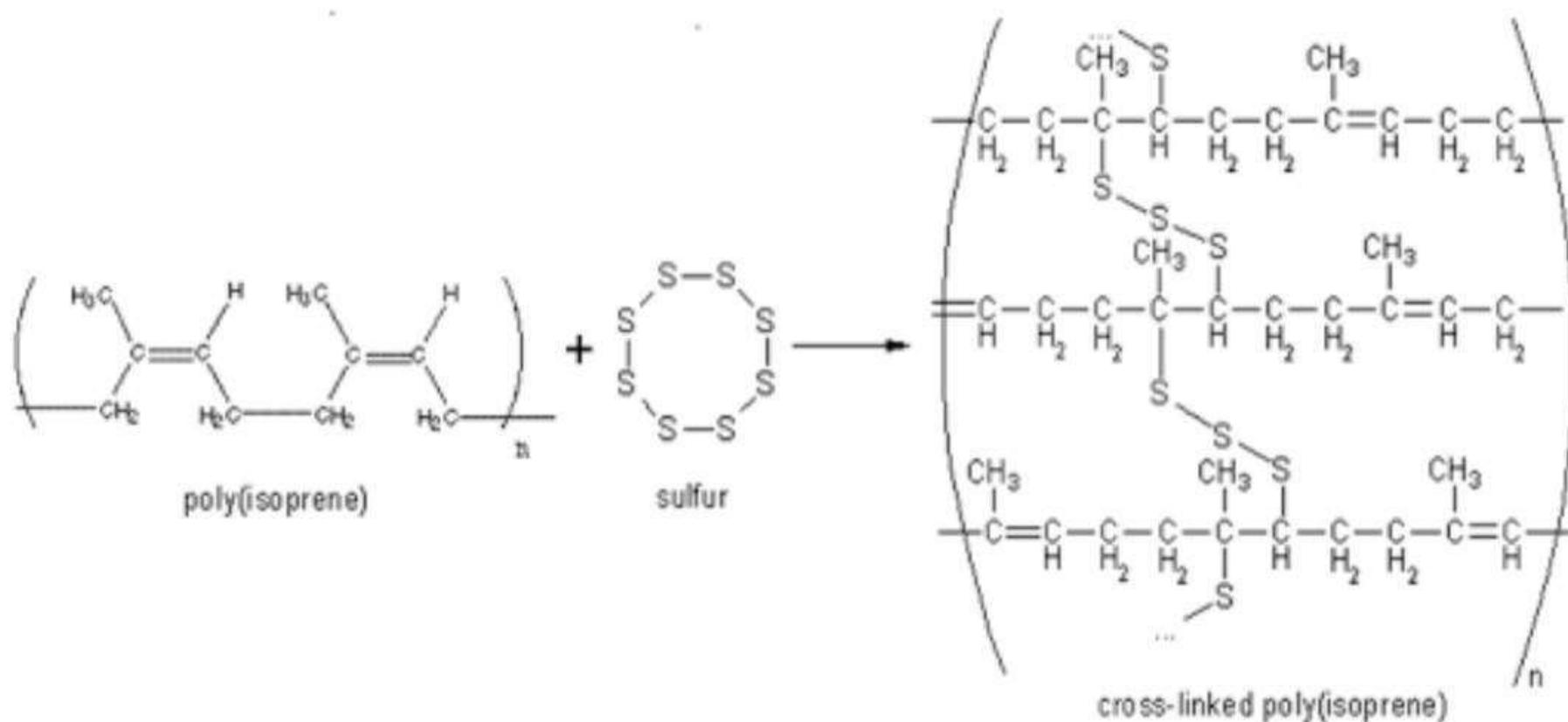
Vulcanization's effect on rubber molecules:

1. Raw rubber;
2. Vulcanized (cross-linked) rubber

Advantages of Vulcanization:

- It has good tensile strength and extensibility.
- It has excellent resilience i.e.it returns to the original shape, when the deforming load is removed.
- It possesses low water absorption tendency.
- It has higher resistance to oxidation, wear and tear abrasion.
- It is better electrical insulator.
- It is resistant to organic solvents (petro, benzene), fats and oils.
- It has slight tackiness.
- It has useful temperature range of -40.C to 100.C

What Happens Chemically During Vulcanization?



Vulcanisation

What Happens Mechanically After Vulcanization?

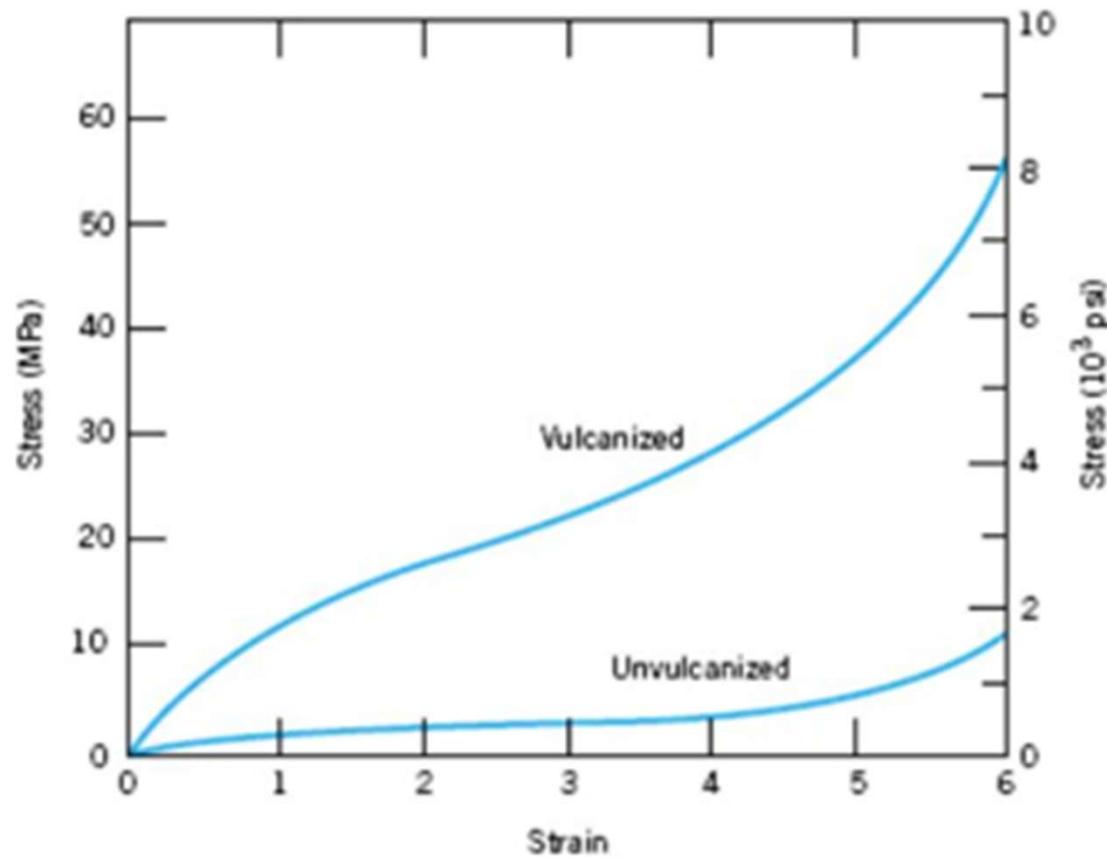
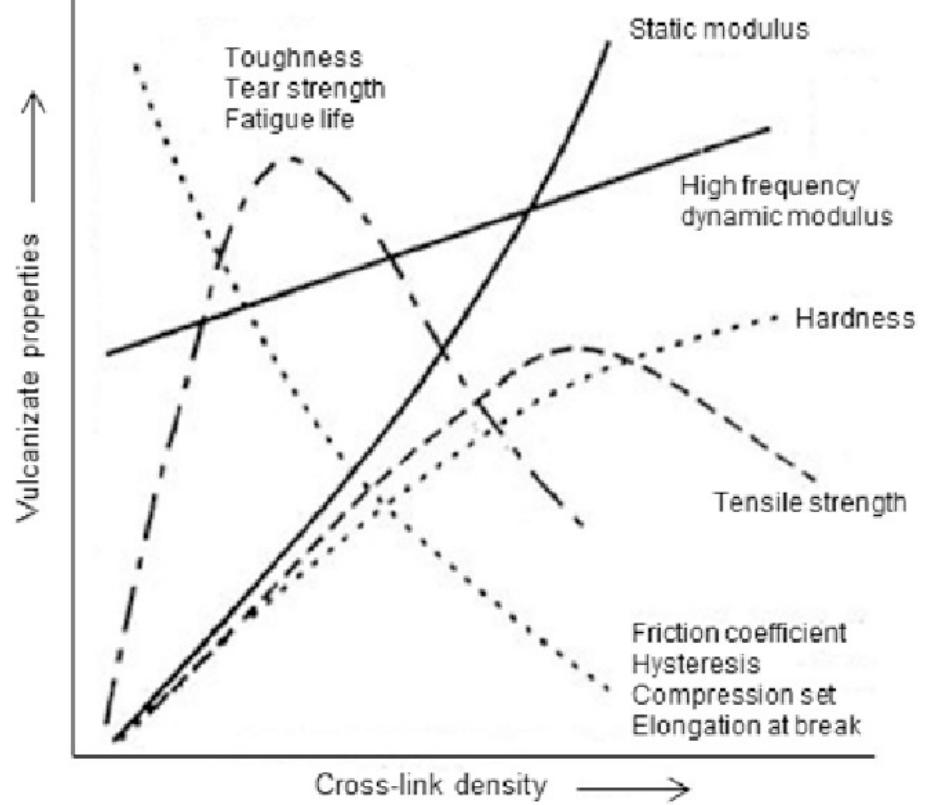
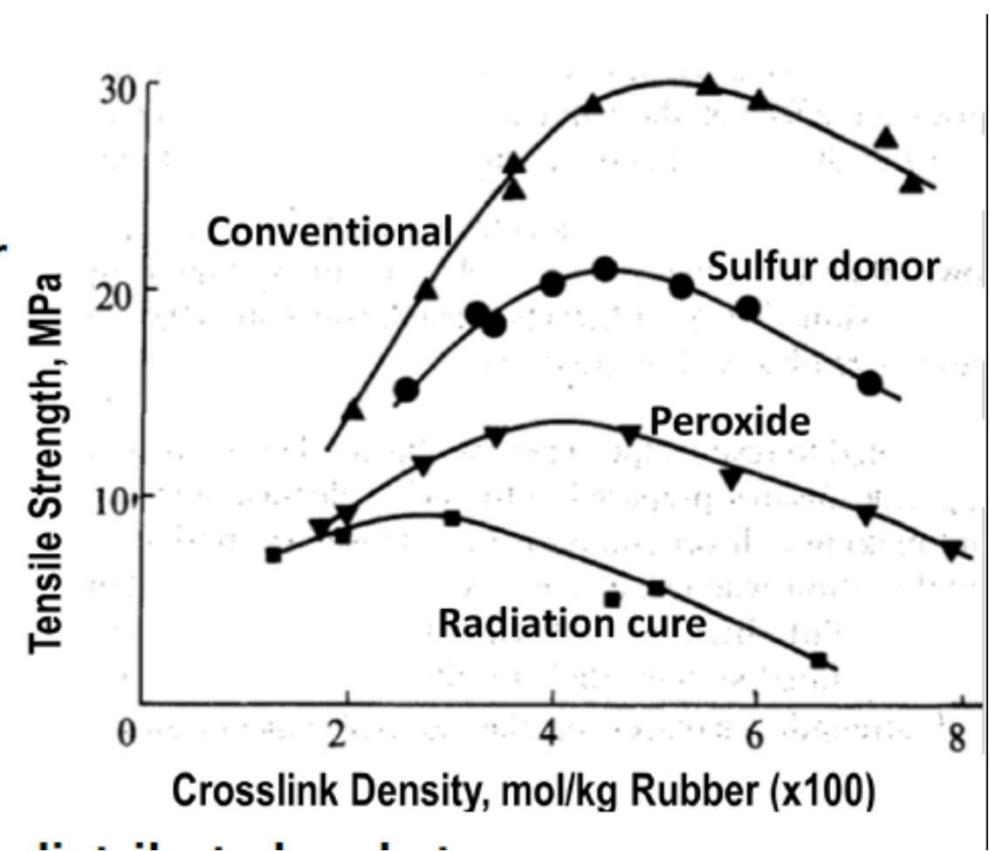
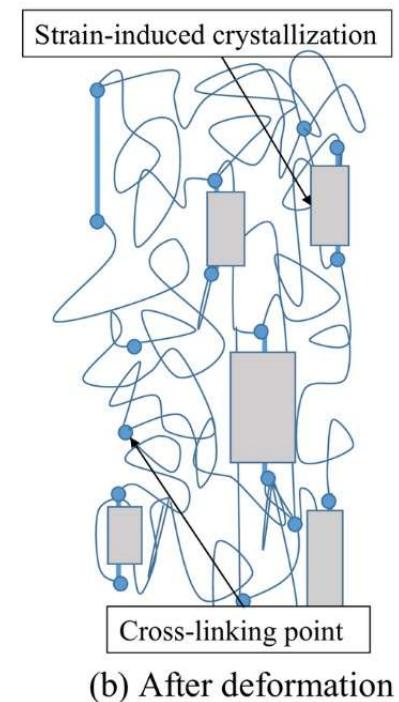
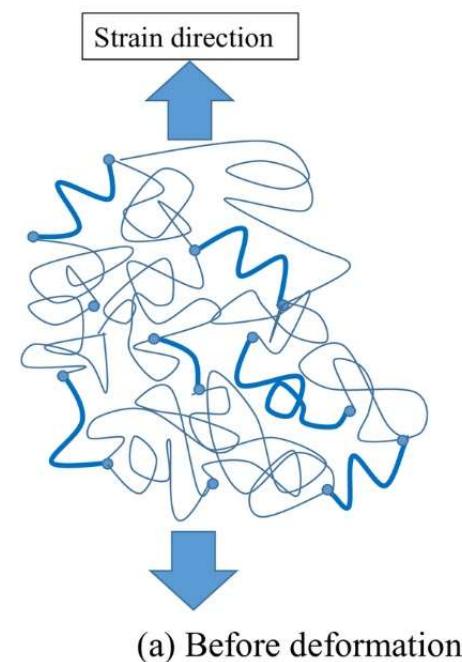
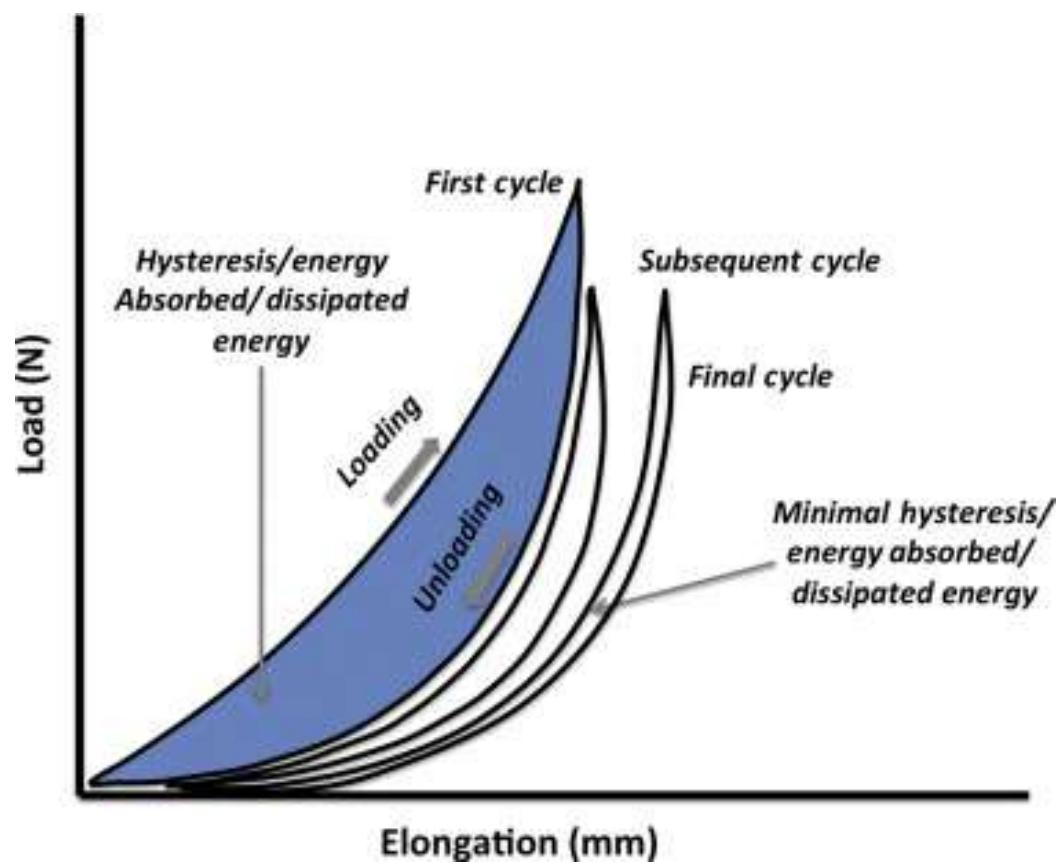


FIGURE 15.15
Stress-strain curves to 600% elongation for unvulcanized and vulcanized natural rubber.

What Happens Mechanically as a Function of Vulcanization?



Hysteresis and Strain Induced Crystallization



Commercial Production of Polyisoprene

The preparation of an all *cis*-1,4-polyisoprene, a duplicate of natural rubber, continued to elude the most extensive efforts of scientists for many more years.

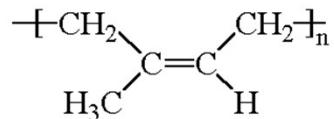
It was not until the mid 1950's that two independent catalyst systems, each capable of polymerizing isoprene to a *cis*-1,4-polymer, were disclosed.

- 1) Home and coworkers, employing a Ziegler-type catalyst prepared from trialkylaluminum and titanium tetra-chloride, polymerized isoprene to an essentially all *cis*-1,4-polyisoprene.
- 2) The other catalyst, based on lithium metal, was discovered by a Firestone Tire and Rubber research team.

In 1960, just a few years after the discovery of the stereospecific catalysts, the first commercial plant for the production of *cis*-polyisoprene with a lithium catalyst was on stream.

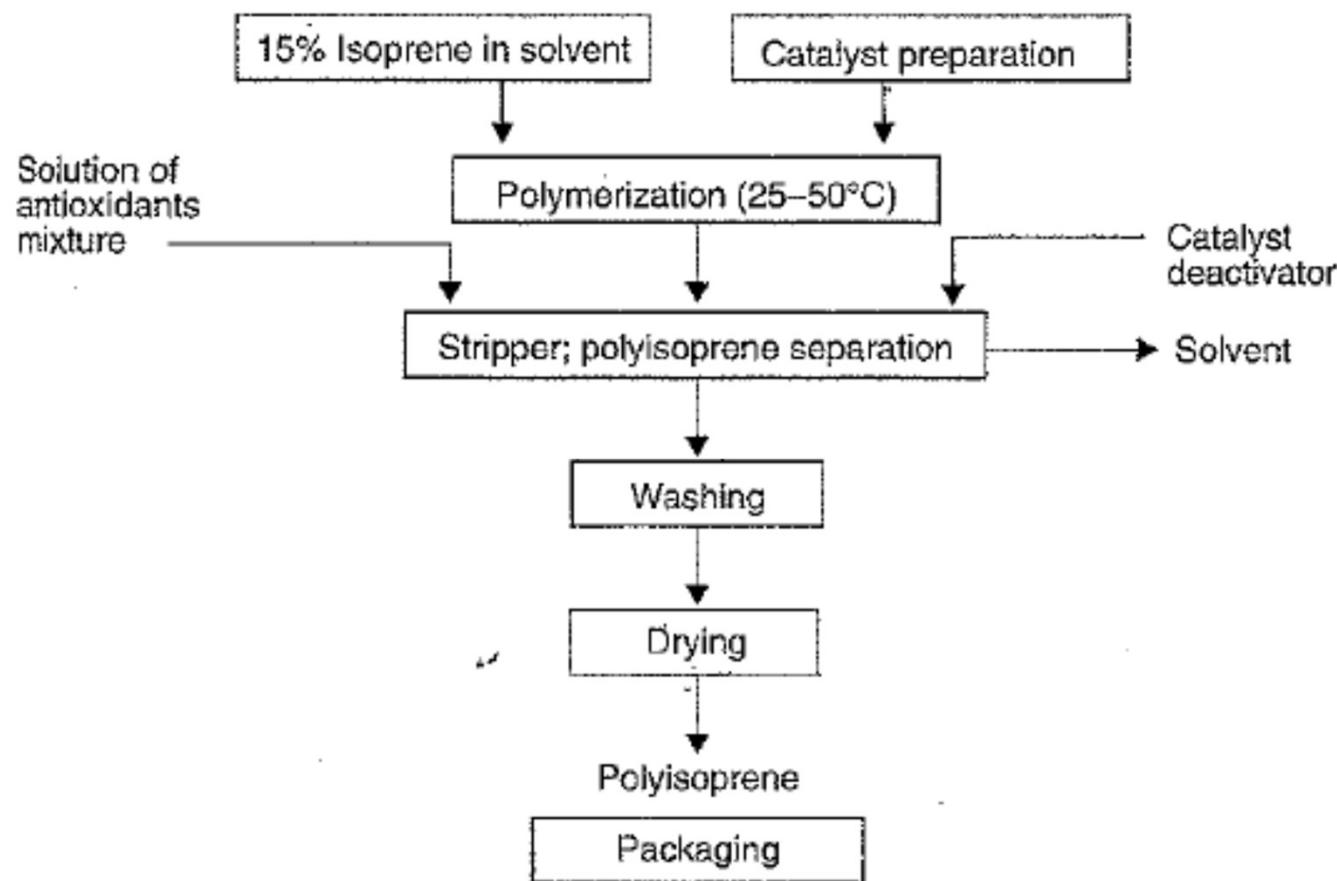
Commercial Production of Polyisoprene

- The only configuration of polyisoprene that is of commercial importance is cis-1,4 polyisoprene.



- Two major polymerization methods exist to commercially produce cis-1,4-Polyisoprene:
 - Ziegler-Natta: comprising trialkylaluminum and titanium tetrachloride,
 - Lithium and Lithium alkyl.
- The properties of synthetic cis-1,4 polyisoprene are very similar to those of cis-1,4 polyisoprene obtained from natural rubber.
- When vulcanized the mechanical properties also are similar.

Polymerization Sequence for Polyisoprene



Comparison of Chemical and Structural Properties of Naturally Produced and Synthetic Polyisoprene

Table 3.8 Analytical data of different polyisoprenes [28]. (Reprinted with permission of the publishers, Butterworth-Heinemann Ltd from *Rubber Technology and Manufacture* edited by C.M. Blow and C. Hepburn, 1982)

Property	Synthetic polyisoprene		
	Ziegler-Natta	Lithium	Natural rubber
1,4 <i>cis</i> units (% wt)	96	92	98–100
Limiting viscosity number (dl/g)	2.5–4.5	8–11	6–7
Gel content (% wt)	10–20	0	High level depending on age
Geometric shape	Branched	Linear	Branched
Stabilizer content (pphr)	1	0.5	2–3
Ash content (% wt)	0.15–0.30	0.05	Approx. 0.5
Total metal content (ppm)	400–3000	70	Approx. 1000
Mooney viscosity [ML(1+4) 100°C]	60–90	—	Approx. 120
Color	White	White	Dark

Mechanical Properties of Naturally Produced and Synthetic Polyisoprene

Table 3.9 Some vulcanize properties [28]. (Reprinted with permission of the publishers, Butterworth-Heinemann Ltd from *Rubber Technology and Manufacture* edited by C.M. Blow and C. Hepburn, 1982)

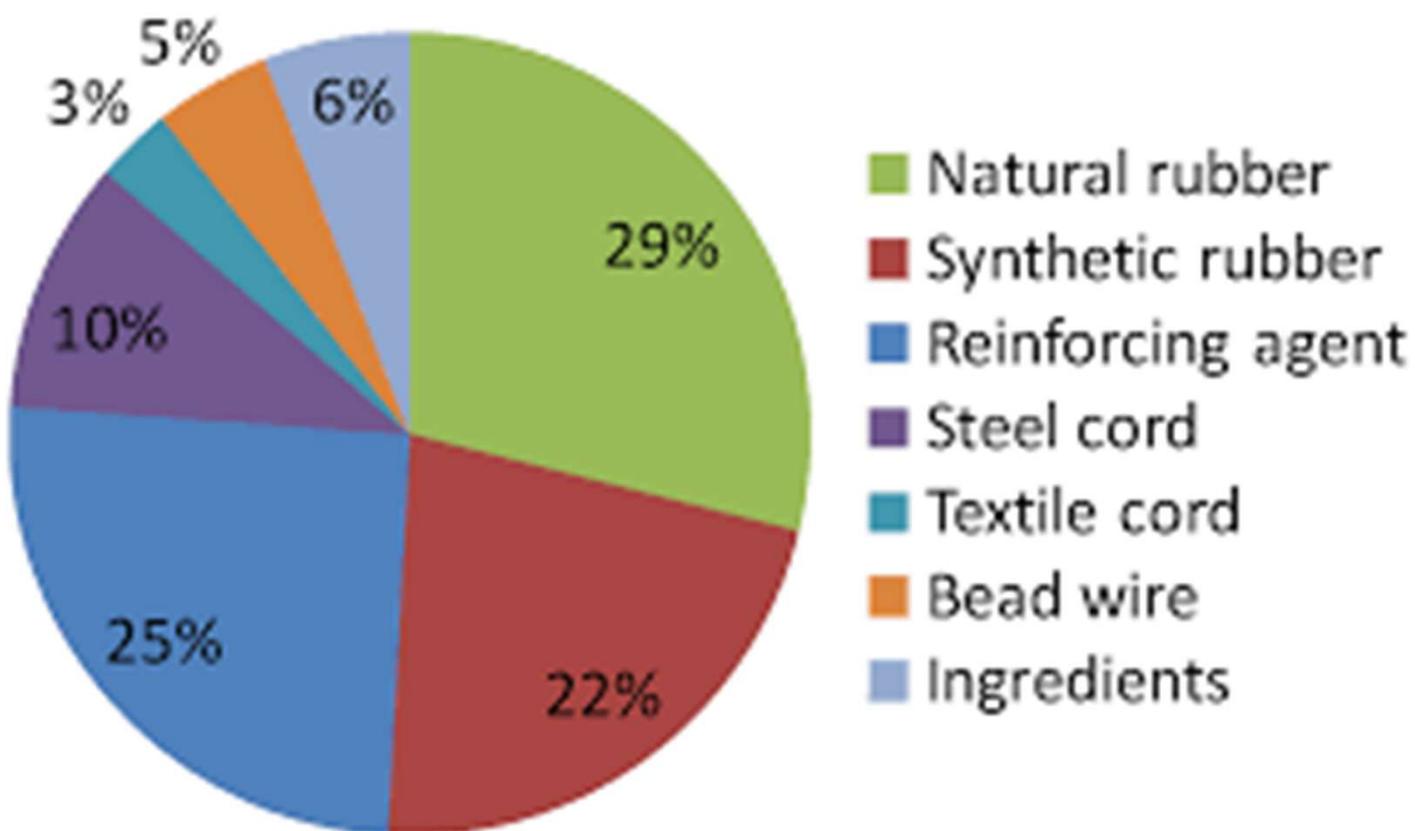
Property	Type of polymer				
	Ziegler– Natta PI	Lithium PI	Natural PI	SBR	PB
Tensile strength (MPa)	30	25	31	25	17
Tear strength (N/mm)	70	60	110	45	35
Heat build-up (°C)	23	21	23	40	33

Comparative Mechanical Properties of Elastomers

	Durometer hardness range	Tensile strength at room temp, psi	Elongation at room temp, %	Temp. range of service °C	Weather resistance
Natural rubber	20–100	1,000–4,000	100–700	-55–80	Fair
Styrene-butadiene rubber (SBR)	40–100	1,000–3,500	100–700	-55–110	Fair
Polybutadiene	30–100	1,000–3,000	100–700	-60–100	Fair
Polyisoprene	20–100	1,000–4,000	100–750	-55–80	Fair
Polychloroprene	20–90	1,000–4,000	100–700	-55–100	Very good
Polyurethane	62–95 A 40–80 D	1,000–8,000	100–700	-70–120	Excellent
Polyisobutylene	30–100	1,000–3,000	100–700	-55–100	Very good

Table 1 Selected properties of some elastomers.

Applications for Polyisoprene - Tires



Additional Applications for Polyisoprene

Cariflex™
Polyisoprene Products



Cariflex IR

- Strong
- Soft
- Pure
- Elastic
- Transparent

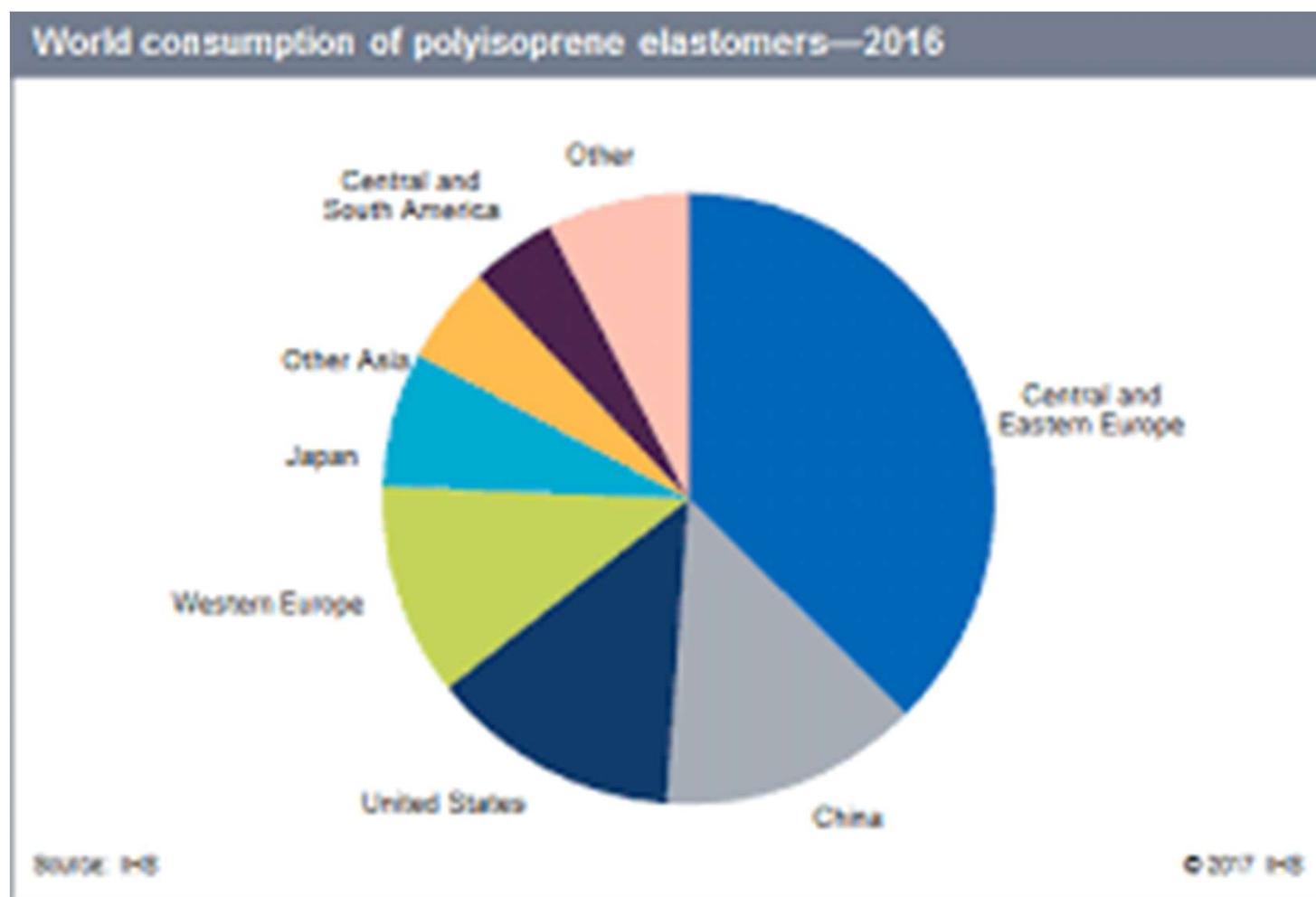
Polyisoprene rubber latex

		
Food & medical packaging	Dental Dams	Catheters
		
Stoppers/Needle Shields	Condoms	Surgical gloves

Solid Polyisoprene rubber

		
Transparent soles	Resealable insulin plugs	Marine coatings

Polyisoprene use Around the World



Alternate Sources for Natural Rubber Latex (Polyisoprene)



Guayule (*Parthenium Argentatum*)



Russian Dandelion
(*Taraxacum kiksaghyz* Rodin)



Fig Tree
(*Ficus Carica*)

Yield from the Alternate Latex Sources

Table 1. Properties and sources of natural rubber producing plants.

Natural producing plant	rubber	Property	Source of rubber	Mw (kDa)	Production (Tones/Yr)	Content of rubber (%)
<i>Hevea brasiliensis</i>		Hevea, rubber yielding tree which is white or yellow latex occurs in latex vessels in the bark.	Bark	1,310	9,000,000	30-40
Guayule shrub <i>P. argentatum</i> Gray		A high protein guayule latex would also be a brown/green color	Root	1,280	10,000	3-12
Russian dandelion <i>Taraxacum (koksgaghyz)</i>		It produces a milky fluid in its roots, which contains a high-quality rubber	Root	2,180	3,000	0-15
Fig tree (<i>Ficus carica</i>)		Nature of latex pale grey in colour.	Bark, leaf	190	--	4

Lesson 15: Polydienes – From Natural Rubber to Synthetic Rubber

Part 1: Natural Rubber, Polyisoprene

Questions?



Dr. Andy Olah, amo5@case.edu, O: 216-368-0606, C: 216-272-0505

“I don't care what you think you're good at, there's a 7-year-old kid on YouTube doing it better”

EMAC 276

Lecture 19: Environmental Stress Cracking (ESC)

Andy Olah, Ph.D. amo5@case.edu

March 5, 2025

FROM: Proponent Testimony In Support of Senate Bill 95

Before the Members of the Ohio Senate Committee on Energy and Natural Resources

Andrerw Olah, Ph.D.

October 25, 2017

“In my introduction to this class I impress upon these upcoming engineers the awareness that all materials have disadvantages based upon the environmental conditions that they can experience.”

“For example, in certain drinking water environments wood rots, steel and iron rusts, and copper corrodes; all specific to the contacting water chemistries. Although plastic materials may be impervious to these conditions there are other environments that the engineer must be aware of when utilizing polymer or plastic materials. Due to these requirements the engineer should have available all approved materials for the specific application in order to match the proper material with the specific end use environmental condition.”

“By allowing engineers to have at their discretion all suitably recognized materials, the engineer can adequately design the best system optimizing mechanical performance and system longevity at a reasonable cost.“

Vast Array of Liquid Media Exist for Polymeric Materials

- Good Solvent – Polymer Dissolves – Clear Solution
- Poor Solvent – Polymer Precipitates - Cloudy
- Oxidative Agent – Polymer Degrades
- Plasticizer – Glassy Polymer Softens Slightly
- Non-solvent – No Polymer Solvent Interaction

- **Environmental Stress Crack Agent**

*Most Environmental Stress Crack Agents
Fall under the Category of a Non-Solvent*



Designation: D543 – 14

**Standard Practices for
Evaluating the Resistance of Plastics to Chemical
Reagents¹**

PRACTICE A—IMMERSION TEST

**11. Procedure I—Weight and Dimension Changes (See
Note 4 and 6.2)**

11.5 Observe the surface of each specimen after exposure to the chemical reagent. Observe and report appearance on the basis of examination for evidence of loss of gloss, developed texture, decomposition, discoloration, swelling, clouding, tackiness, rubberiness, crazing, bubbling, cracking, solubility, etc. See Terminology D883 for proper descriptive terminology.

**Traditional Solvent-Polymer Tests only
Looked at the Interactions Under
Static (Unstressed) Conditions**

12. Procedure II—Mechanical Property Changes

12.2 Determine the mechanical properties of identical non-immersed and immersed specimens in accordance with the standard methods for tensile tests prescribed in the specifications for the materials being tested (see Note 7). Make mechanical properties tests on nonimmersed and immersed specimens prepared from the same sample or lot of material in the same manner, and run under identical conditions. Test immersed specimens immediately after they are removed from the chemical reagent. Where specimens are exposed to reagents at elevated temperature, unless they are to be tested at the elevated temperature, they shall be placed in another container of the reagent at the standard laboratory temperature for approximately 1 h to effect cooling prior to testing (see Note 7).

Cracking of Stressed Polyethylene

EFFECT OF CHEMICAL ENVIRONMENT

J. B. DECOSTE, F. S. MALM, AND V. T. WALLDER

Bell Telephone Laboratories, Inc., Murray Hill, N. J.

"In a number of applications for polyethylene, particularly cable sheaths and cosmetic containers, it has been found that under certain conditions failure of the polyethylene results in a cracking of the plastic. Considerable information is available to show that in an unstressed condition polyethylene is highly resistant to a wide variety of chemical environments such as alcohols, soaps, and fatty oils. However, when polyethylene is exposed to these environments under polyaxial stress it fails by cracking."



Figure 1. Environmental Stress Crack in Polyethylene Cable Sheath

Coste, J.B., Malm, F.S., and Wallder, V.T. Industrial and Engineering Chemistry, 43(1),
117-121, 1951

Stress Cracking (Crazing) of Polystyrene – Part 1

Ziegler and Brown
The Dow Chemical Company

“In recent years, many people have purchased plastic articles assuming, . . . that they were well made. Some of these people have been well pleased but, unfortunately, others have not.”

“Among the latter were come users of plastic kitchen utensils who, although they avoided heat, nevertheless watched small internal cracks develop over a period of time, . . . and sometimes cause complete failure.”

“Still others witnessed gradual degradation of such miscellaneous plastic parts as battery cases, coat hangers, brush backs, bottle closures, and food containers.”



“These plastic parts failed because of stress cracking or crazing.”

E.E. Ziegler, W.E. Brown, Plastics Technology, July 1955, 341-364.

Stress Cracking (Crazing) of Polystyrene – Part 2

Ziegler and Brown
The Dow Chemical Company

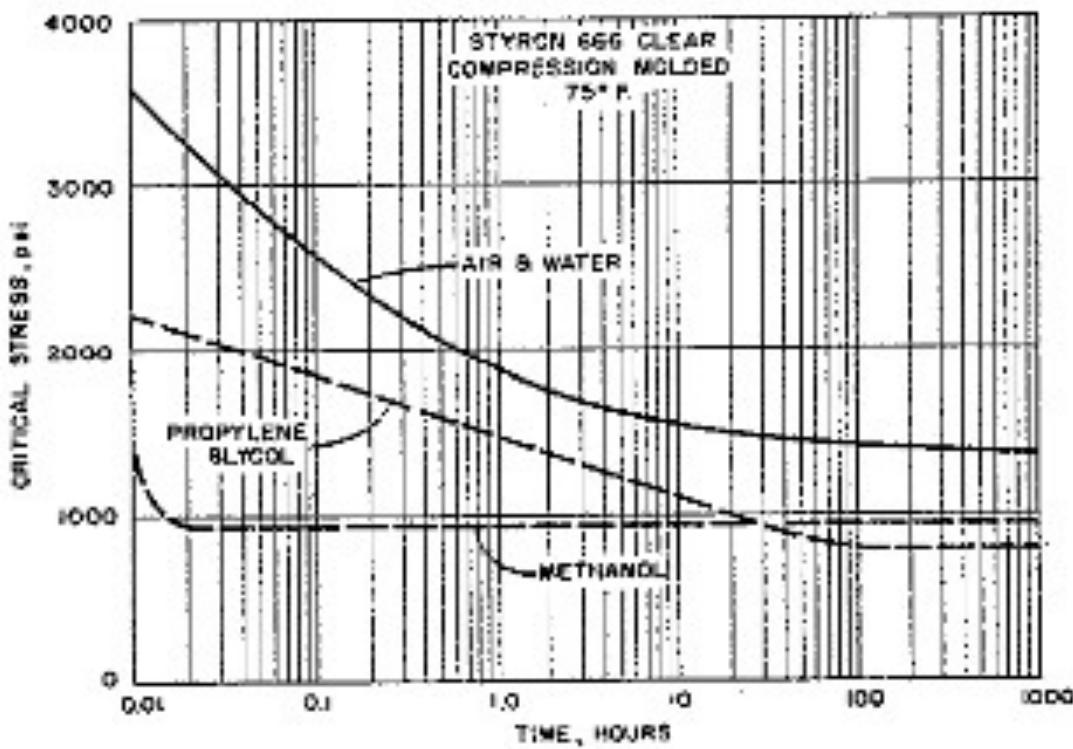
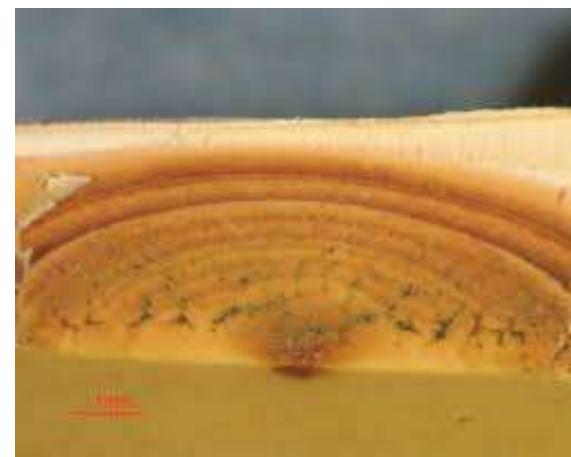
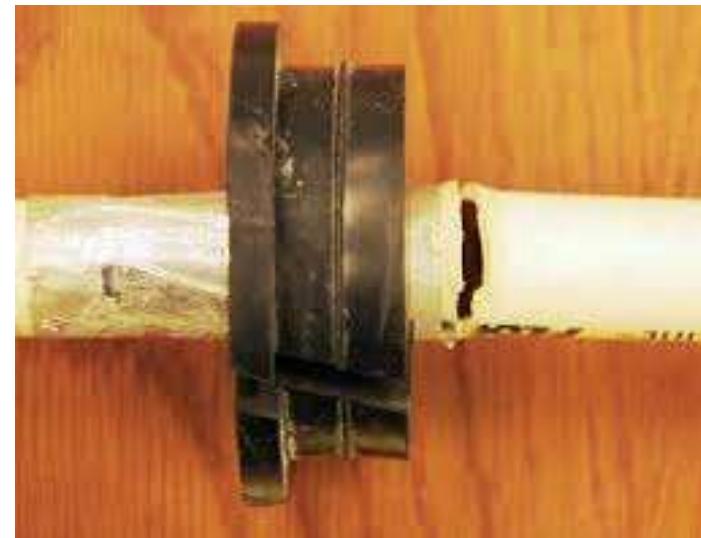
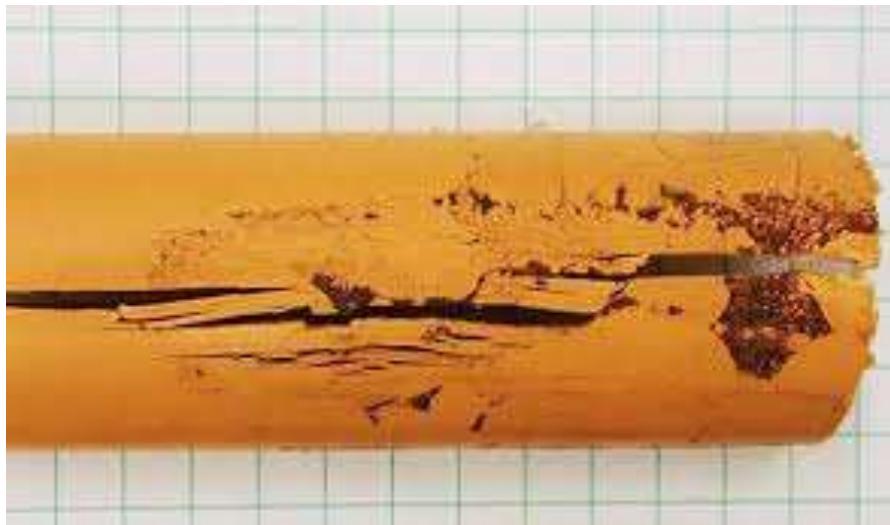


Table 4. Effect of Dairy Products on Stress Cracking of Styron 666 and Q-767 at 75° F.

Reagent	Equilibrium Critical Stress, Psi.	
	Styron 666	Q-767
Air	1,500	4,550
Water	1,500	3,600
Evaporated milk	900	4,100
Skim milk	750	2,300
Homogenized milk	450	2,300
Cream	450	2,100
Butter	450	2,100

E.E. Ziegler, W.E. Brown, Plastics Technology, August 1955, 409-415.

Examples of Environmental Stress Crack Field Failures



Definition of ESC

Environmental stress cracking (ESC) occurs because of the combined effects of mechanical stress and chemical exposure.

- ESC results in the brittle failure of plastics at significantly lower stresses than would normally be expected.
- Prediction of ESC is extremely difficult.
- The chemicals responsible for ESC can be present by design but are more often secondary fluids such as cleaning agents or lubricants.
- ESC can occur years after the products have been manufactured making identification of the precise causes difficult.
- ESC failure is a major problem when assessing the long-term behavior of polymeric components
- ESC can be extremely expensive in terms of:
 - lost production,
 - in service failures,
 - litigation.



Definition of ESC

The mechanisms involved in the ESC failure of polymeric materials have been extensively reported in the literature.

- Nucleation occurs preferentially at sites of stress concentration or at local microstructural inhomogeneity.
- Large local tensile stresses present in such regions lead to the formation of micro-voids that evolve into crazes.
- These crazes are void regions that are held together by highly drawn fibrils, which bridge the craze allowing stress to be transmitted across the craze and preventing the craze from propagating.
- Once nucleated the craze grows both in length and width, by stretching the fibrils and draw new material in from the surrounding bulk polymer.
- Stretching of the fibrils is believed to be governed by the disentanglement of the molecules. This localized yielding is believed to control the drawing of new material into the crazes.
- Stretching of the fibrils weakens them until eventually the fibrils fail producing a crack which can ultimately lead to the complete failure of the component.

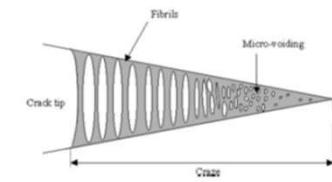


FIG. 1. Schematic diagram of the craze structure in polyethylene.

Definition of ESC

- It is believed that ESC occurs by a process of local weakening of the polymer due to infusion of an active environment.
- The weakening leads to easier craze formation and growth when subject to stress.
- A large amount of work has been conducted in an attempt to predict such failure.
 - 1) The first has been to determine which combinations of polymers and environments will cause ESC.
 - Much of this work has concentrated on thermodynamic compatibility, through the use of solubility parameters, and has met with some success, although quantitative predictions have not been successful.
 - 2) The second area has been to determine what conditions of stress and strain are required for ESC failure to occur.

The major problem is that ESC failure is a very complex process involving:

- 1) craze initiation,**
- 2) craze growth, and,**
- 3) craze breakdown,**

It has been virtually impossible to formulate failure criteria that successfully encompass all of these features.

Initial Test Methods Evaluating ESC have Focused on Test Specimens having an Induced Bending Stress

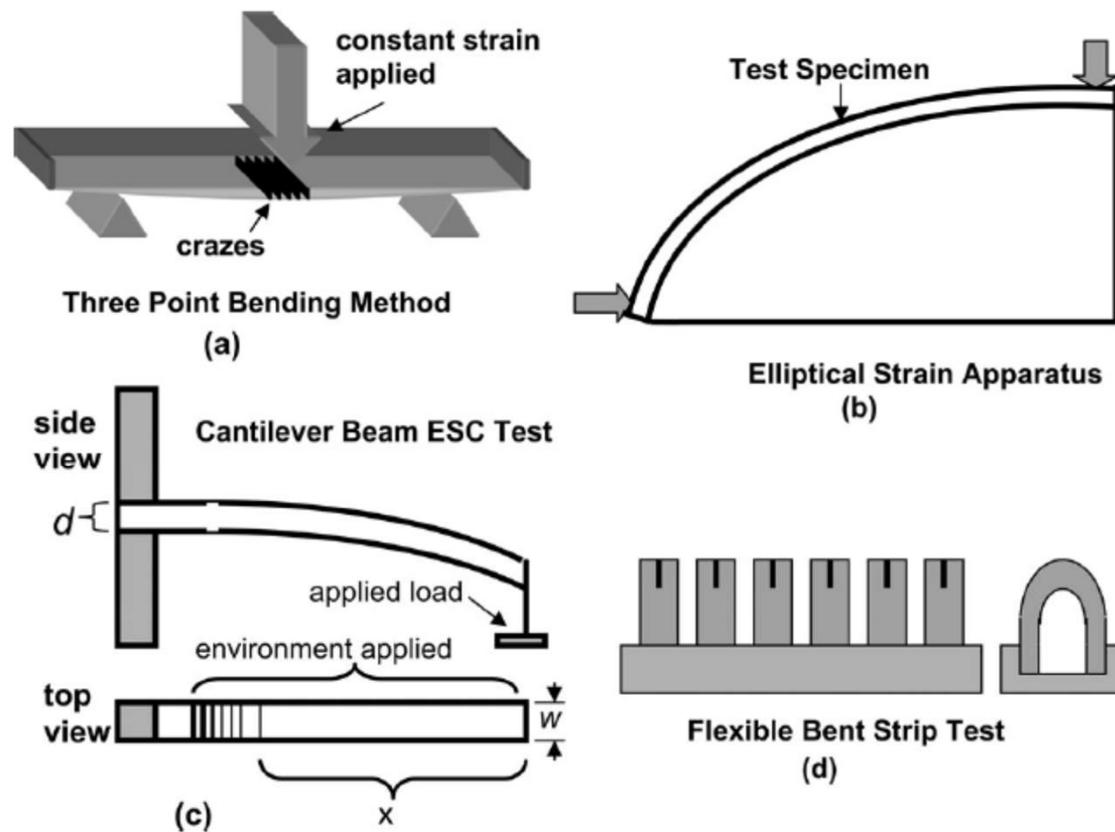
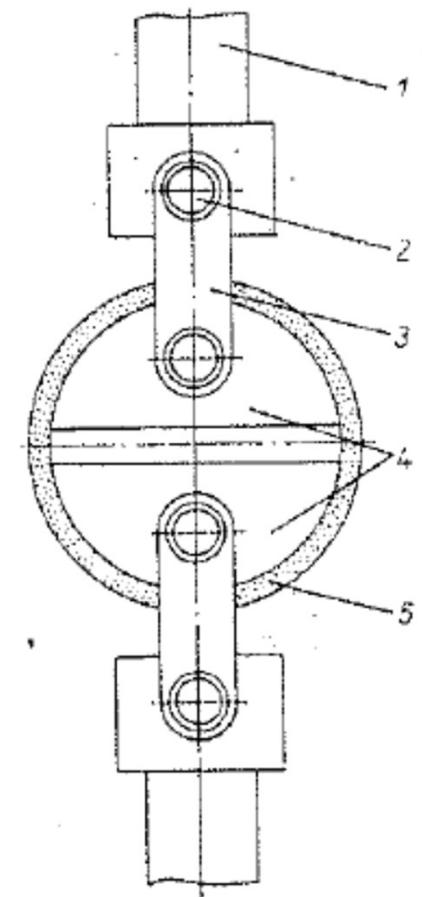
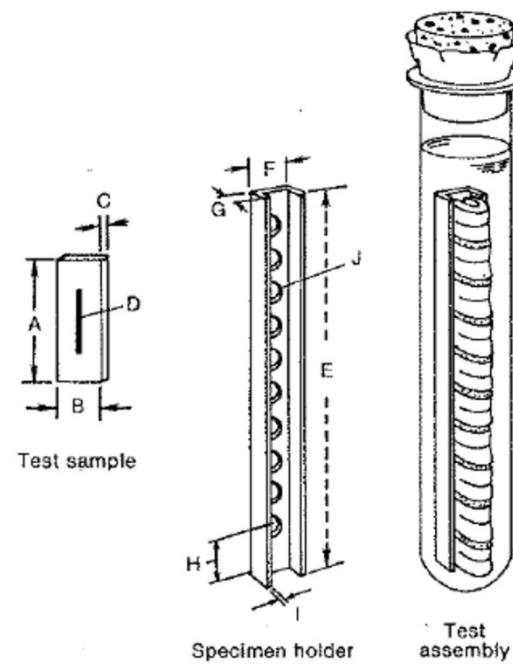
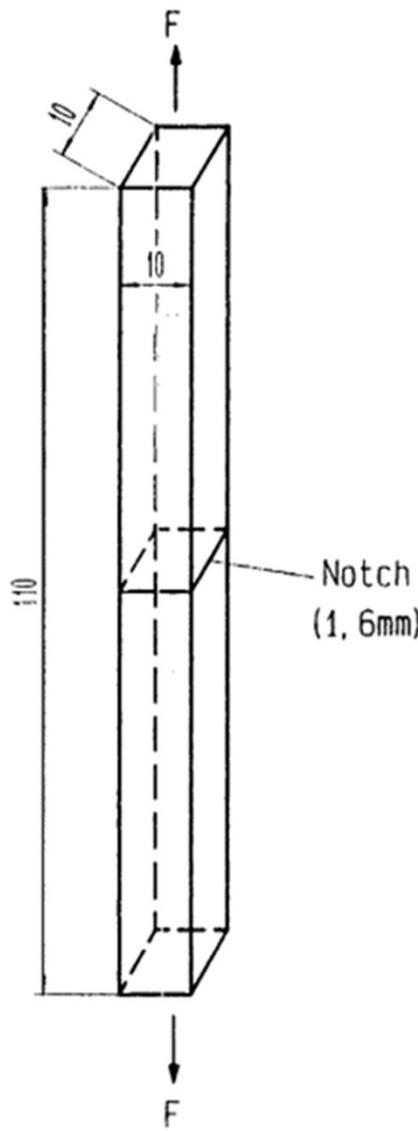


FIG. 5. (a-d) Illustration of various test methods to access environmental stress crazing/cracking.

Other ESC Test Devices

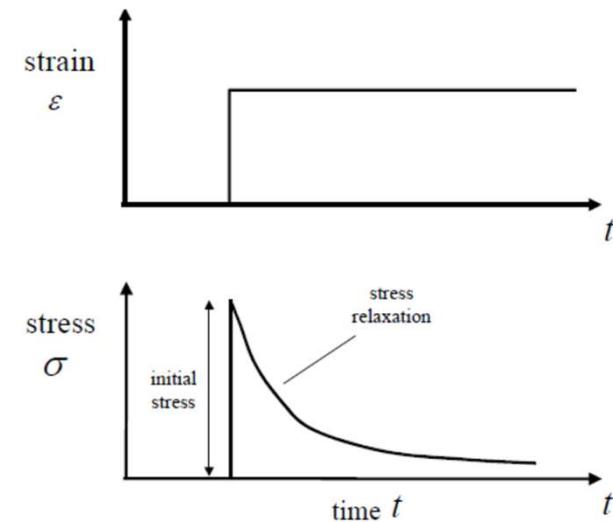
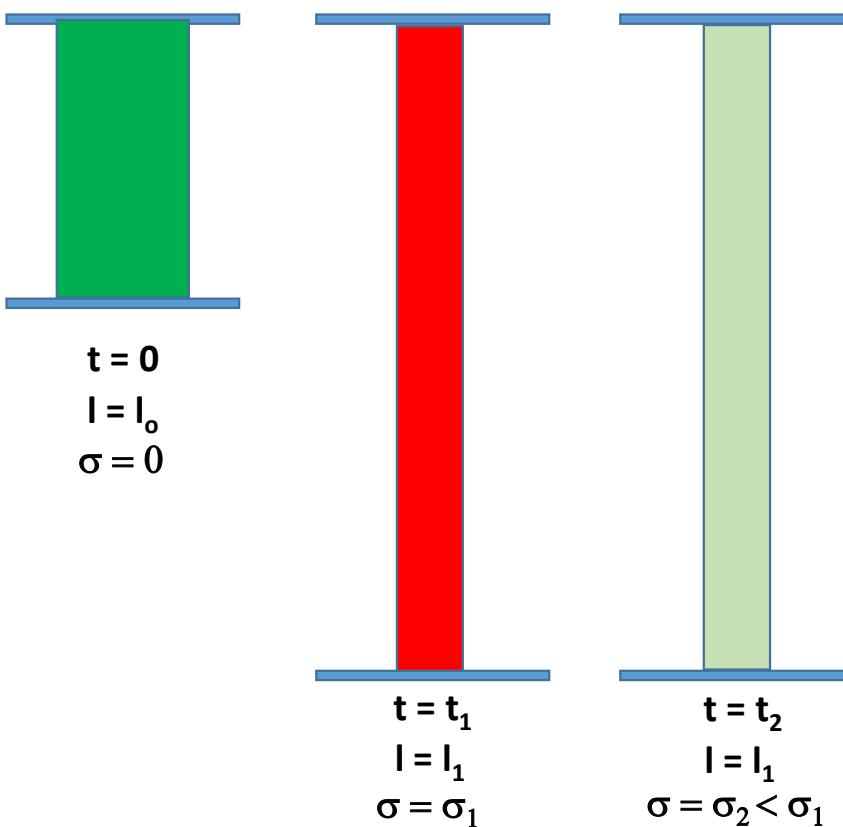


Viscoelastic Performance of Polymeric Materials

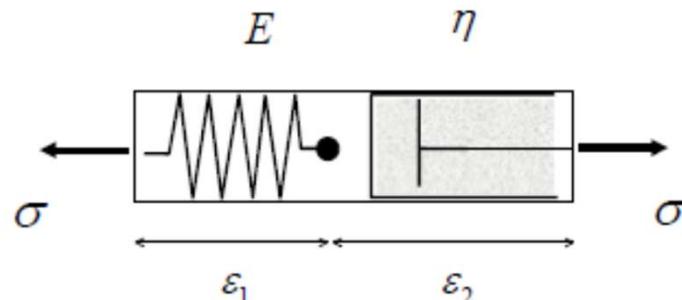
- Stress Relaxation – Constant Strain (deformation) :: Stress Reduction (load)
 - Example: Strings on Musical Instruments
 - Others?
- Creep – Constant Stress (load) :: Strain Change (deformation)
 - Example: Pressure Vessels: Pipe
 - Others?

Both “stress relaxation” and “creep” are time dependent phenomena.

Stress Relaxation



Stress Relaxation



$$\varepsilon_1 = \frac{1}{E} \sigma$$

$$\dot{\varepsilon}_2 = \frac{1}{\eta} \sigma$$

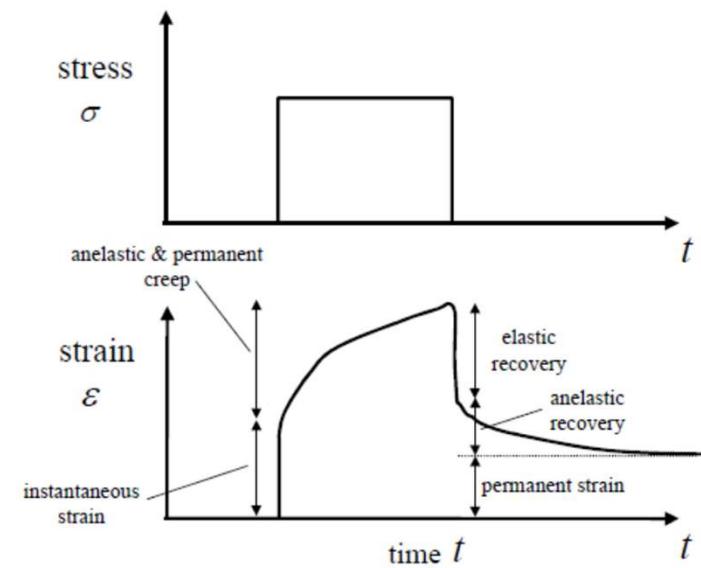
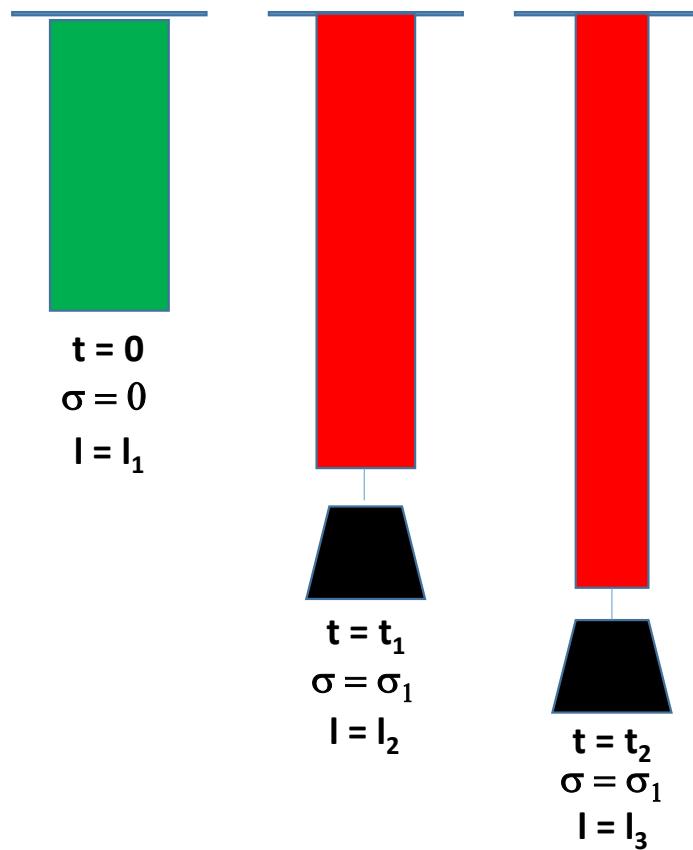
$$\varepsilon = \varepsilon_1 + \dot{\varepsilon}_2$$

$$\dot{\varepsilon} = \frac{1}{E} \dot{\sigma} + \frac{1}{\eta} \sigma$$

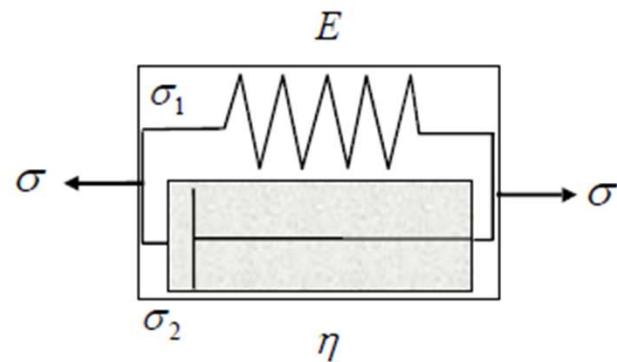
$$\sigma + \frac{\eta}{E} \dot{\sigma} = \eta \dot{\varepsilon}$$

$$\frac{\sigma(t)}{\epsilon_0} = E_{rl}(t) = E_0 \exp(-t/\Theta_{rl})$$

Creep



Creep



$$\varepsilon = \frac{1}{E} \sigma_1$$

$$\sigma = \sigma_1 + \sigma_2$$

$$\sigma = E \varepsilon + \eta \dot{\varepsilon}$$

$$\dot{\varepsilon} = \frac{1}{\eta} \sigma_2$$

$$\frac{\epsilon(t)}{\sigma_0} \equiv D_{\text{rt}}(t) = D_0 \{1 - \exp(-t/\Theta_{\text{rt}})\}$$

Overview

- Introduction
- Historical Perspective
- Definitions of ESC
- Testing & Difficulties
- Macro Characterization of ESC Mechanism
- Micro Characterization of ESC Mechanism
- Known Macromolecular Remediation
- Future Opportunities

Studies of Crack Initiation: Polycarbonate in Ethanol

Arnold, J.C., Journal of Material Science, 330, 665-660, 1995.

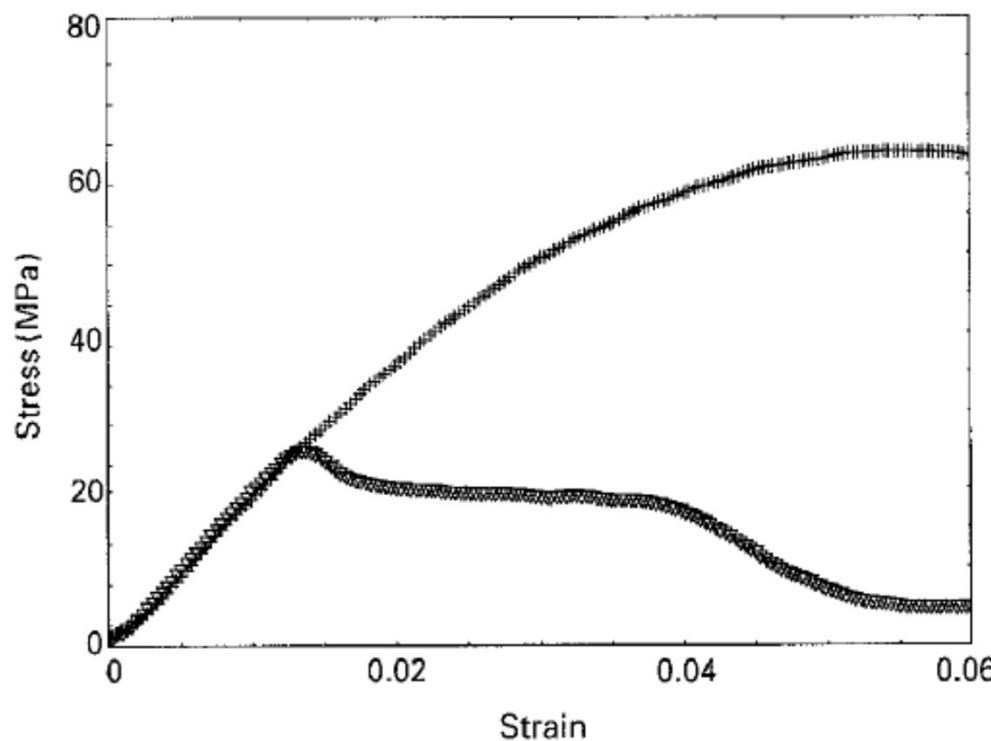
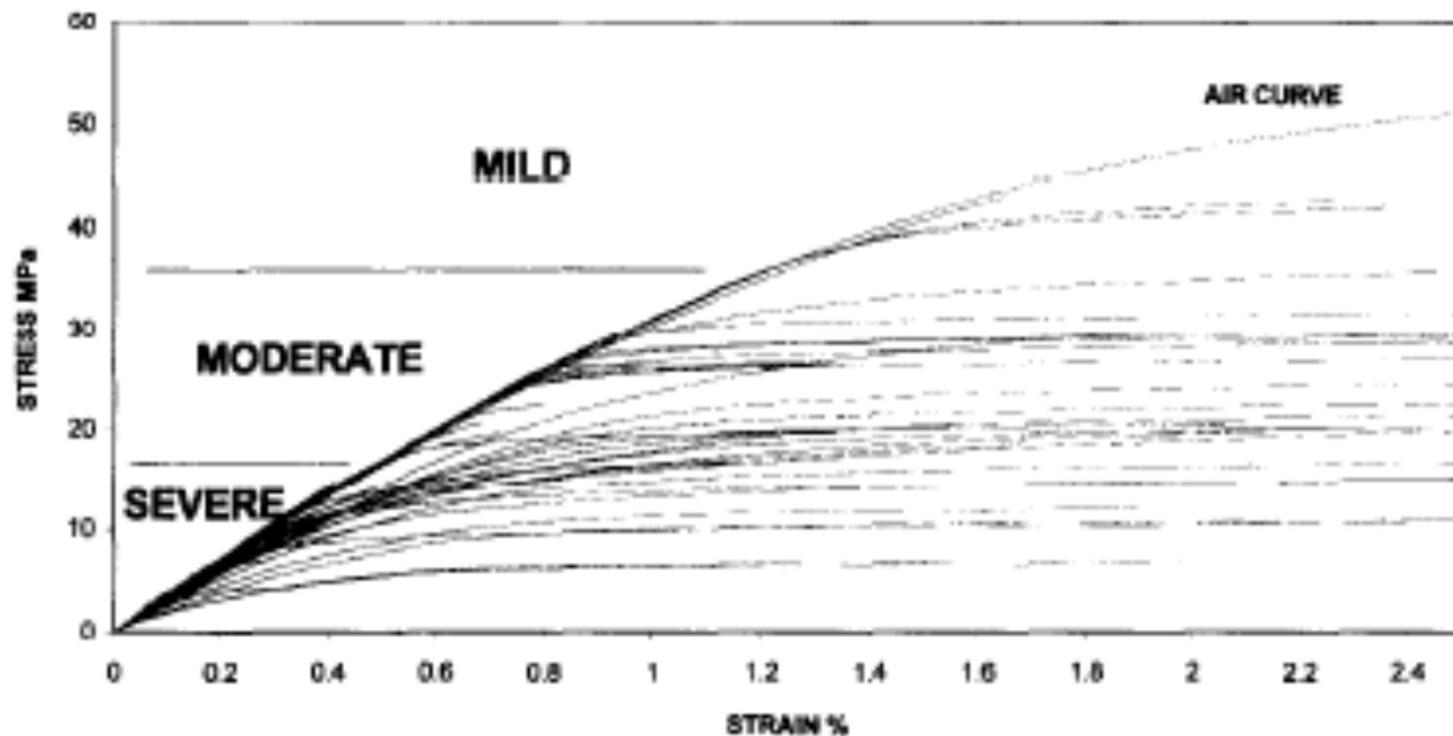


Figure 2 The variation of stress with strain for samples tested in (+) air and (∇) ethanol at a strain rate of $9.2 \times 10^{-6} \text{ s}^{-1}$.

Test Methods for Assessing Environmental Stress Cracking of Amorphous Thermoplastics

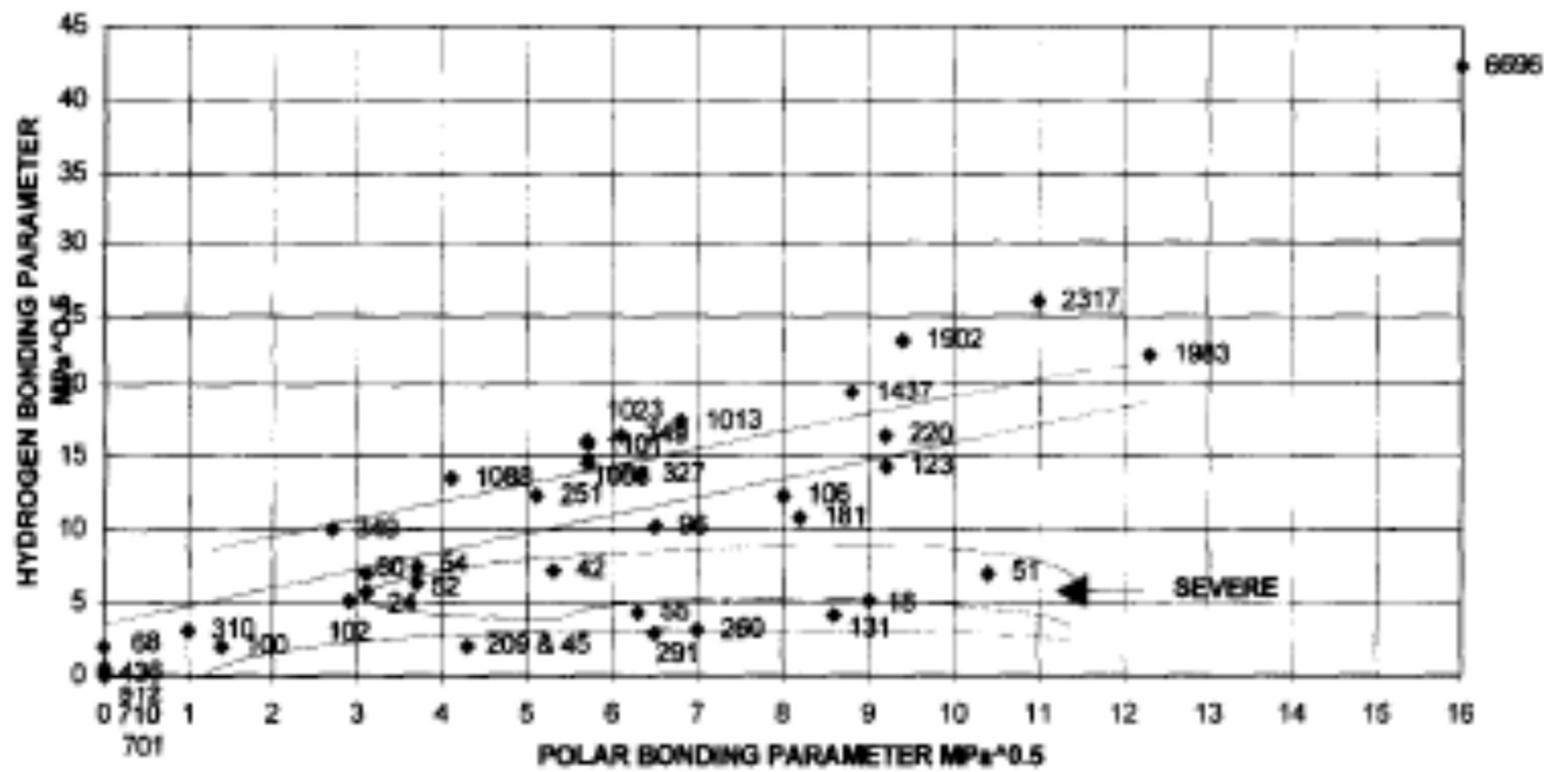
Hough and Wright, Polymer Testing, 15 (1996) 407 - 421



Monotonic 4 MPa/h stress-strain characteristics of UPVC in air and 41 fluids at 20 °C.

Test Methods for Assessing Environmental Stress Cracking of Amorphous Thermoplastics

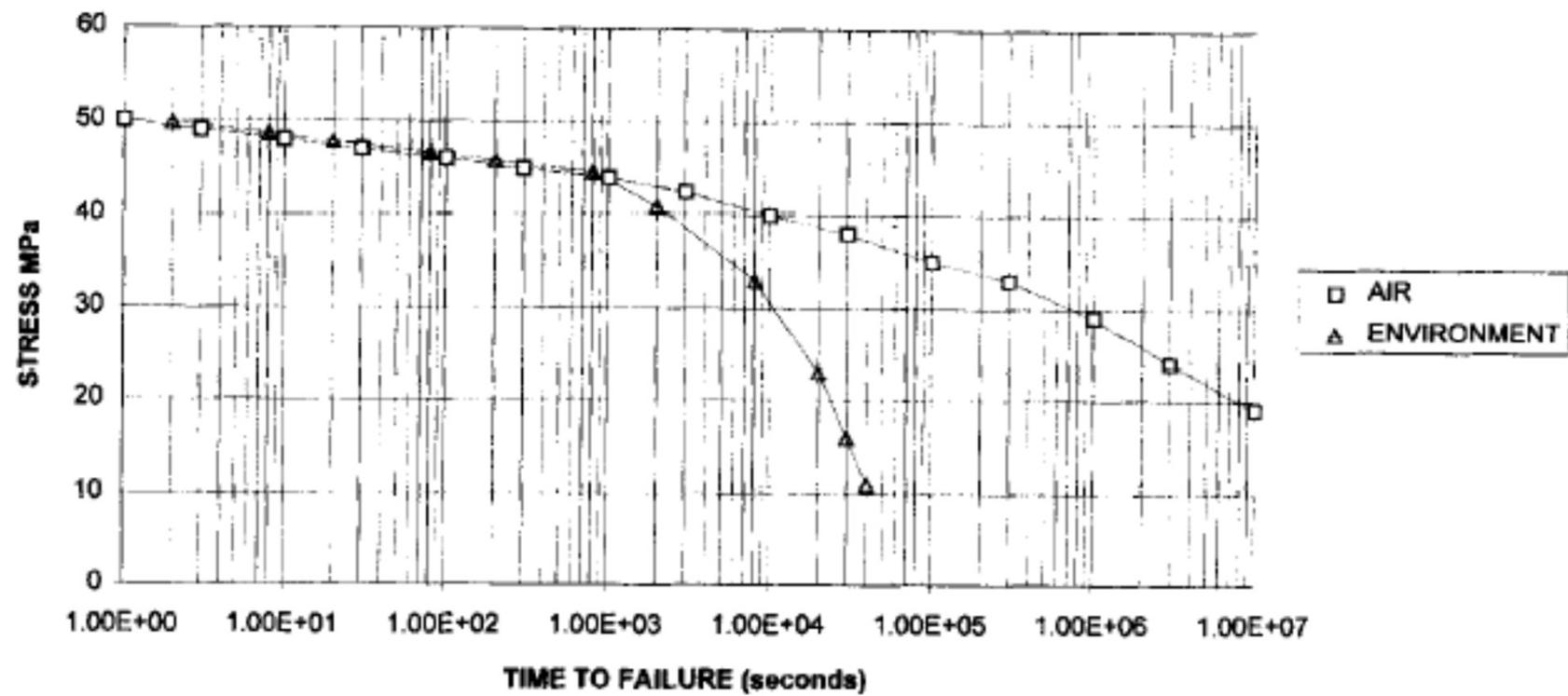
Hough and Wright, Polymer Testing, 15 (1996) 407 - 421



PVC 'Severity Index' for various fluids on the hydrogen bonding versus polar bonding plot.

Test Methods for Assessing Environmental Stress Cracking of Amorphous Thermoplastics

Hough and Wright, Polymer Testing, 15 (1996) 407 - 421

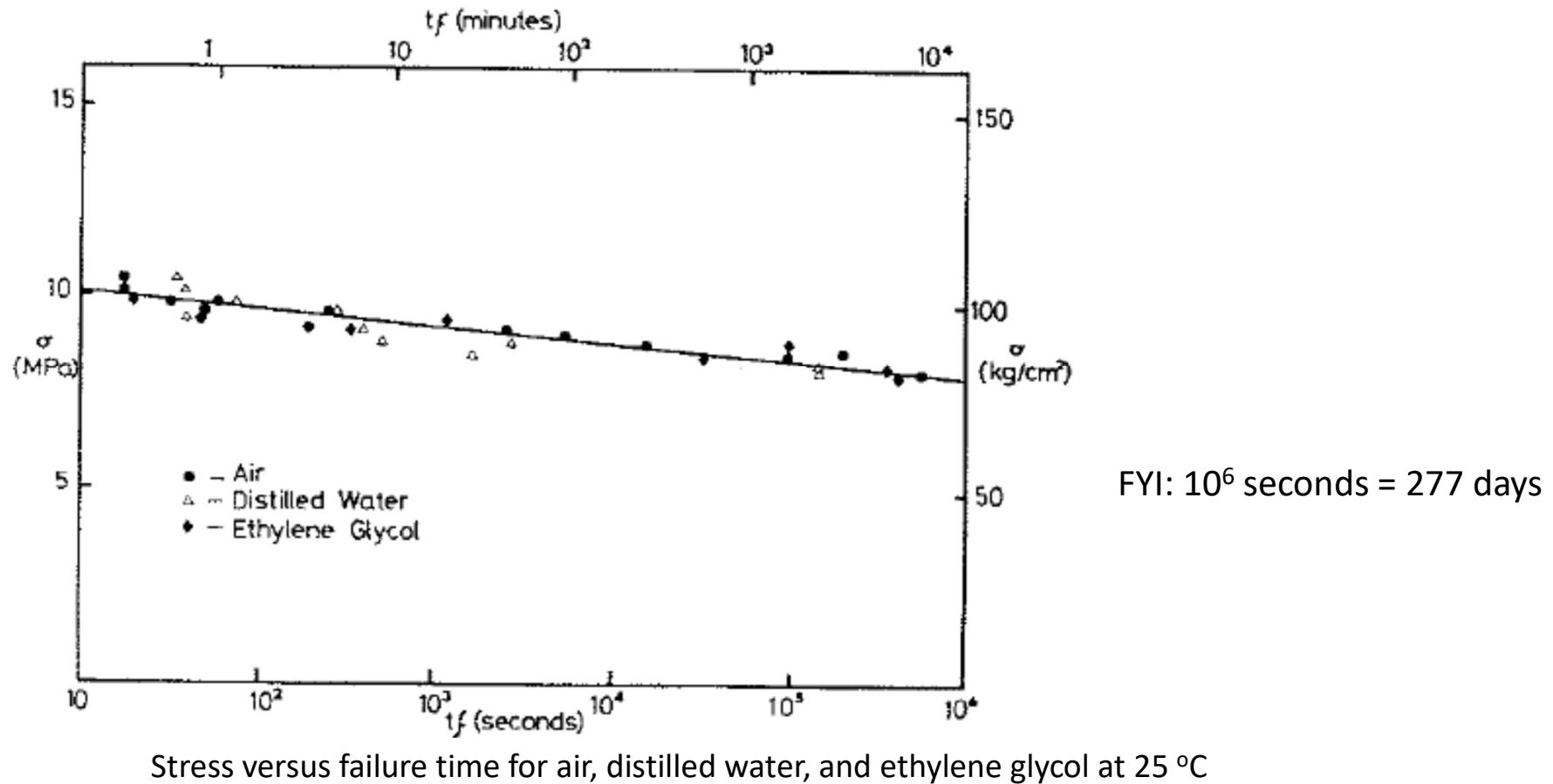


Hough, M.C., Wright, D.C., Polymer Testing, 15, 407-421, 1996

Environmental Stress Cracking of Polyethylene: Criteria for Liquid Efficiency

Shanahan and Schultz,

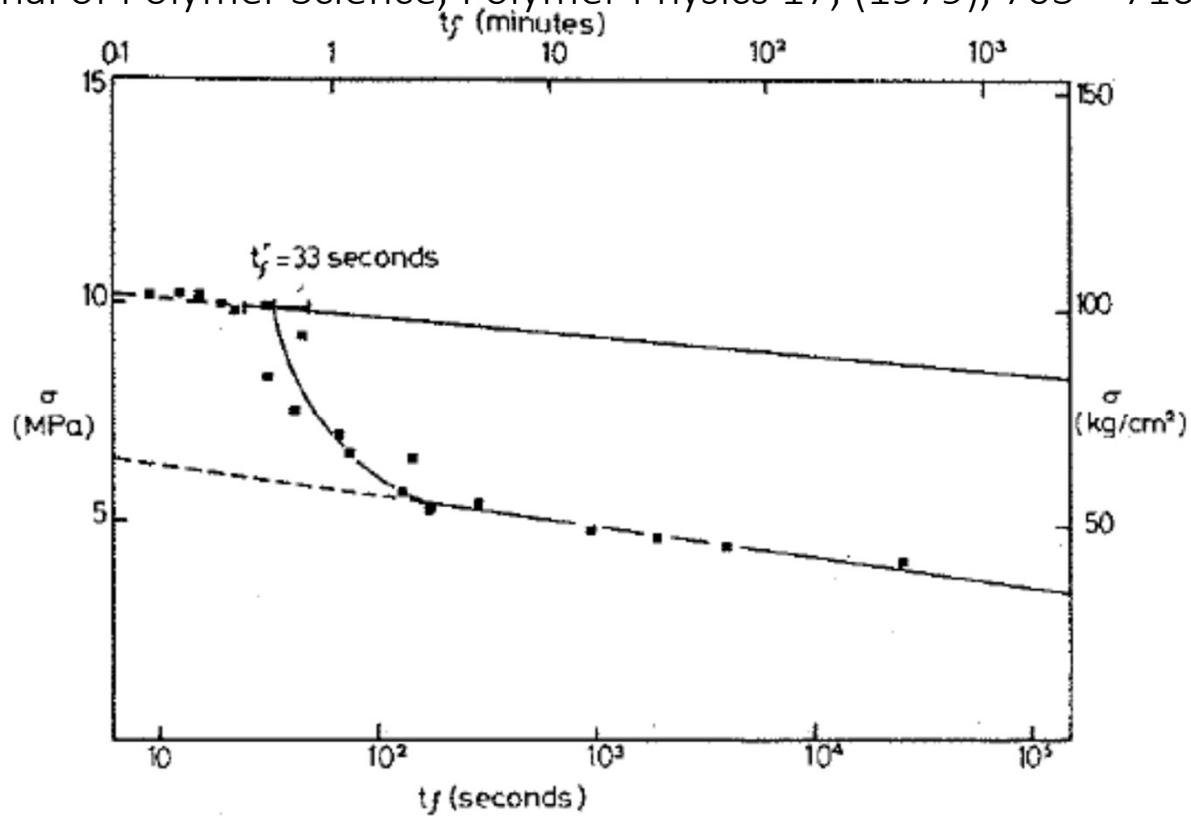
Journal of Polymer Science. Polymer Physics 17. (1979). 705 – 710.



Environmental Stress Cracking of Polyethylene: Criteria for Liquid Efficiency

Shanahan and Schultz,

Journal of Polymer Science, Polymer Physics 17, (1979), 705 – 710.



Stress versus failure time for polyethylene in PDMS (340 cP viscosity)

Environmental Stress Cracking of Polyethylene: Criteria for Liquid Efficiency

Shanahan and Schultz,

Journal of Polymer Science, Polymer Physics 17, (1979), 705 – 710.

TABLE I

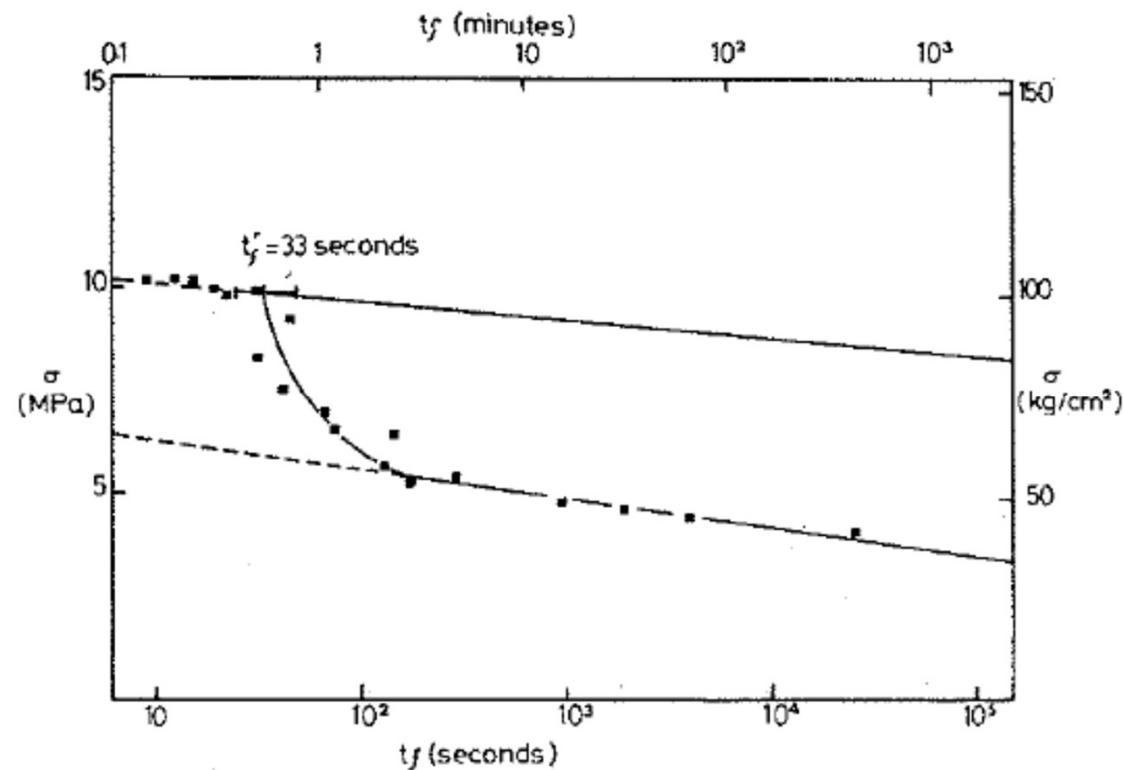
Liquid	t_f^r (sec)	$(t_f^r + \Delta t_f^r)$ (sec)	$(t_f^r - \Delta f^r)$ (sec)	η (cP) (at 25°C)	S (mN/m)
Tricresyl phosphate	24	33	18	80	-5.6
Diiodomethane	9	12	6	2.5	-16.9
Paraffin oil	7.2	12	4.8	35.5	6.5
PDMS ($\eta = 340$)	33	48	24	340	13.7
PDMS ($\eta = 970$)	72	114	54	970	13.6
Distilled water	—	—	—	0.9	-87.1
Ethylene glycol	—	—	—	16.3	-30.8

The Three Regimes of ESC

- 1. High Stress Regime** – ESC and normal necking-type fractures are in competition. Necking-type fractures are observed since that process is faster.
- 2. Intermediate Stress Regime** – depending upon the liquid environment a transition region is encountered. The speed of penetration of the liquid within a growing crack largely controls overall time to failure.
- 3. Low Stress Regime** – “pure ESC” is obtained since the liquid is continually present at the fracture front.

Environmental Stress Cracking of Polyethylene: Criteria for Liquid Efficiency

Shanahan and Schultz,
Journal of Polymer Science, Polymer Physics 17, (1979), 705 – 710.



Stress versus failure time for polyethylene in PDMS (340 cP viscosity)

Overview

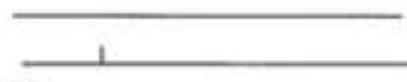
- Introduction
- Historical Perspective
- Definitions of ESC
- Test Methods
- Macro Characterization of ESC Mechanism
- Micro Characterization of ESC Mechanism
- Known Macromolecular Remediation
- Future Opportunities

Microstructure of Different Polyethylene Materials

HDPE

Density: 940-970 kg/m³

Comonomer content: 0-2.5 wt-%



MDPE

Density: 930-940 kg/m³

Comonomer content: 2.5-5 wt-%



LLDPE

Density: 915-930 kg/m³

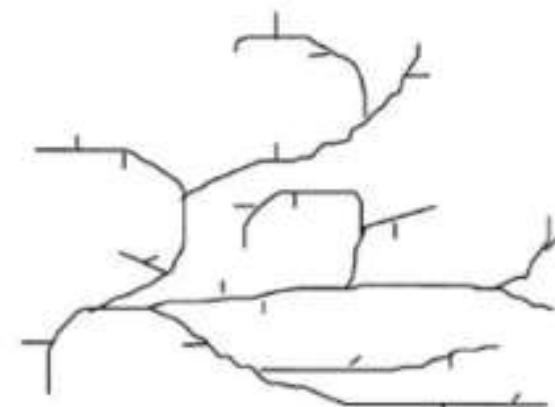
Comonomer content: 5-12 wt-%



VLDPE

Density: 860-915 kg/m³

Comonomer content: 10-35 wt-%



LDPE

Density: 910-930 kg/m³

No comonomer

Figure 2.1: Molecular structure of different type of polyethylene (1)

Morphology of Polyethylene - A Semicrystalline Polymer

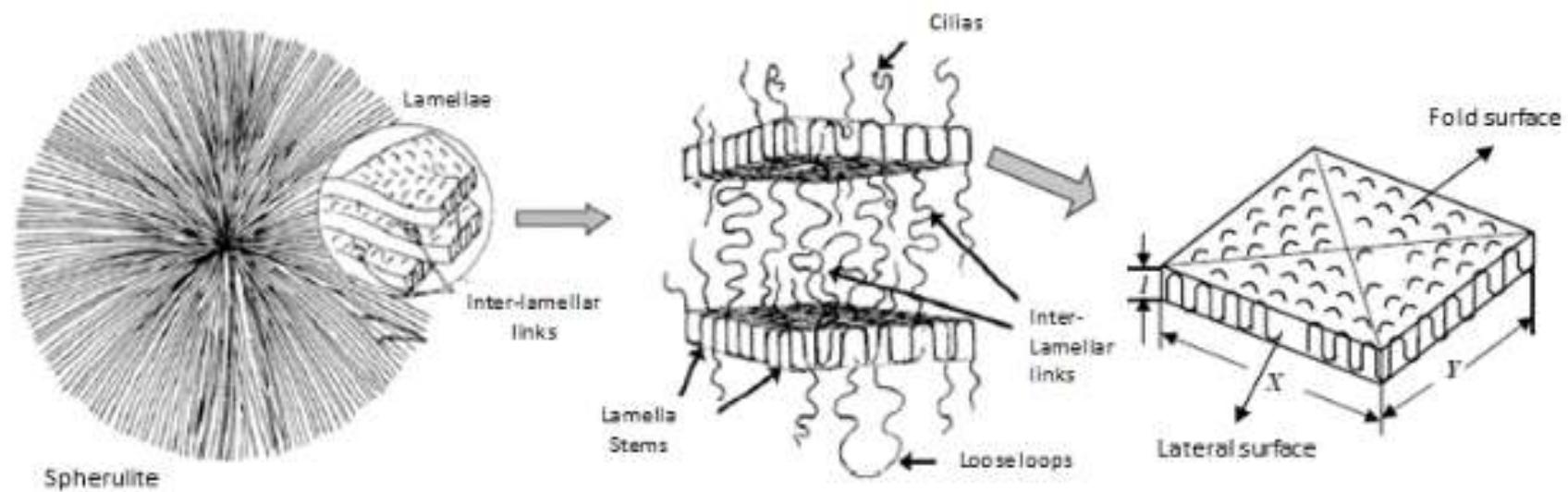


Figure 6.6: Spherulitic and lamellar structure of melt crystallized PE, adapted from (7, 26)

Influence of Uniaxial Stress upon Polyethylene Morphology

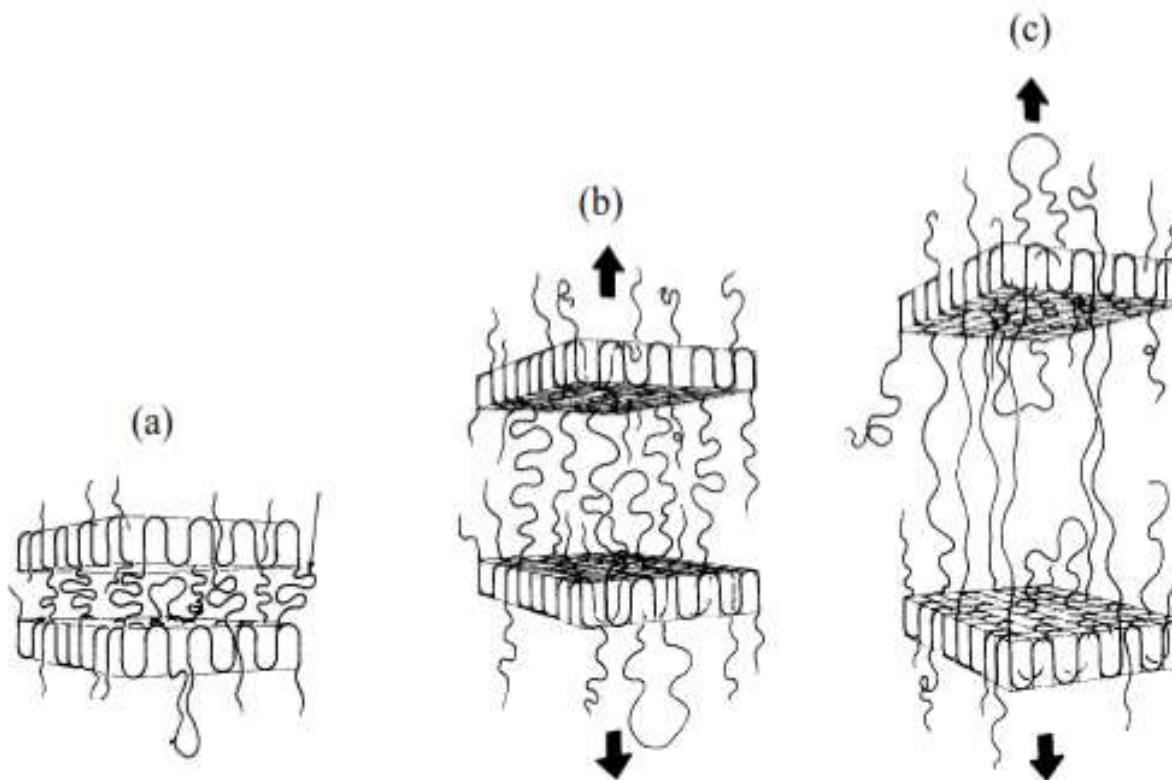


Figure 2.3: Brittle fracture of polyethylene; (a) Unstressed lamella structure (b) Stretch and break of tie-molecules (c) Separation of lamellae (17)

Morphology and Terminology for Crazing, Cracking and ESC

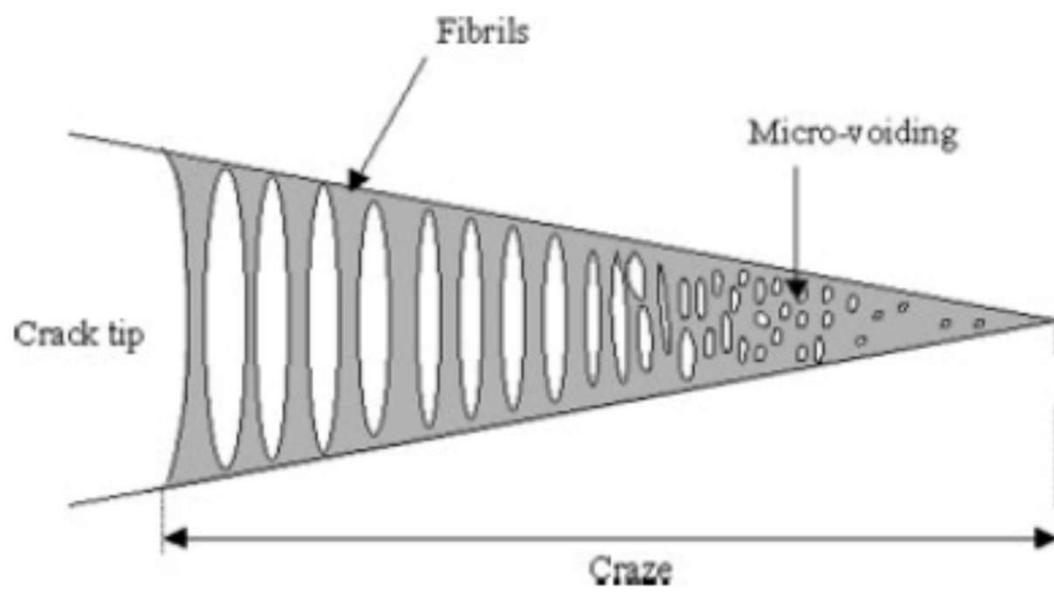
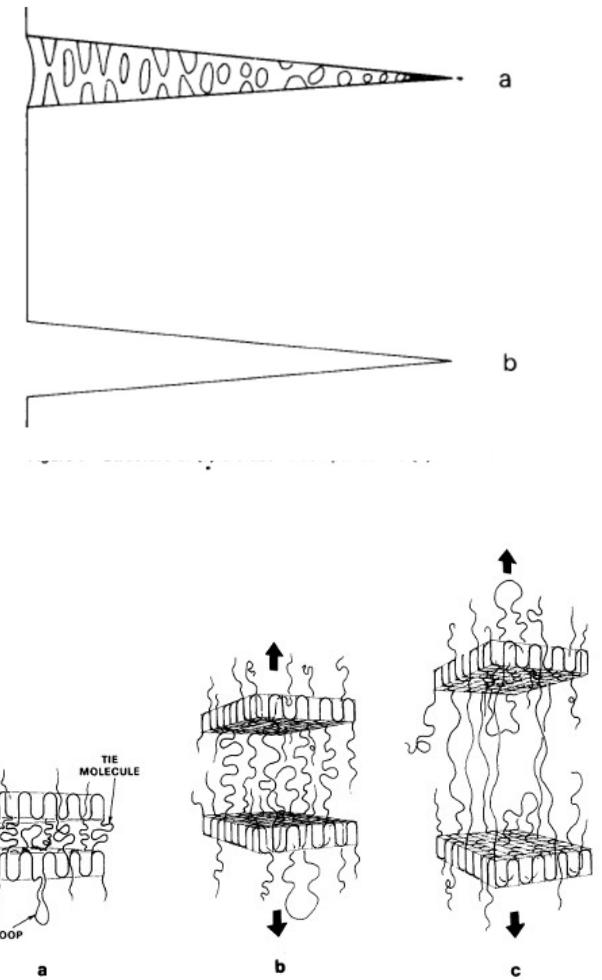
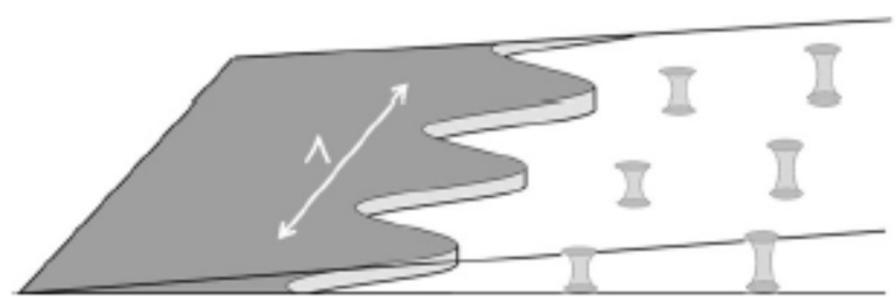
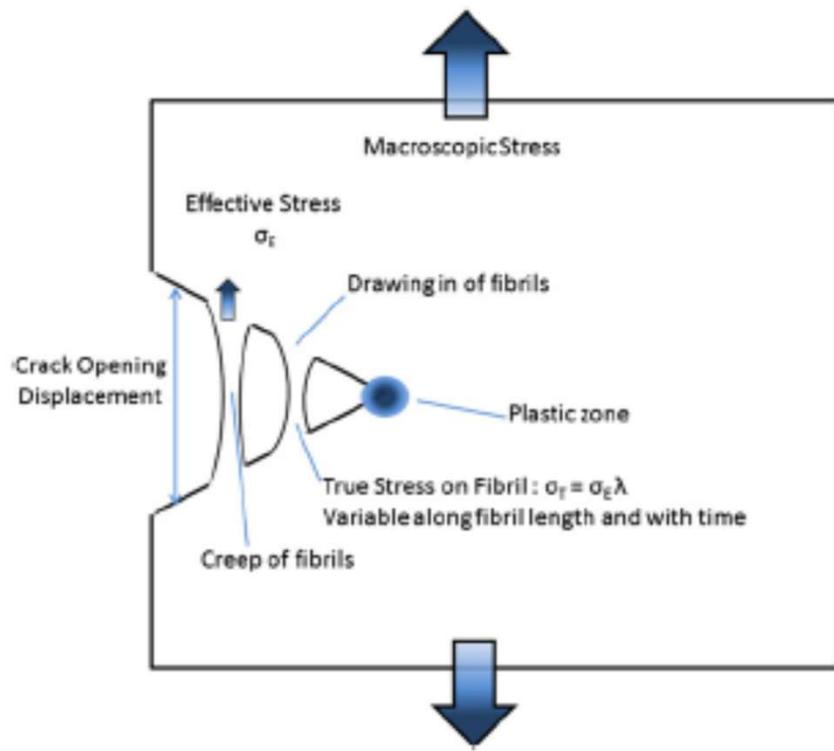


FIG. 1. Schematic diagram of the craze structure in polyethylene.

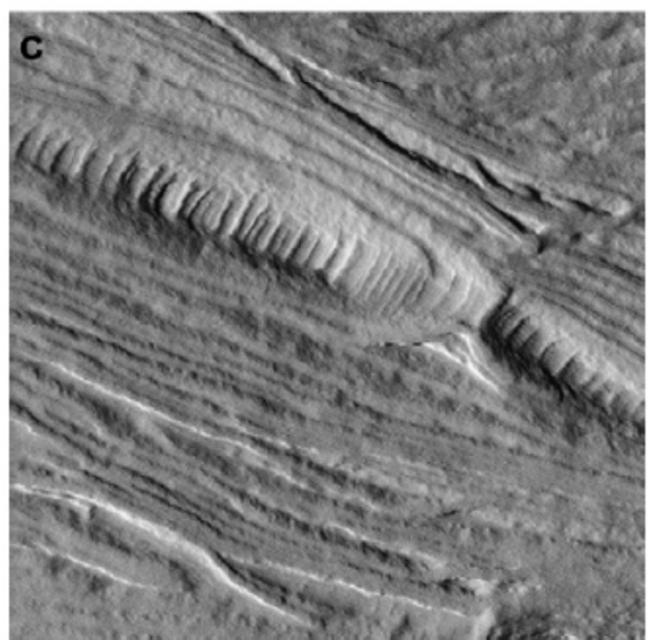
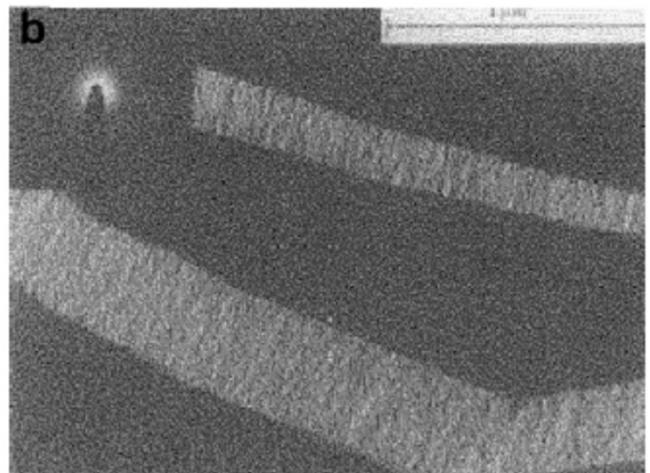


Deblieck, van Beek, Remerie, Ward, Polymer, 52 (2011) 2979 - 2990



Stress induced melt at a craze tip transforms into fibrils via a surface tension driven Taylor meniscus instability.

Craze-crack and craze propagation represented schematically. The propagation goes from left to right. The principal stress acts in the up-down direction.

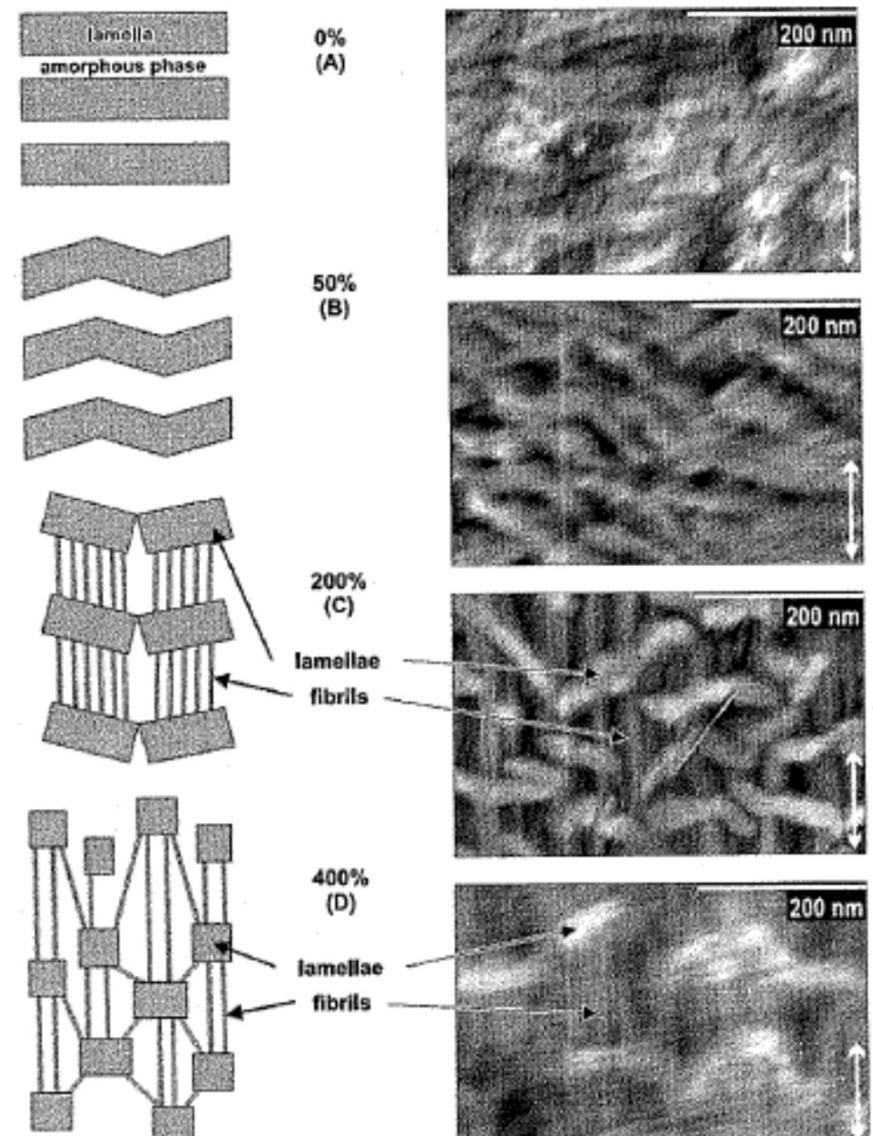


- a) Craze fibrillar network and the craze-crack transition in PE (upper) in addition multiple crazing around the craze tip is revealed (lower).
- b) Crazing as observed by TEM in a thin film of spherulitic isotactic polystyrene at room temperature
- c) Crazing and coalescence of crazes as observed by tapping mode AFM. The width of the image is 1.5 microns.

The Structural Evolution of High-Density Polyethylene during Crazing in a Liquid Medium

Yarysheva, Rukhlya, Yarysheva, Bagrov, Volynskii, Bakeev
European Polymer Journal, 66, (2015), 458 - 469.

AFM images of (A) initial HDPE and that drawn to (B) 50%, (C) 200%, and (D) 400% in water-ethanol solution. The stretching direction coincides with the extrusion axis and is denoted by the arrows in the images. The scheme constructed based on the images is shown in the left hand part of the figure.



Liquid Induced Stress Depression

Two different stress contributions exist in polymer fibrils undergoing craze-crack propagation: a) the material strength of the fibril, and b) a surface strength contribution based on the surface tension of the material and the surrounding environment.

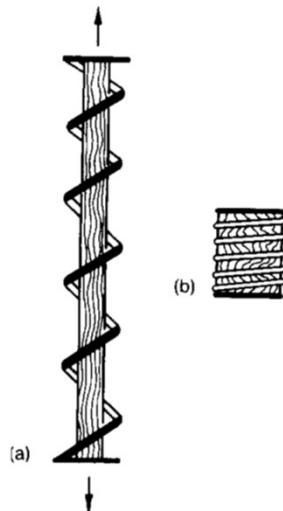


FIG. 11. Schematic illustration of possible coexistence of surface forces (spring) together with conformational property of the fibrillar mass so that the fibril is always in an extended state; (a) loaded or (b) unloaded.

Fiber Strength Contribution - $F_E = \frac{\pi D^2}{4} E \epsilon$

Surface Strength Contribution - $F_S = \pi D \gamma$

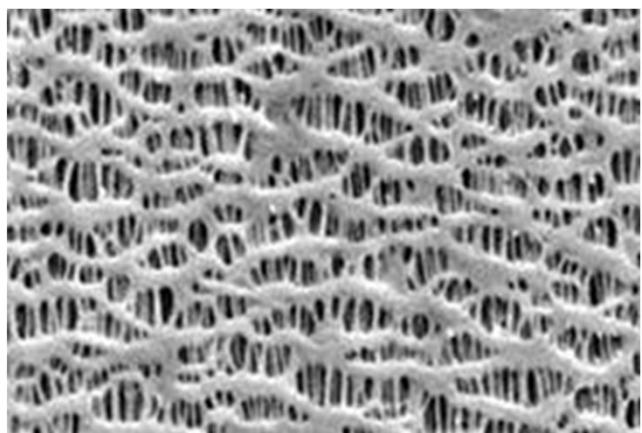
$$F_T = F_E + F_S = \frac{\pi D^2}{4} E \epsilon + \pi D \gamma$$

$$\Delta \sigma_f = \sigma_{SA} - \sigma_{SL} = \frac{4}{D} (\gamma_{SA} - \gamma_{SL})$$

$$\Delta \sigma = \frac{4 A_f \gamma_{LA} \cos \theta}{\bar{D}}$$

Chou, C.J., Hiltner, A., Baer, E., *Polymer*, 27, 369 – 376, (1986)
Moet, S., Palley, I., Baer, E., *J. Appl. Phys.*, 51, 5175 – 5183, (1980)

Liquid Induced Stress Depression on Celgard®



Celgard®

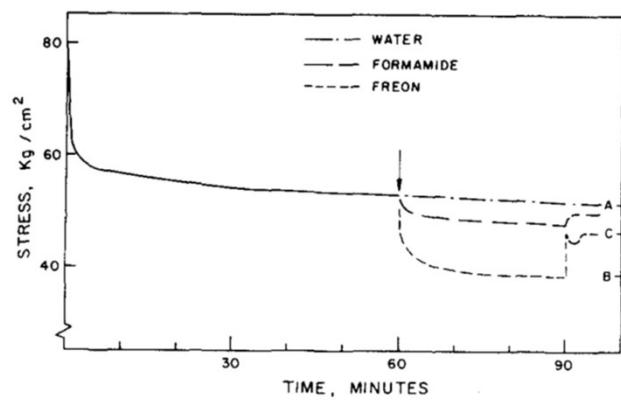
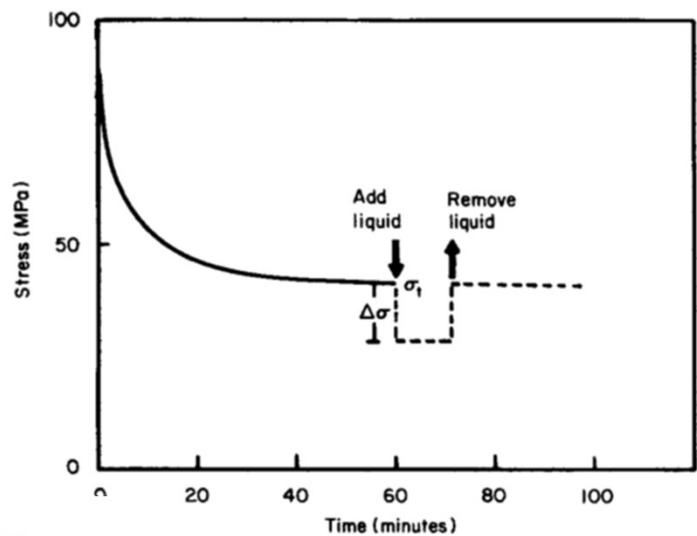


FIG. 9. Stress-relaxation behavior of hard-elastic HIPS in air for 1 h and then in liquid (arrow) for 30 min, after which the liquid is removed.



Liquid Induced Stress Depression

TABLE I. Depression of retractive stress caused by immersion in liquid environments as a function of their surface tension, solubility parameters, and viscosity.

Liquid	Viscosity (cP)	Surface tension (dyn/cm)	Solubility parameter (cal/cm ³)	Total (kg/cm ²)	Depression of retractive stress Reversible (kg/cm ²)
Water	1.0	72.0	23.61	0	...
Formamide	3.3	58.2	19.2	4.5	4.0
Acetic acid	1.2	28.8	10.1	45.7	13.2
Methanol	0.6	24.5	14.5	25.9	16.6
Ethanol	1.0	23.0	10.0	31.3	24.7
Silicone oil ^a	8300	21.3		13.5	...
Silicone oil	830	21.1	4.9 to	19.8	...
Silicone oil	8.3	19.7	5.9	21.4	...
Silicone oil	1.7	19.2		30.5	13.7
<i>n</i> -hexane	0.3	18.4	7.3	53.9	23.7
Freon (E-3) ^b	2.2	14.2	5.2 ^c	13.5	7.8

^aPolydimethylsiloxane.

^cEstimated from heat of vaporization.

^bFluorocarbon liquid (DuPont Co.).

Chou, C.J., Hiltner, A., Baer, E., Polymer, 27, 369 – 376, (1986)

Moet, S., Palley, I., Baer, E., J. Appl. Phys., 51, 5175 – 5183, (1980)

Overview

- Introduction
- Historical Perspective
- Definitions of ESC
- Test Methods
- Macro Characterization of ESC Mechanism
- Micro Characterization of ESC Mechanism
- Known Macromolecular Remediations
- Future Opportunities

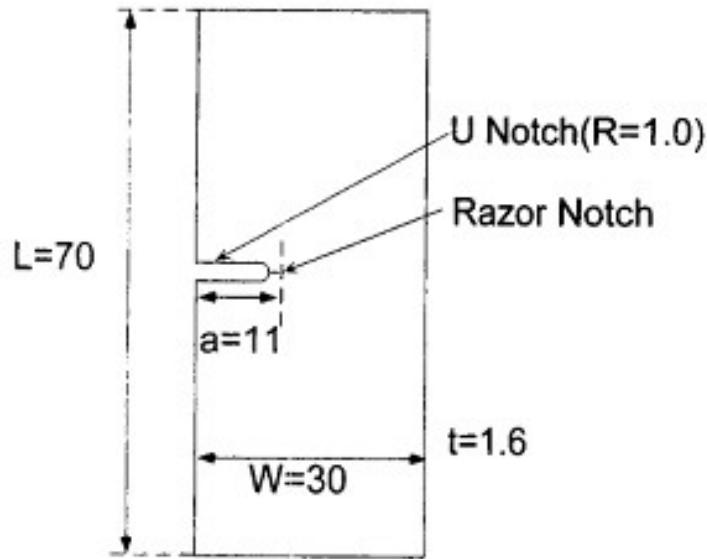
Molecular Mechanisms **for** Reducing the Effects of ESC

Drawing Parallels from Polymer Science on Craze-Crack Mechanics (Polystyrene, PVC, Polyethylene):

- Polymer Blends
- Molecular Weight of the Polymer
- Crosslinking
- Branching of the Polymer
- Rubber Modification
- Fiber Reinforcement

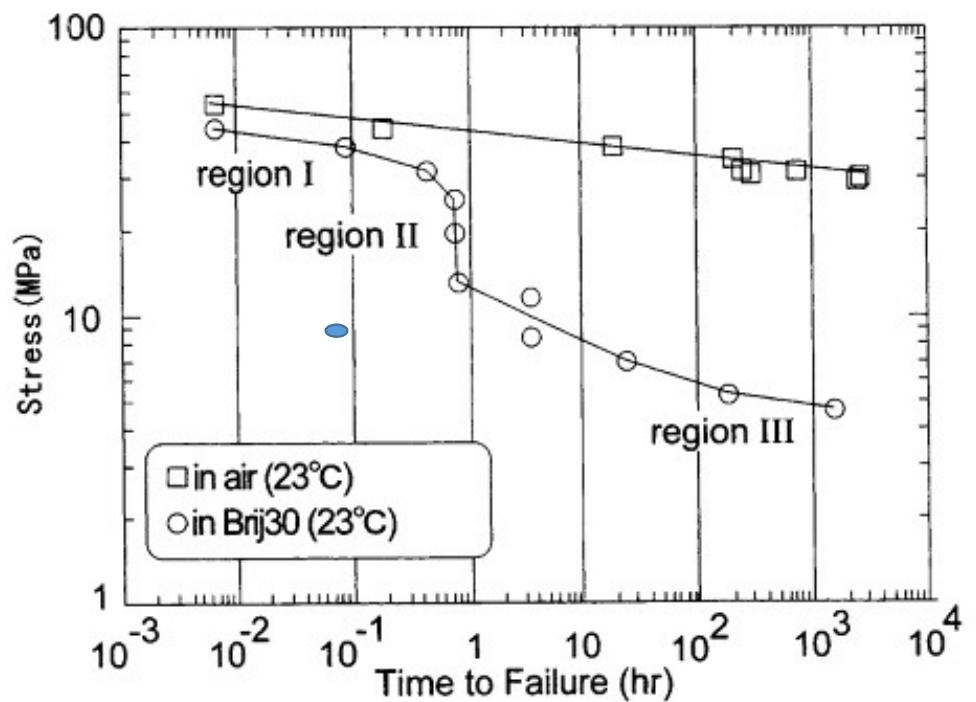
Environmental Stress Cracking of Poly(Acrylonitrile-Butadiene-Styrene)

Kawaguchi, Nishimura, Miwa, Abe, Kuriyama, Narisawa, Polymer Eng. & Sci., 39(2), (1999), 268 – 273.



The schematic of the specimen for ECT tests.

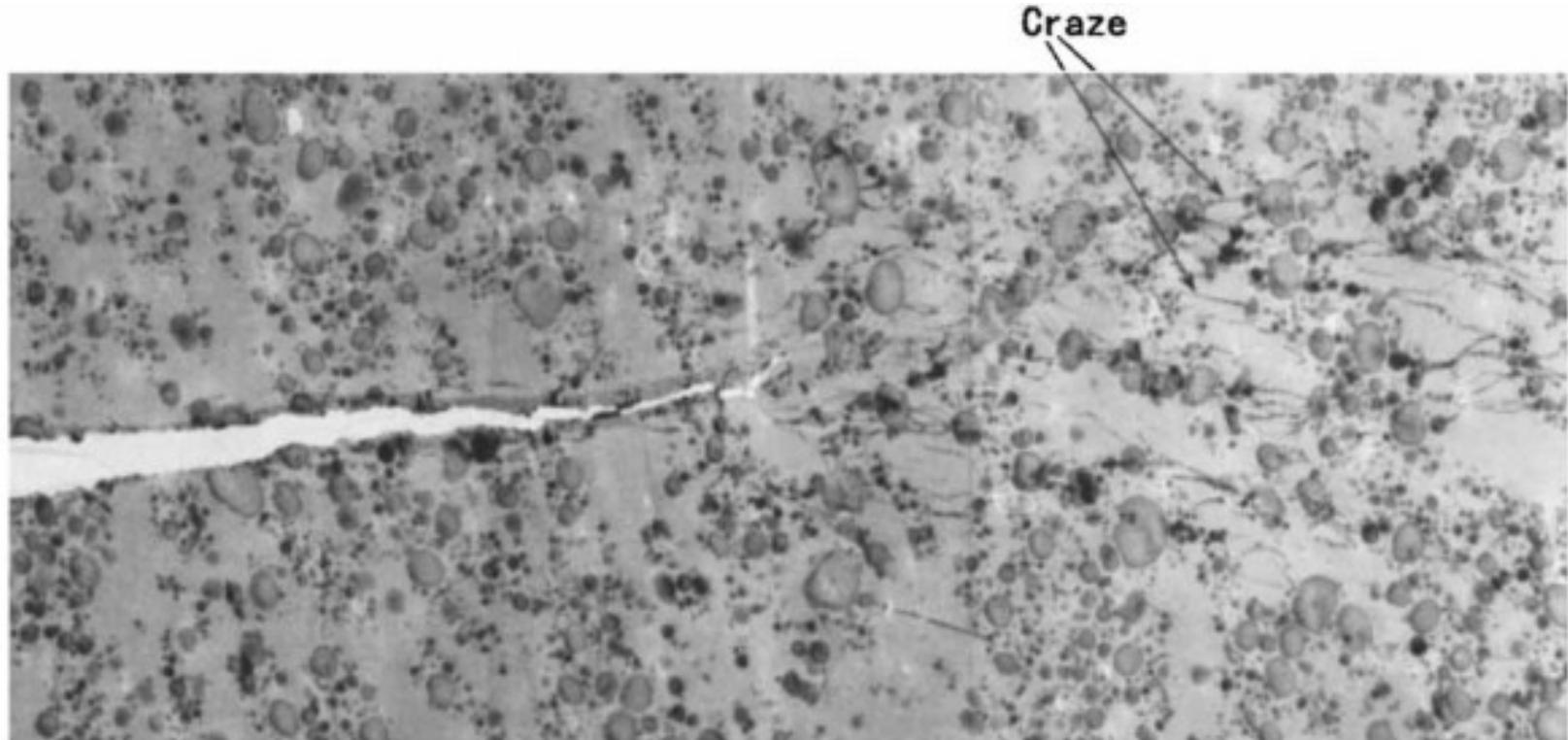
ECT - Constant load tensile creep test –
edge crack tension.



The result of creep tests in air and nonionic surfactant.

Environmental Stress Cracking of Poly(Acrylonitrile-Butadiene-Styrene)

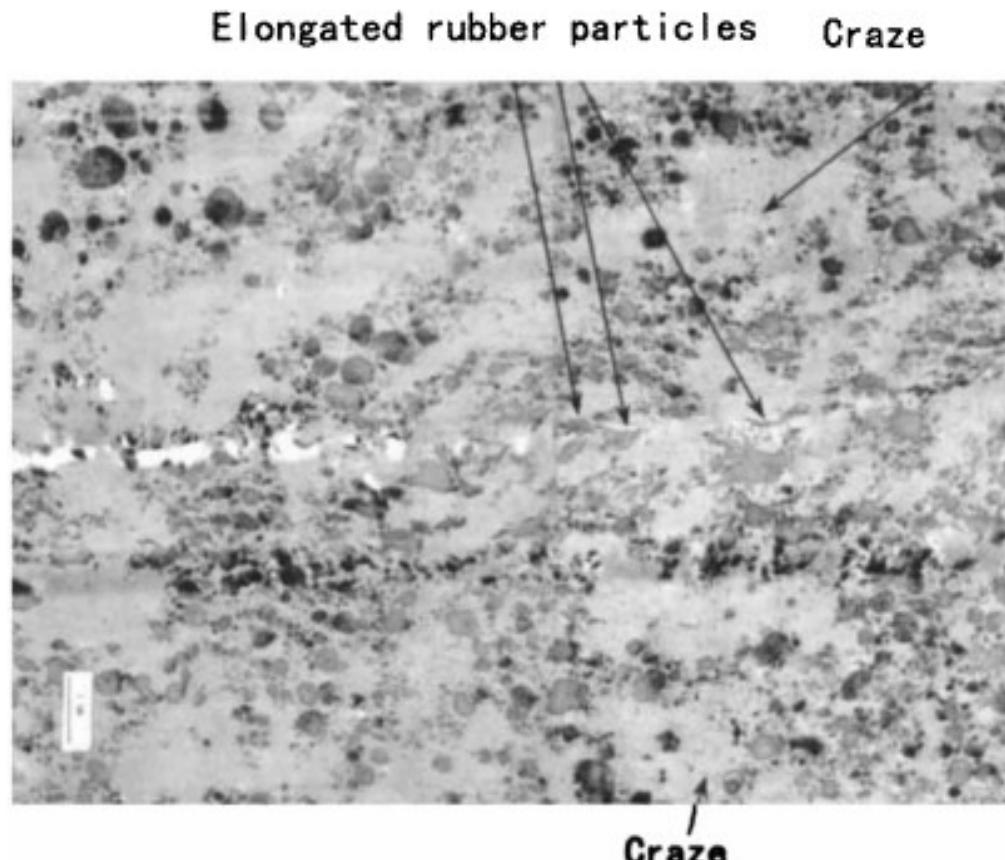
Kawaguchi, Nishimura, Miwa, Abe, Kuriyama, Narisawa, Polymer Eng. & Sci., 39(2), (1999), 268 – 273.



TEM image of the crack tip in an ECT test.

Environmental Stress Cracking of Poly(Acrylonitrile-Butadiene-Styrene)

Kawaguchi, Nishimura, Miwa, Abe, Kuriyama, Narisawa, Polymer Eng. & Sci., 39(2), (1999), 268 – 273.

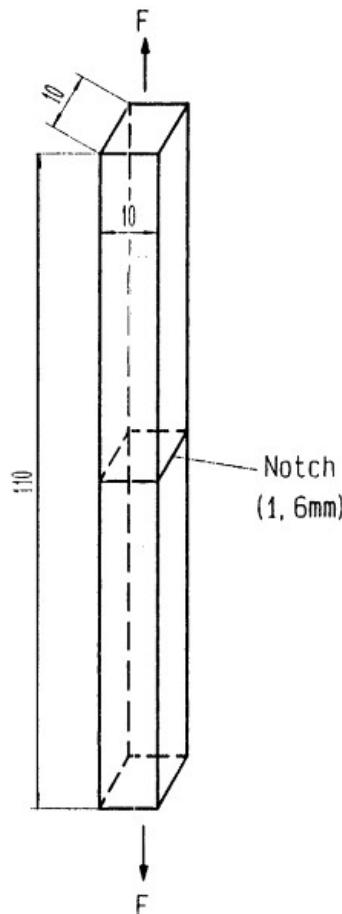


TEM image of the crack tip.

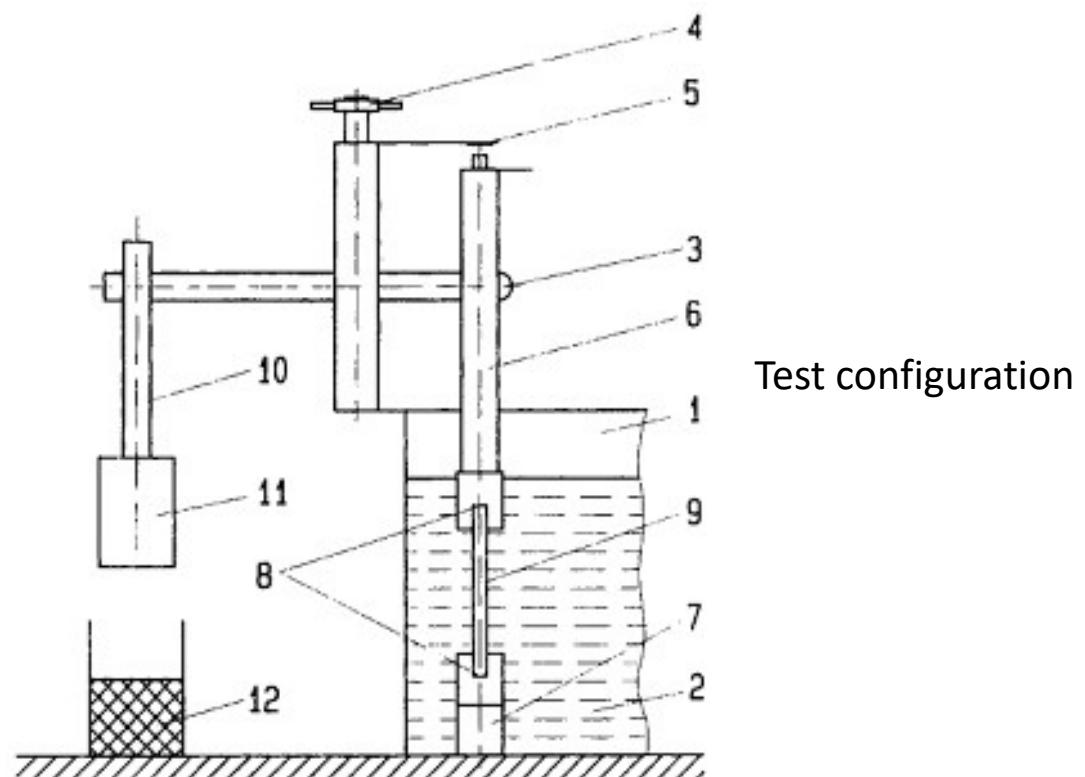
Environmental Stress Cracking Resistance of Blends of High-Density Polyethylene with Other Polyethylenes

Schellenberg, Feinhold, Polymer Eng. & Sci., 38(9), (1998), 1413 – 1419.

Test piece geometry

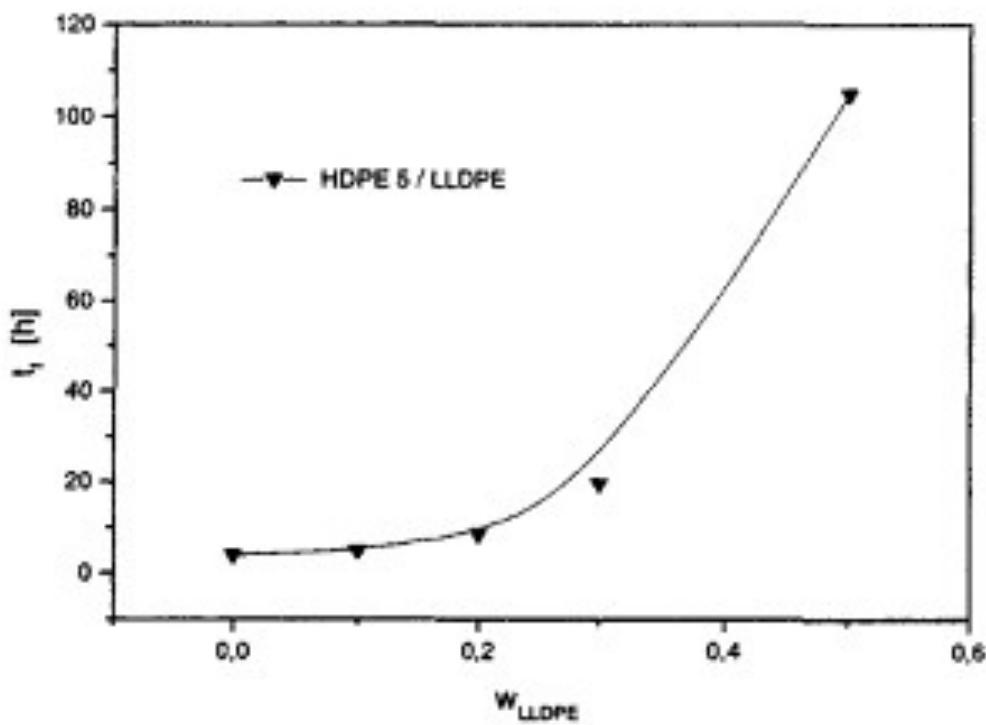


Test configuration

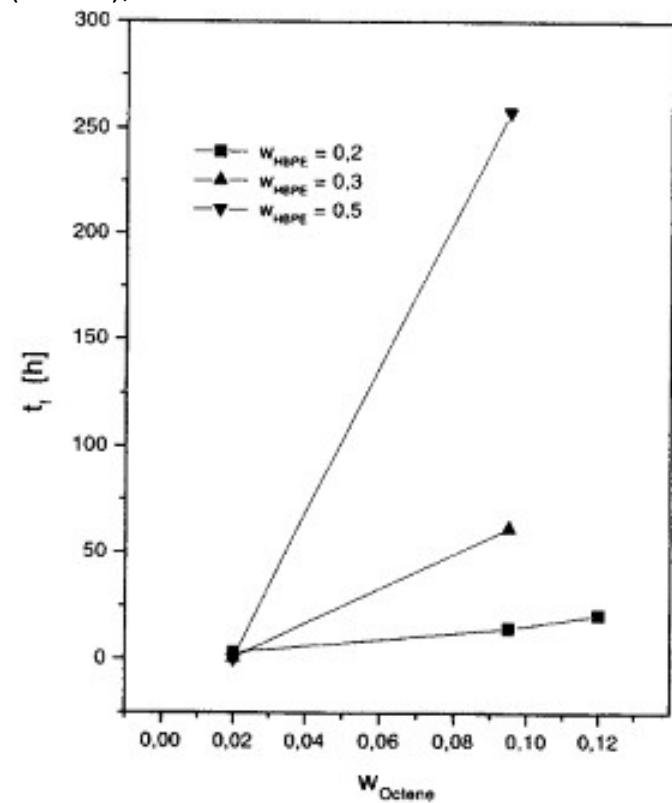


Environmental Stress Cracking Resistance of Blends of High-Density Polyethylene with Other Polyethylenes

Schellenberg, Feinhold, Polymer Eng. & Sci., 38(9), (1998), 1413 – 1419.



Dependence of failure time t_f on weight fraction of LLDPE (W_{LLDPE}) in HDPE/LLDPE blends (test load 6 Mpa).



Dependence of failure time t_f on weight fraction of octene in HBPE (W_{Octene}) in HDPE/HBPE blends for various blend compositions (W_{HBPE}) (test load 6 Mpa).

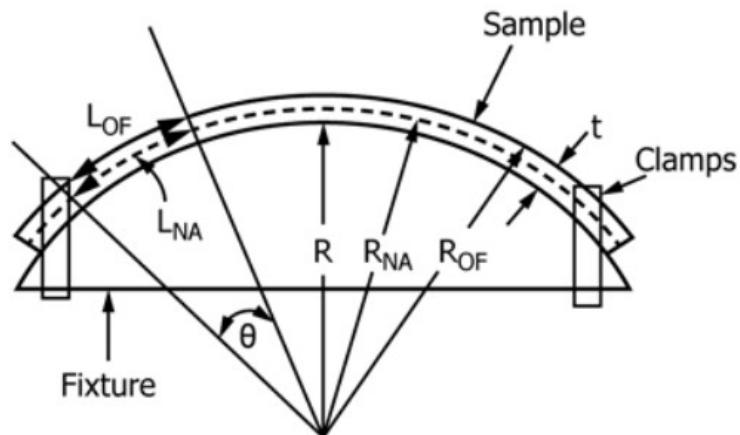
Summary: Opportunities

- Environmental Stress Cracking will continue to cause problems with commercial thermoplastics.
- Although much has been learned regarding ESC there has not been a solution for designing materials that are impervious to ESC.
- Until testing standardization has been introduced, the correlation of data from different laboratories will be difficult.
- Millions of dollars will continue to be spent on ESC field failures
- There exists an opportunity to further the understanding and resolution of ESC by well structured investigations.



Designation: D543 – 14

Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents¹



R = radius of jig

R_{NA} = radius of neutral axis

R_{OF} = radius of outer fiber

t = thickness of specimen

θ = arbitrary angle

L_{OF} = length of outer fiber

L_{NA} = length of neutral axis

considering a portion of test bar determined by angle θ

PRACTICE B—MECHANICAL STRESS AND REAGENT EXPOSURE

19.2 Expose the strained test specimens, along with one set of 0.0 % strain (unstrained) specimens, to the reagent being evaluated for compatibility. The test specimens can be immersed in liquid reagents, or alternately, a wet patch method can be used. The wet patch method involves applying a cotton patch (cheesecloth) over the test specimens and saturating the patch with liquid. For volatile reagents, reapply the liquid as necessary to provide continuous saturation. Greases can be wiped directly onto the specimen surface.

FROM: Proponent Testimony In Support of Senate Bill 95

Before the Members of the Ohio Senate Committee on Energy and Natural Resources

Andrerw Olah, Ph.D.

October 25, 2017

“In my introduction to this class I impress upon these upcoming engineers the awareness that all materials have disadvantages based upon the environmental conditions that they can experience.”

“For example, in certain drinking water environments wood rots, steel and iron rusts, and copper corrodes; all specific to the contacting water chemistries. Although plastic materials may be impervious to these conditions there are other environments that the engineer must be aware of when utilizing polymer or plastic materials. Due to these requirements the engineer should have available all approved materials for the specific application in order to match the proper material with the specific end use environmental condition.”

“By allowing engineers to have at their discretion all suitably recognized materials, the engineer can adequately design the best system optimizing mechanical performance and system longevity at a reasonable cost.“

Lecture 18: Environmental Stress Cracking

Questions?



5

Dr. Andy Olah, amo5@case.edu, C: 216-272-0505

"My kids and grandkids keep laughing about me losing my memory.
They won't be laughing at Thanksgiving when there's no eggs under the tree."