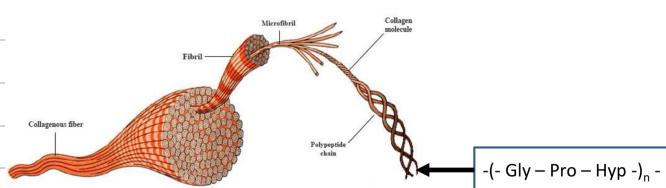


Lessons From Biology: Hierarchical Structures (HS[s])

- **Hierarchical Structures:** Build up of structural layers/components that combine into a larger/scaled phase
 - ↳ Example: Tendons = Procollagen \rightarrow Micro Fibril \rightarrow Sub Fibril $\rightarrow \dots \rightarrow$ Tendons
 - Assemblies of molecular units of fiber aggregates that are embedded or in contact with other phases
 - Present in probably all complex systems, especially natural ones
 - 3 basic principles
 1. Scale: Structure is organized in discrete levels or scales
 2. Interaction: Levels of structural organization held together by specific interaction b/w components
 3. Architecture: Levels organized into an oriented hierarchical composite system
 - Uniaxial Mechanical System: Tendons

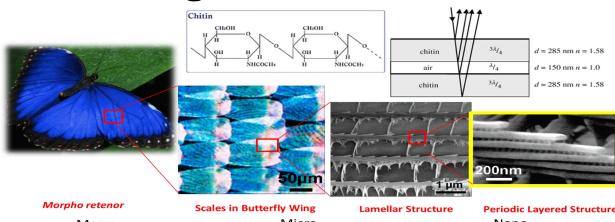
Structure of collagen



- Operates reversibly at uniaxial tension
 - Hierarchical Structure absorbs energy & protects the tendon as a whole from catastrophic failure

Other examples: Human Hair

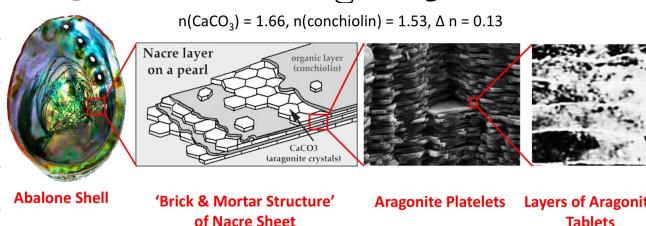
• Photonic Layered Systems : Butterfly Wings



- Periodic Structure creates photonic band gap that gives a brilliant blue color
 - Periodicity is different in different butterflies, thus giving color to two wings
 - The color is not due to a pigment

Other examples: **Eggs of Butterflies**

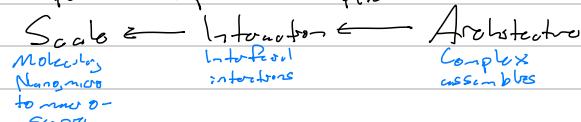
Organic/humic Layered Systems: Nan Shells



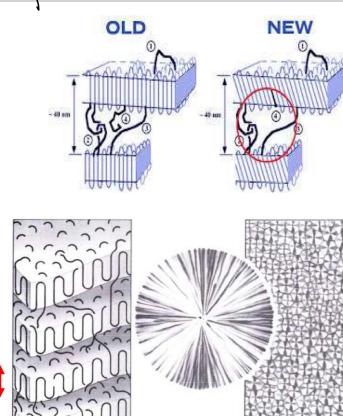
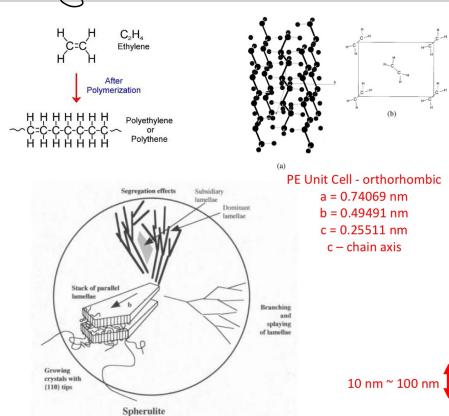
- Organic cement act as ductile fraction preventing crack growth
 - Elasto Modulus: 70 GPa in dry, 60 GPa in wet states
 - Tensile Strengths: 170 MPa in dry, 130 MPa in wet states
 - Flexural strength (between 100 and 200 MPa) is comparable to many other ceramics
 - Other Estimates: Bone (Young's Modulus b/w 8 and 24 GPa)

- Hierarchical structures in Plants: Wood, Collarose, Bamboo

Important Components in Hierarchical Structures



Polymer Morphological Structures



• Hierarchical Structures Elsewhere

\rightarrow The Effect of T_0

→ Management Systems

→ Hierarchical Structures

o Protein MS based on Amino Acid Seq.

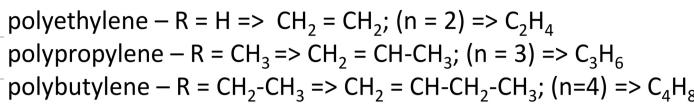
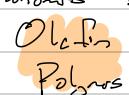
- A linear seq. of a large number of amino acids forms primary protein structure
- The Intramolecular interactions among specific segments of the amino acids in the primary structure forms the Secondary structure

Polystyrene and Styrofoam

Vinyl Polymers Not to be confused with PVC materials

• Most common type of polymers derived from "vinyl-type" monomers: $\text{CH}_2=\text{CHR}$

- Olefin polymers are a subgroup of vinyl monomers produced from alkenes having a C_nH_{2n} monomer structure
- Vinyl Polymers
 - polystyrene - $\text{R} = \text{C}_6\text{H}_5$
 - polyvinyl chloride - $\text{R} = \text{Cl}$
 - polyvinyl acetate - $\text{R} = \text{O}_2\text{CH}_3$
 - polyacrylonitrile - $\text{R} = \text{CN}$



Polystyrene

- $T_g = 100^\circ\text{C}$, can be increased by forming a copolymer
- Polymerized by free radical polymerization

Rand. • Atactic: $T_g \approx 100^\circ\text{C}$

Alt. • Syndiotactic: rapidly semi-crystalline $T_g = 100^\circ\text{C}$, $T_m = 270^\circ\text{C}$ can crystallize, but weak

Same. • Isotactic: slowly semi-crystalline $T_g = 100^\circ\text{C}$, $T_m = 240^\circ\text{C}$ crystalline domain

↳ None have crystallization temperature!

Recall • Amorphous = without structure, no repeating

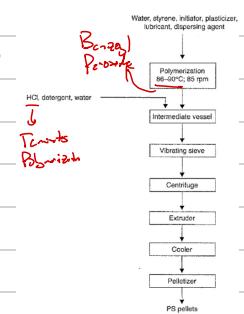
• Semi-crystalline = regions of both crystalline & amorphous

• Chain rotation motion of Polymers @ $T > T_g$ but frozen @ $T < T_g$
 ↳ Phenyl group spinning on the backbone

Unmodified Polystyrene is quite brittle

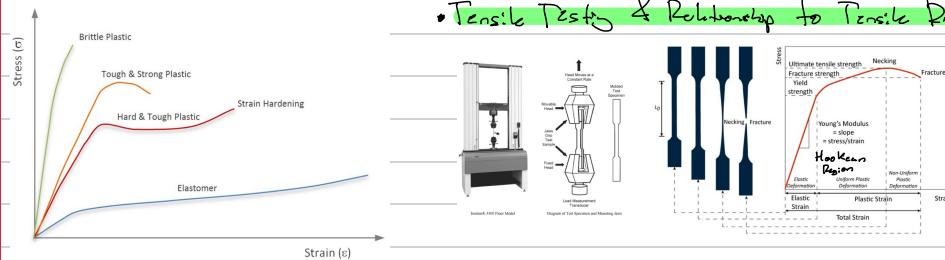
• Thermally insulating XPS for insulation and EPS for coolers and packaging
 ↳ Extruded ↳ Expanded

Flow Diagram
Process flow diagram of
Polymerization of
PS



Polystyrene Continued - SAN, ABS, & HIPS

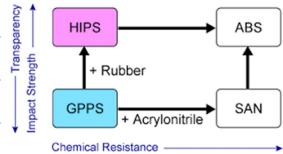
• Tensile Testing & Relationship to Tensile Properties of Plastics



• Stress-Strain Curves are polymers' finger prints

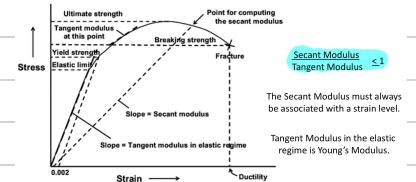
◦ Tensile Properties of polymers (fingerprints) their mechanical performance

• Polystyrene Derivatives for Improved Performance



GPPS = General Purpose Polystyrene

↳ The topic of the previous lecture

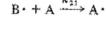
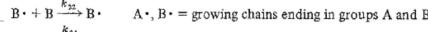
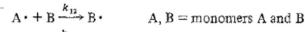


Reactivity Ratios for Free Radical Polymerization

Assumptions 1. Concentration of free radicals doesn't change over time

2. Only two monomers react on a polymer chain determines reactivity

3. Chain propagation is the only reaction of importance (disregard initiation and termination)



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

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

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

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

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

Product of r_1 and r_2

a) $r_1 \cdot r_2 \approx 1$ - Random Copolymer

b) $r_1 \cdot r_2 < 1$ - Alternating Copolymer

c) $r_1 \cdot r_2 > 1$ - Block Copolymer

Products of Monomer Reactivity Ratios in Copolymerization

Monomer	Styrene	Vinyl Acetate	Vinyl Chloride	Methyl Methacrylate	Vinylidene Chloride	Methyl Acrylate	Acrylonitrile
Butadiene	1.0	0.55	0.39	1.0	0.61	0.80	0.84
	0.71	0.34	0.24	0.16	0.12	0.09	0.02
	0.30	0.24	0.30	0.96	0.61	0.75	0.25
	0.19	0.16	0.12	0.75	0.61	0.75	0.13
	0.10	0.14	0.90	0.75	0.96	0.80	0.24
	0.04	0.14	0.90	0.75	0.96	0.80	0.34
	0.02	0.02	0.25	0.13	0.24	0.84	0.64

$r_1 \cdot r_2 < 1 \rightarrow$ Alternating Copolymer

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	1.50 ± 0.05	4
Vinyl acetate	Acrylonitrile	0.061 ± 0.013	4.05 ± 0.3
Vinyl acetate	Vinyl chloride	0.23 ± 0.02	1.68 ± 0.08
Vinylidene chloride	Isobutene	3.3	0.05

SAN

• Styrene-Acrylonitrile Copolymer

↳ Typically 70% Styrene and 30% Acrylonitrile

• Advantages:

◦ Excellent rigidity

◦ Excellent Load-bearing capability

◦ Chemical resistance

◦ High Thermal Stability

◦ Good Appearance and Clarity

◦ Good Thermal Resistance

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

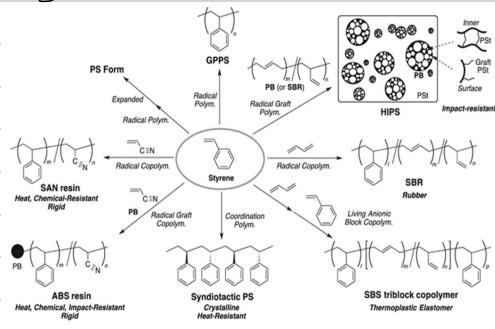
Uses:

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

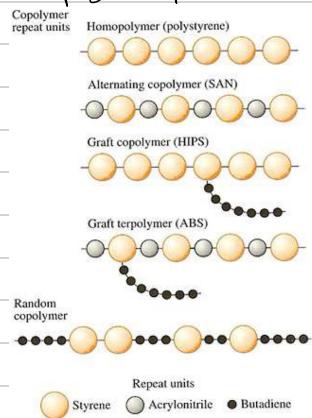
ABS

- Acrylonitrile Butadiene Styrene Copolymer
- Loss of Transparency, Increased Impact Strength

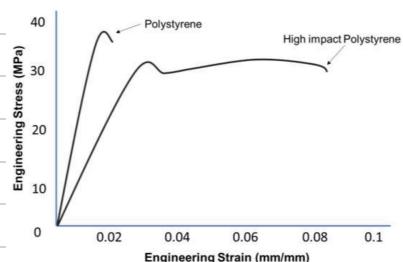
Styrene Forms



Copolymer Repeat Units



Impact Modification - ABS & HIPS

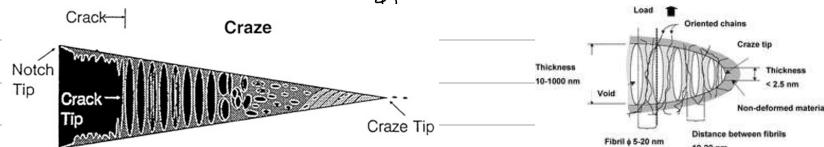


ABS is a generic term

- ↳ The only thing needed to be called ABS is that it needs acrylonitrile, Butadiene and styrene. The structure is independent of the monomer arrangement (the arrangement of the 3 is not specific to ABS)
- ↳ If looks for ABS, look into the product, not just to name

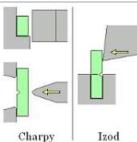
Failure Mechanism Differences

- Crazing: Occurs prior to a crack
- Shear Bands - Slip bands regions
- Crack-Craze Morphology in PS

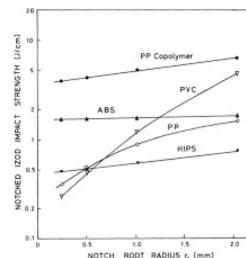


Craft & Izod Impact Test Method

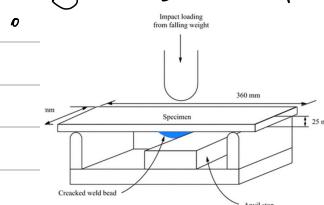
- Sharp Notch → Low Impact Strength
- Wide Notch → Higher Impact Strength



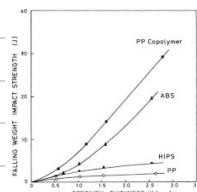
Results:



Falling Weight Impact Test Method



Res. Izs:



Energy Disruption Mechanisms in Rubber Modified Structures

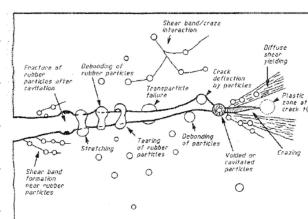
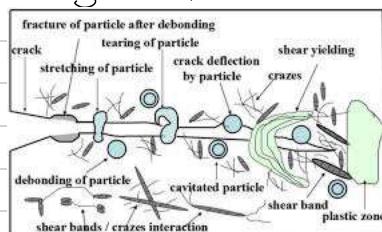
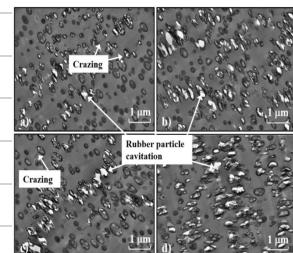


Fig. 3.1 Crack toughening mechanisms in rubber filled modified polymers.

- By Encapsulated Rubber in ABS and HIPS:



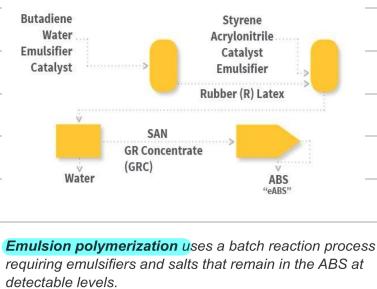
Methods for producing ABS polymers

- 1. Direct polymerization:
 - Process: Original process discussed previously having all three monomers are polymerized
- 2. Graft Copolymerization (In Situ Bulk Polymerization):
 - Process:
 - This is the most common method. It involves polymerizing styrene and acrylonitrile in the presence of polybutadiene. This creates a structure where the polybutadiene acts as a backbone, with styrene and acrylonitrile chains grafted onto it.
 - Mechanism:
 - The polybutadiene, a rubbery polymer, provides impact resistance and flexibility. The styrene and acrylonitrile contribute to stiffness, strength, and heat resistance.

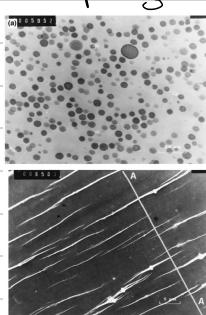
- 3. Mechanical Blending (Blending of SAN and Polybutadiene):
 - Process: In this method, a styrene-acrylonitrile copolymer (SAN) is mechanically mixed with polybutadiene. This approach creates an ABS blend, which might be preferred for specific applications or to achieve certain cost-effectiveness.
- 4. Emulsion Polymerization:
 - Process: A specific type of graft polymerization, where butadiene is first polymerized in an aqueous medium, and then styrene and acrylonitrile are grafted onto the butadiene particles.
- 5. Mass Polymerization:
 - Process: Another patented process that also leads to the production of ABS. All reactants are sequentially introduced into reactor.

Emulsion Polymerization of ABS

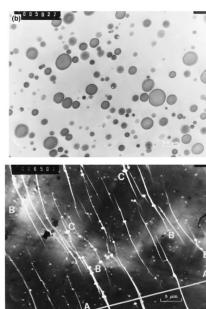
EMULSION POLYMERIZATION



Morphology & craze structures in Emulsion ABS



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

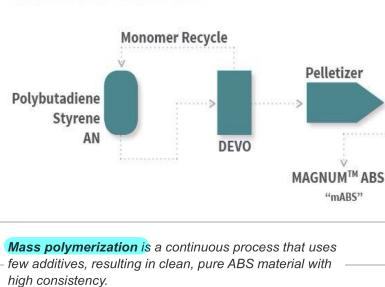


E2:
PB ~ 68%
ST ~ 24%
AN ~ 8%

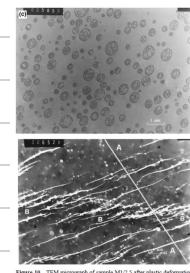
Figure 9 TEM micrograph of sample E2 2.5 after plastic deformation

Mass Polymerization of ABS ← "Put it all together!"

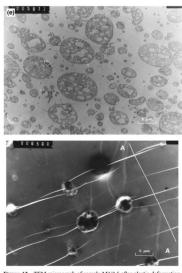
MASS POLYMERIZATION



Morphology & craze structures in Mass ABS



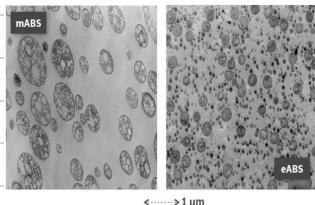
M1:
PB ~ 11%
ST ~ 65%
AN ~ 23%



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

Figure 11 TEM micrograph of sample M2 2.5 after plastic deformation

Comparison of Mass & Emulsion Polymerized ABS



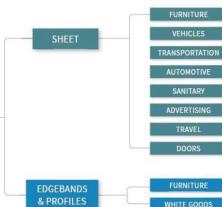
Morphology is the result of in situ formation of rubber particles during the SAN matrix polymerization. Pictured below are examples where:

- 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.

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.

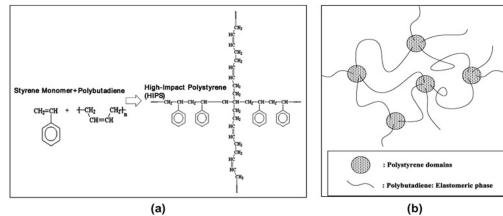
eABS: rubber particles are smaller and dense because they are in essence produced in a separate process (rubber latex and GRC production) from the SAN matrix polymerization. This allows a higher control on the rubber particle size and hence the possibility to produce smaller rubber particles, which can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

Applications of ABS



HIPS Structure and Morphology

- Doesn't have Acrylonitrile



- Various morphologies can be imprinted into HIPS

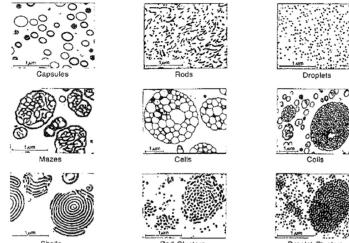


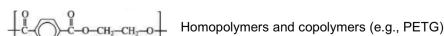
Figure 14. Particle structures observed in HIPS. (Reproduced with permission from ref. 32. Copyright 1992 Hanover.)

Plant to Slide Annotations for PVC

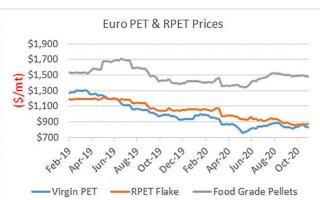
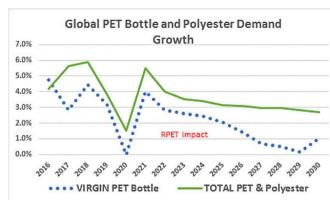
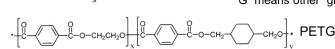
Lectures 6, 7 and most of 8 are all slide-only annotations

Polyesters

Poly(ethylene terephthalate) (PET)



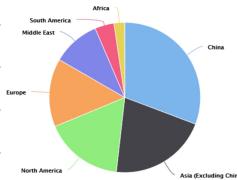
"G" means other "glycols"



World Production & Consumption

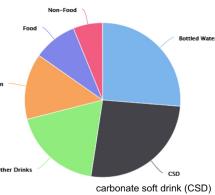
Global PET Production Capacity

Total Capacity 30.3 million tons (2017)



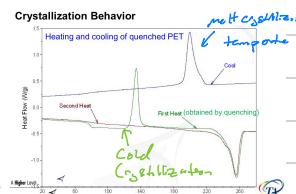
Global PET Consumption by End-Segment

Total Consumption 21.5 million tons (2016)



Typical Properties (Thermal, Mechanical, Electrical)

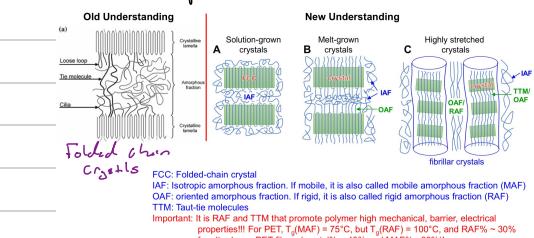
Glass transition temperature T_g	K	DSC	(72-100°C) 342-388
Melting temperature T_m	K	DSC	(265-280°C) 338
Heat of fusion ΔH_f	kJ mol ⁻¹	DSC	24.1
Breaking strength σ_b	N/mm ²	Tensile	50
Tensile (Young's) modulus E	N/mm ²	Tensile	1,700
Flexural modulus (rigidity) E_f	N/mm ²	3-point flexure	2,000
Ultimate strain ϵ_u	%	Tensile	180
Yield strain ϵ_y	%	Tensile	4
Impact strength I_{90}	J m ⁻¹	Notched IZOD, ASTM D28-86	90
Hardness		Rockwell	80B
Deflection temperature	K	HDT	
Thermal expansion coefficient	K ⁻¹	TMA	9.1×10^{-5}
Water absorption	%	After 24h	0.5
Dielectric strength	kV mm ⁻¹	Thermal	15.7
Dielectric constant	10 ⁹ Hz	1/8 in	3.8
Volume resistivity	ohm cm	At 1 psi	330
		At 60 psi	344
		After 24h	20
		After 24h	0.5
		ASTM D257	0.1×10^{12}



<http://www.american-decay.com/Downloads/Applications/Notes/13221-Differential-Scanning-Calorimetry-DSC-as-an-Analytical-Tool-in-Plastics-Failure-Analysis.pdf>

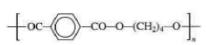
- Crystallinity ranges from 0% to 45%;
- Amorphous PET is transparent – PET preform or parison;
- Crystalline PET is non-transparent – heat resistant products.

Rigid Amorphous Fractions for Better Properties

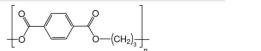


PBT & PTT

Poly(butylene terephthalate) (PBT)



Poly(trimethylene terephthalate) (PTT)



Polyester	Structure of Repeat Unit	Trade Name
Polyethylene terephthalate (PET/PETE)		
Polybutylene terephthalate (PBT)		Dynel [®] DuPont [®] Celanese [®]
Polytrimethylene terephthalate (PTT)		Cetron [®] Celanese [®] DuPont [®]
Polyethylene naphthalate (PEN)		Zeneal [®] Teijin

Physical Property	PET	PTT	PBT
Chemical structure			
Specific Gravity measured as per ASTM D792 specifications)	1.40	1.35	1.34
T_g (°C)			
Using DSC for injection molded samples at a heating rate of 10 °C min ⁻¹)	265	227	228
T_d (°C)	80	45-60	25
Onset of decomposition temperature by using TGA (°C)	350	373	378

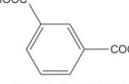
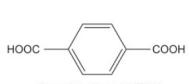
*indicates that the same experimental conditions were used in both

PBT & PTT

Glycol-Modified PET (PETG) Copolymers

Diacid	+	Diol	→	Polyester
TPA	+	EG	→	PET
TPA	+	EG + CHDM	→	PETG (copolyester where EG > CHDM)
TPA	+	CHDM + EG	→	(copolyester where CHDM > EG)
TPA + IPA	+	CHDM	→	PCTG (copolyester)
TPA	+	CHDM	→	PCT

EASTMAN



Property	Unit	PETG	PCTG	PCTA
Density	g/cc	1.27	1.23	1.2
Transparency	%	91	89	91
Glass transition temperature	°C	81	83	87
HDT at (0.46 MPa or 66 psi)	°C	70	74	75
HDT at (1.8 MPa or 264 psi)	°C	63	64	65
Tensile strength @ break	MPa	28	30	51
Tensile elongation	%	110	330	300
Flexural modulus	GPa	2.1	1.8	2
Impact strength, notched, 23°C	J/m	101	No break	80
Processing temperature	°C	250-270	250-270	230-280
Softening point	°C	85	88	—

Bisphenol A-free – To replace PC



aligners



milk/water bottles



medical containers

1. PCT has rather stiff chains, $T_g=130^\circ\text{C}$ and $T_m=290^\circ\text{C}$. It has good weathering and water resistance and is used for film and fibers.
2. PCTA is amorphous ($T_g \sim 100^\circ\text{C}$), and has a high clarity and good mechanical and processing characteristics.
3. A similar copolyester (PETG/PCTG) is prepared from terephthalic acid and a mixture of CHDM and EG.

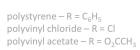
The Polyolefin Family

What is an Olefin Polymer

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

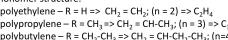
$$\text{CH}_2 = \text{CHR}$$

Where,



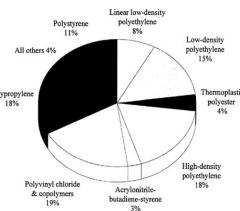
Not to be confused with poly(vinyl chloride) (PVC) materials which have traditionally been identified as "Vinyls", i.e., vinyl siding, vinyl records, etc.

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



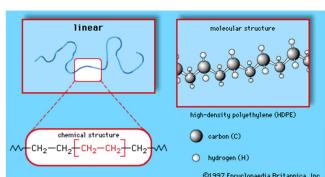
Polyolefin Resin Market Share

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



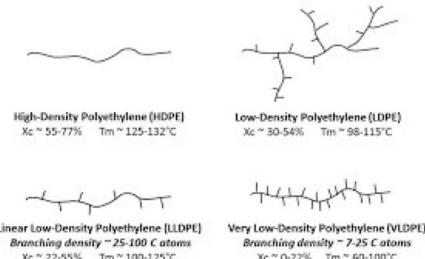
Polyethylene

Mono Simple Polymer



Branching

- Most of most PE products is branching

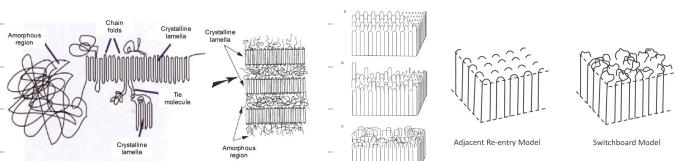


Reasons for PE's varying structure

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

Morphology

- Semi-crystalline: Different morphology forms



Polyethylene Transitions

What is the Gamma Thermal Transition in Polyethylene

The gamma transition (Γ) in polyethylene refers to a low-temperature relaxation process involving localized movements of the CH_2 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 CH_2 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 malleable, elastic state. In this context, the gamma transition often serves as a precursor to the broader glass transition observed below it.

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 effect of the Γ transition on the local movement of polymer chains influences its overall flexibility and toughness in the low-temperature range. Because 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 (β) 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.

Observations: 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 relaxation or the glass transition of the crystalline phase, is a relaxation process associated with the segmental mobility of chain units within the crystalline region of the polymer.

Segmental Mobility: The α -transition involves the movement of relatively short segments of the polyethylene chains within the crystalline domain. This movement can be described as the rotation and/or translation of these segments along their 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 aging 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 300 to 300 $(30$ to 120°C).

Factors Affecting α -Transition: The intensity and temperature of the α -transition can be affected by various factors like branching, crystallite size, 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.