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

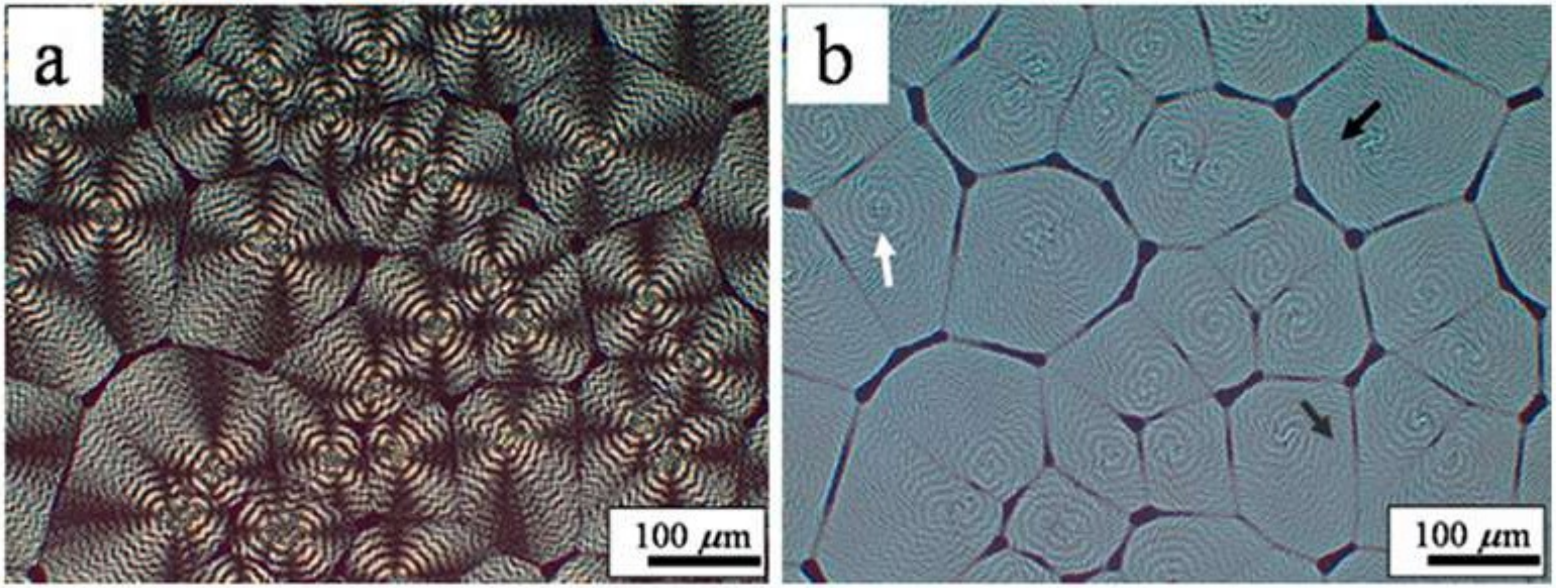

Figure 8. POM (**a**) and OM (**b**) micrographs of $PCL_{84.4k}$ CEBS formed from a 50 $mg \cdot mL^{-1}$ solution-cast film. Reproduced from [49] with permission from the Royal Society of Chemistry.

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/cryst7040115

Review of Optical Properties of Spherulites

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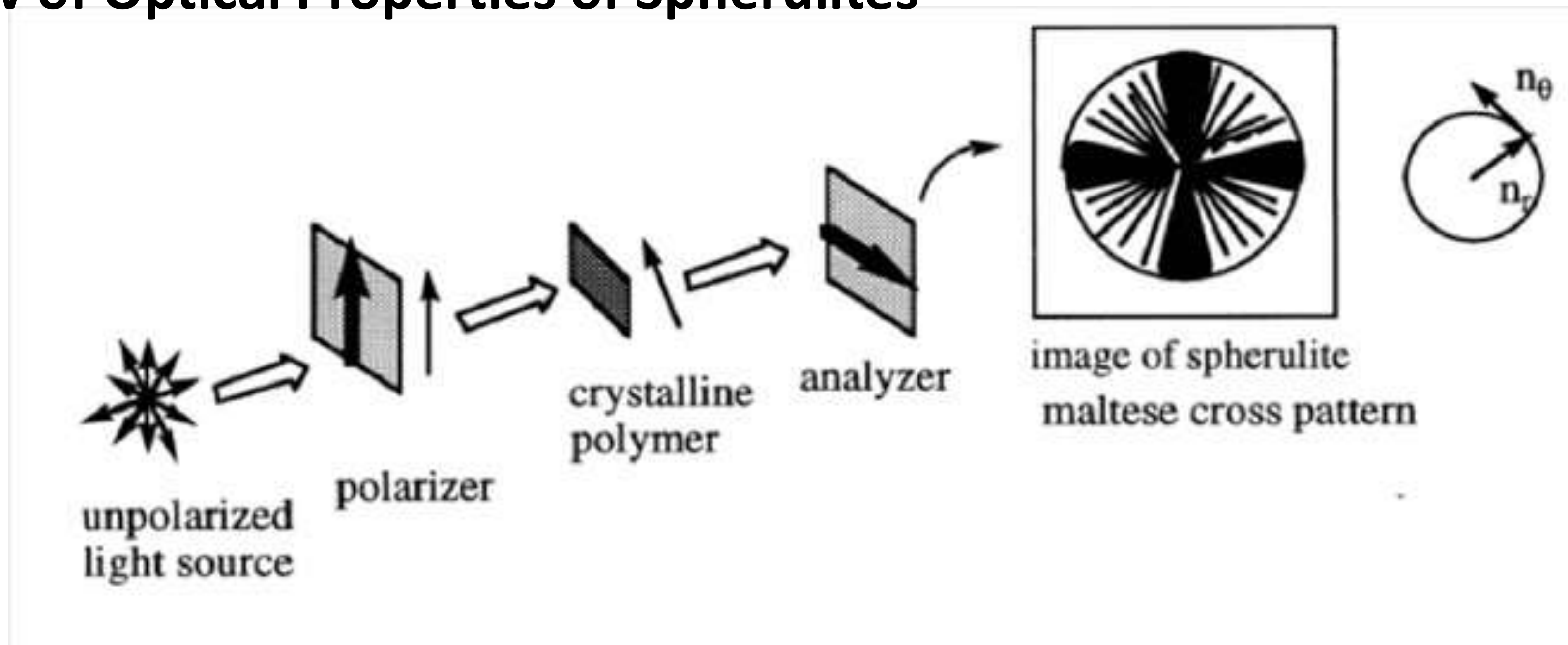
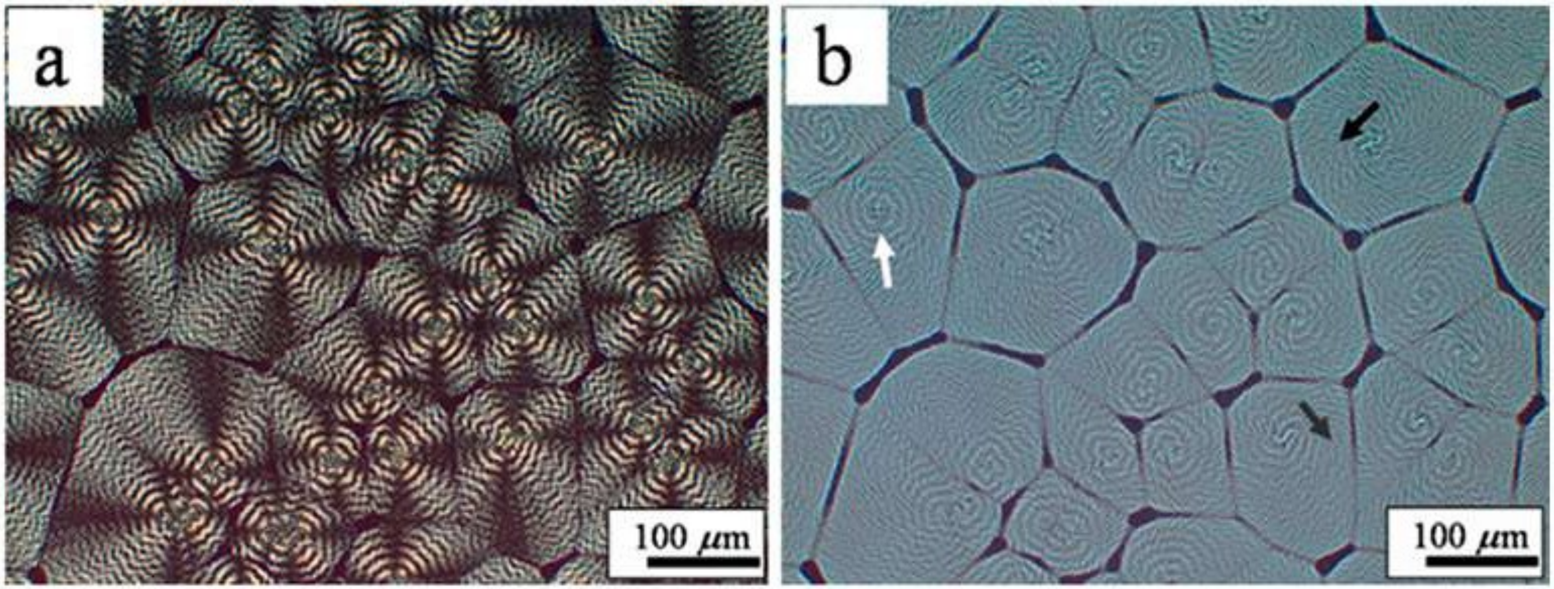


The Maltese cross is seen because polymers are birefringent. **Polarised light cannot travel through a crystalline polymer if the direction of the polarisation of the light is perpendicular to the direction of carbon chain in the polymer.** As a result, when a sample is studied under crossed polars,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



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Colloid and Polymer Science (2019) 297:771–779
https://doi.org/10.1007/s00396-019-04503-8

ORIGINAL CONTRIBUTION

Review of Optical Properties of Spherulites

Banded spherulites and twisting lamellae in poly–ε–caprolactone

Wilhelm Kossack[1] · Friedrich Kremer[1]

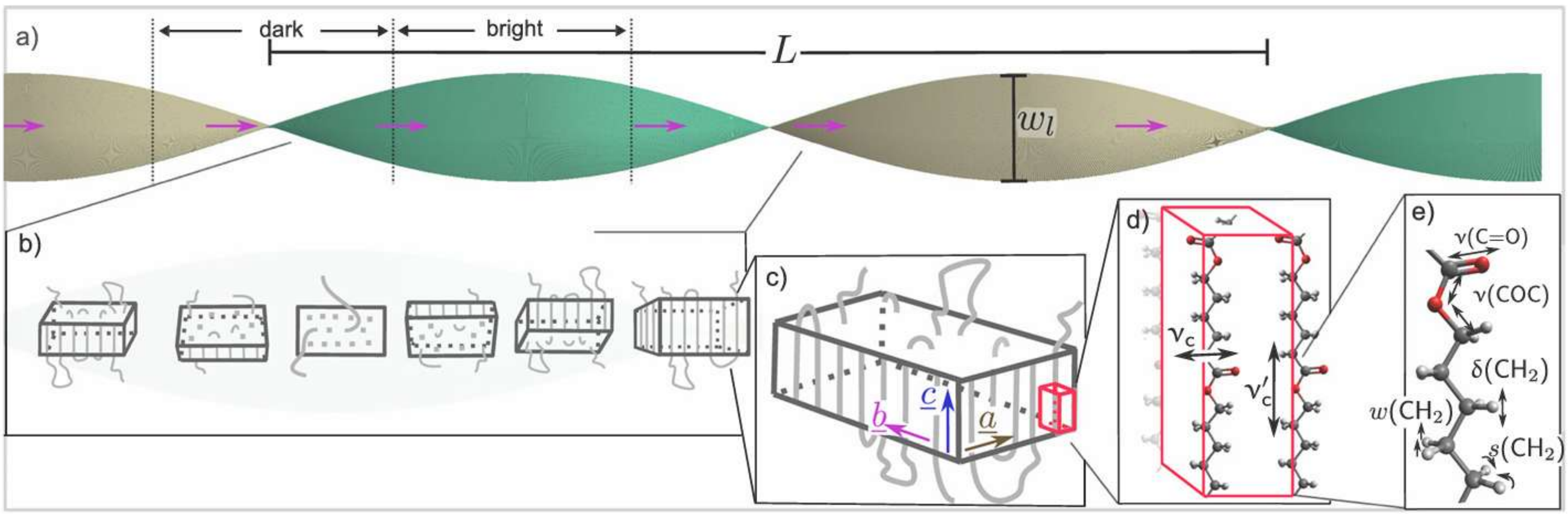


Fig. 7 Proposed model of a helicoidally growing lamellae (a twisted ribbon) within a spherulite of PCL. Green and beige coloring is a guide for the eye and marks the two sides of the lamellae. Lamellar growth direction ($\underline{b}$) is indicated by magenta arrows. Orientation of parts of the growing 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 momoner (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

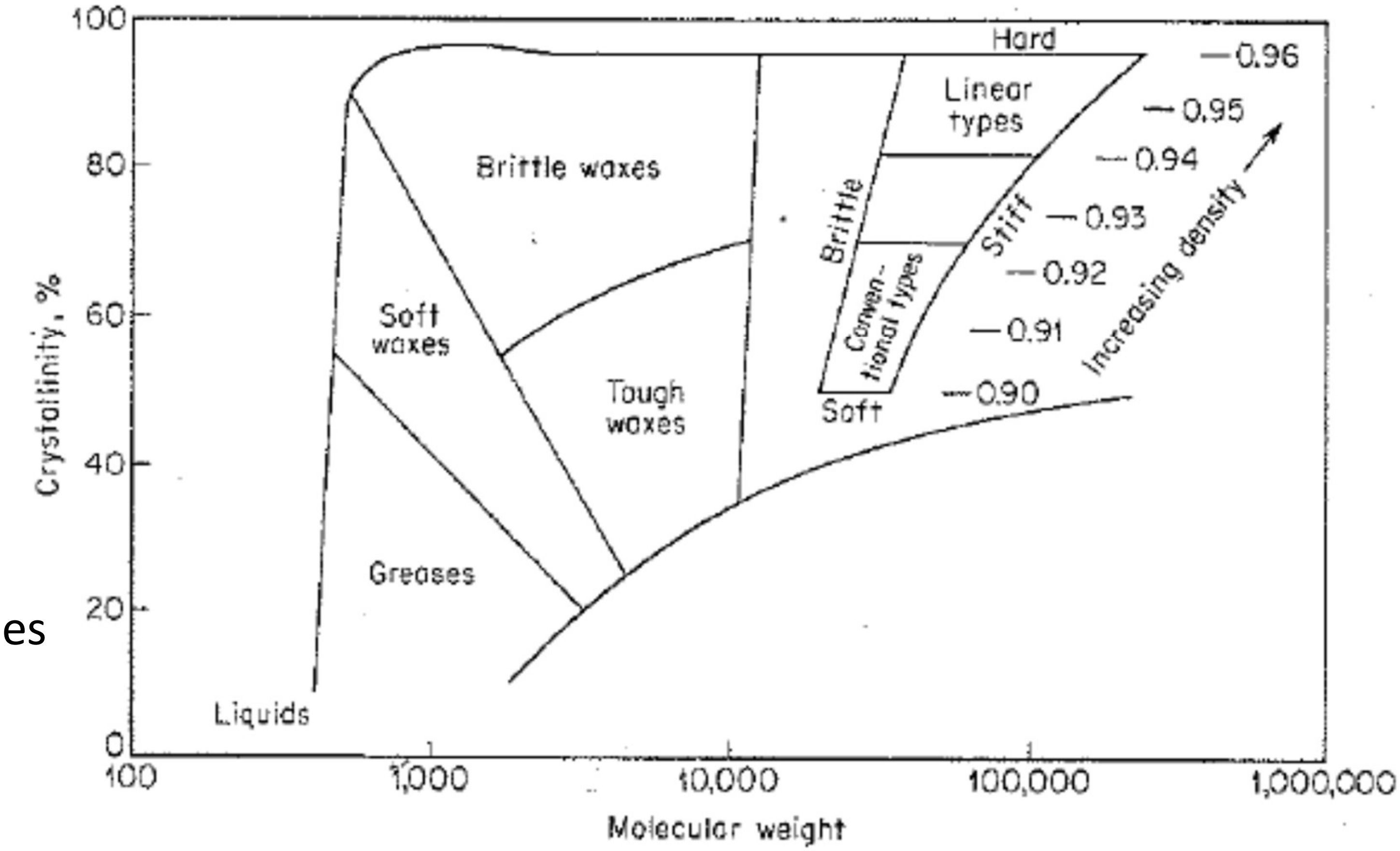


FIGURE 13-1
Relationships between crystallinity, molecular weight, and mechanical properties of polyethylene [3]. (After Kratz and Lyle, *Encyclopedia of Chemical Technology*, First Suppl., Interscience, 1957.)

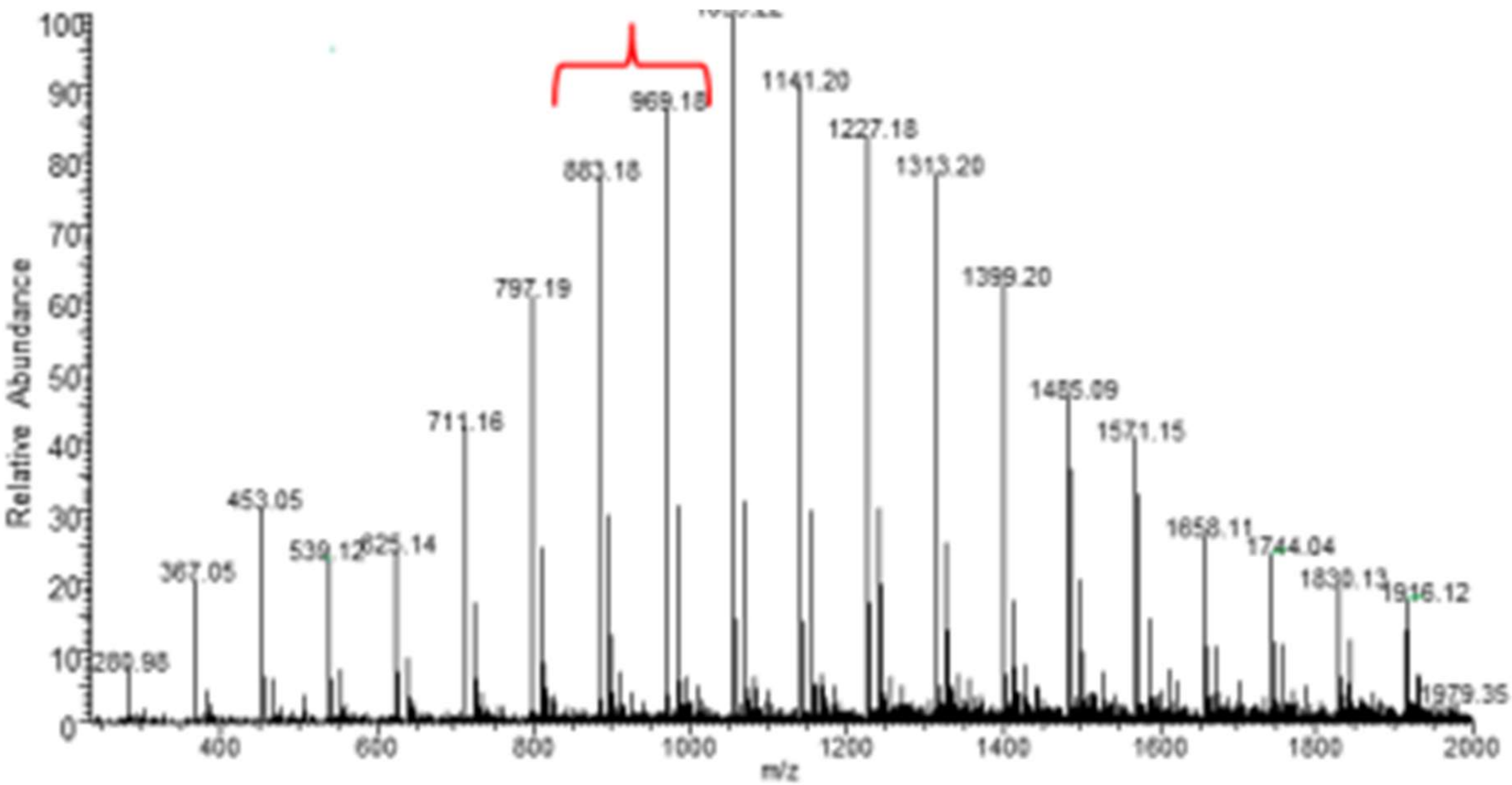
Ultralow Molecular Weight Polyethylene

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.

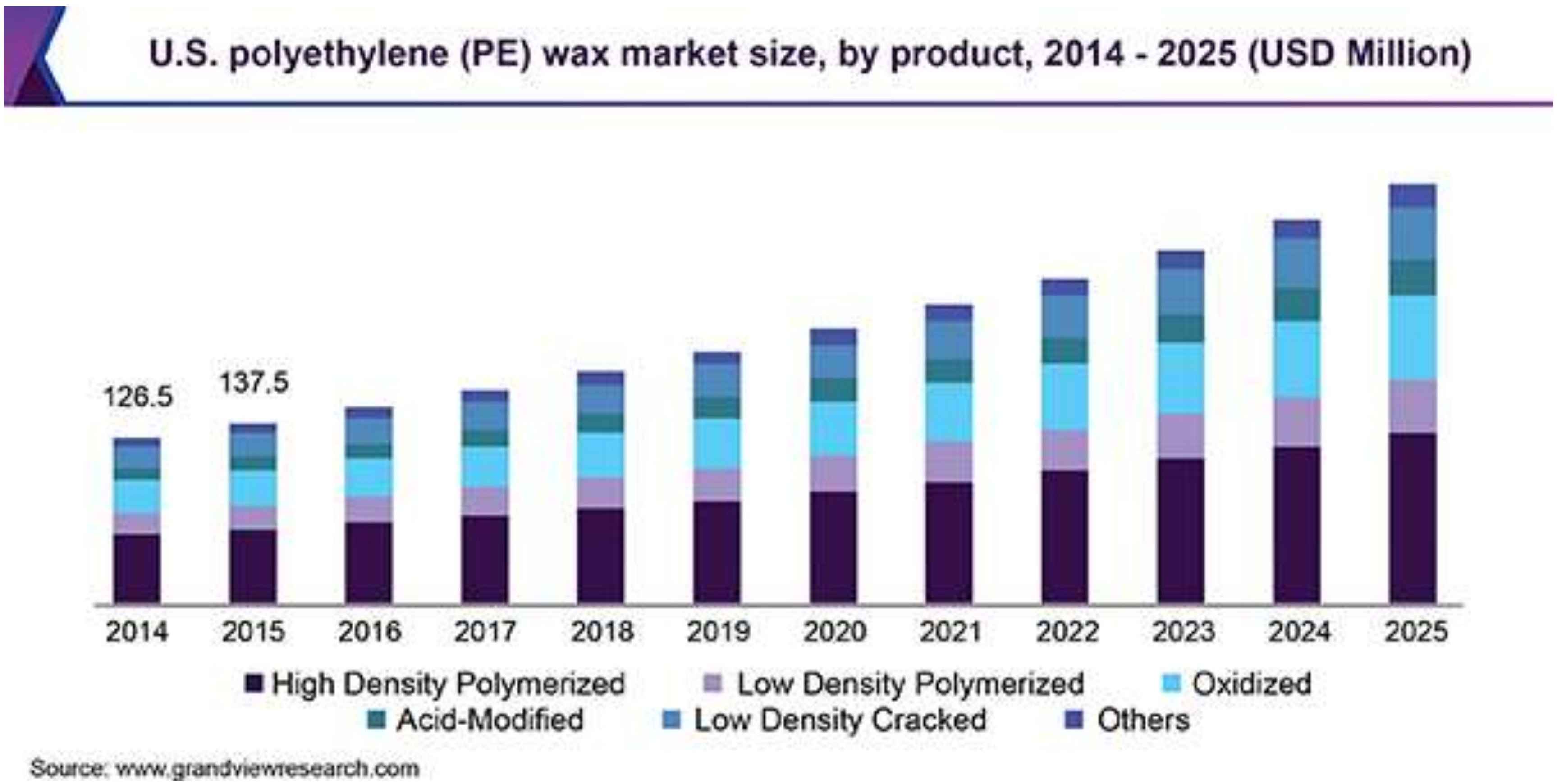
PE Wax is available from on-purpose production and as a byproduct of polyethylene production. This material is available in both HDPE and LDPE forms.

MW Distribution of OPE Wax

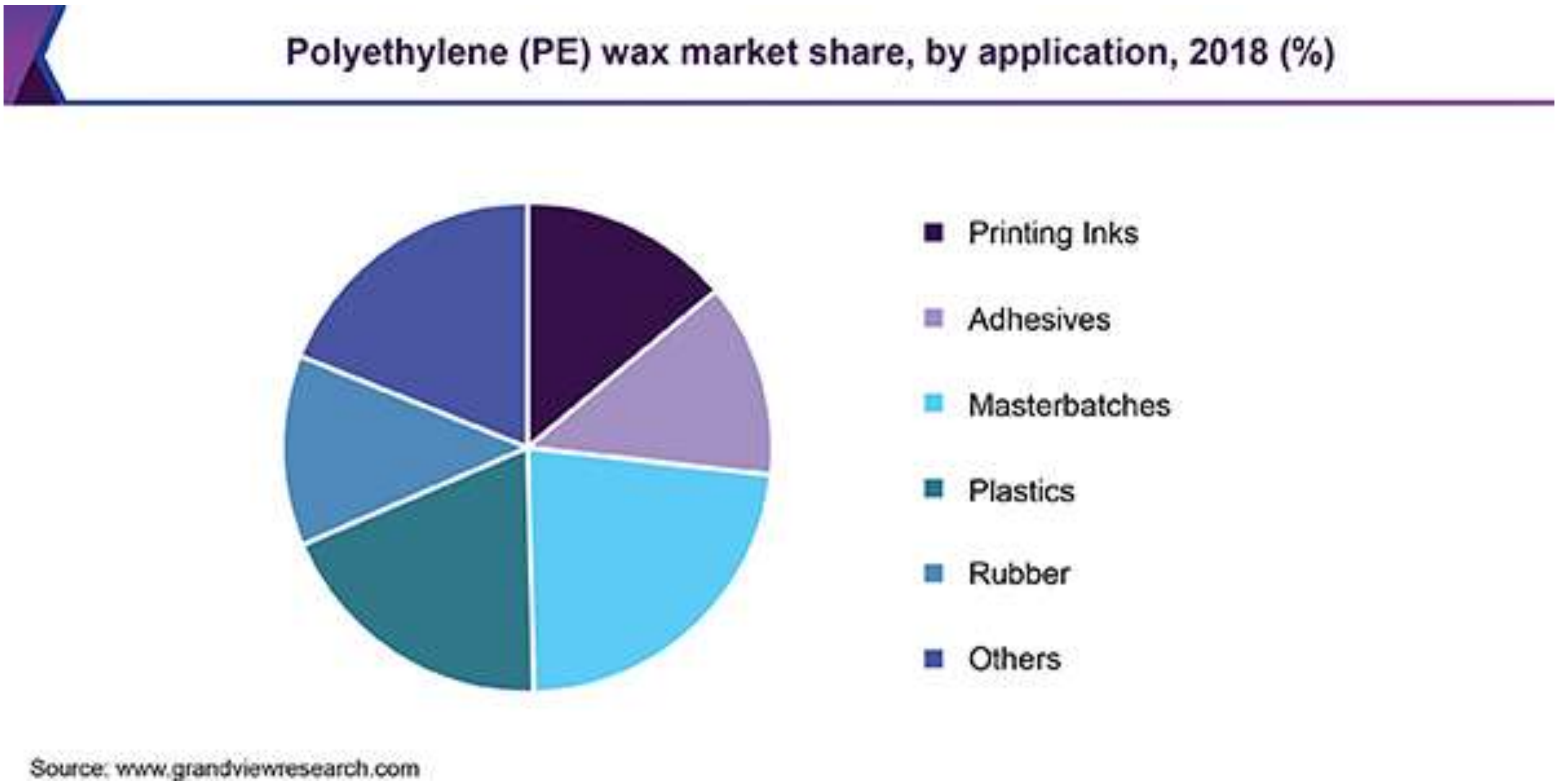


Polyethylene Waxes	Melting Point (°F)	Melting Point (°C)	Viscosity at 300°F, cPs	Penetration, at 77 °F , dmm
Indrapol 31	230-240	110-116	10-50	3 typ
Indrapol 70	235-245	113-118	60-100	2 typ
Indrapol 100-C	212-248	100-120	30-70	9 max
Indrapol 235	225-245	107-118	55 max	9 max
Indrapol 400-C	239-250	115-121	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)

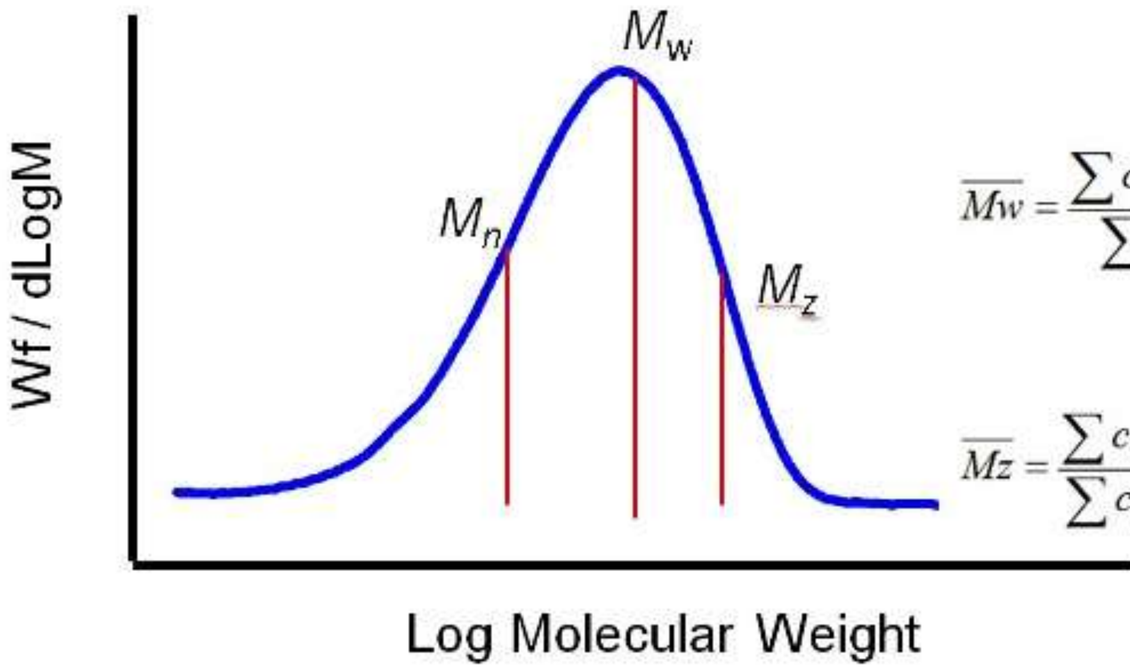


Applications of ULMWPE



Review of Molecular Weight and Molecular Weight Distribution

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



$$\overline{Mw} = \frac{\sum c_i M_i}{\sum c_i} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

$$\overline{Mz} = \frac{\sum c_i M_i^2}{\sum c_i M_i} = \frac{\sum N_i M_i^3}{\sum N_i M_i^2}$$

Viscosity Average Molecular Weight (M_v)

VISCOSITY MEASUREMENT

Ubbelohde Viscometer, for measuring viscocity of dilute solution

upper and lower level

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

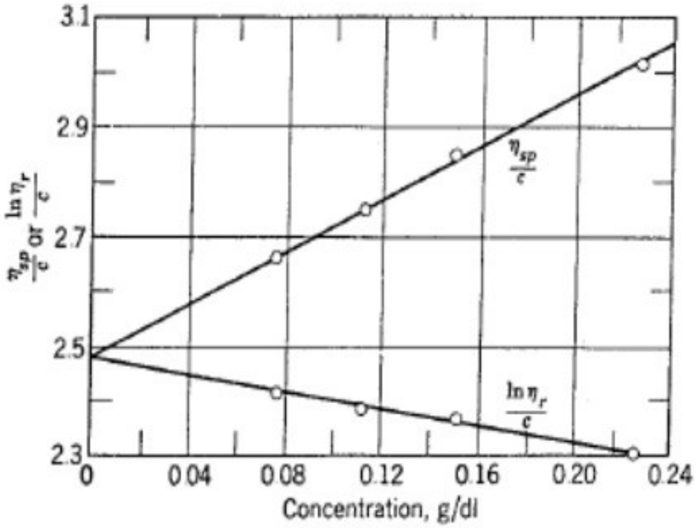
$$\eta = k\rho t$$

k = viscometer constant
ρ = density of solution
t = flow time

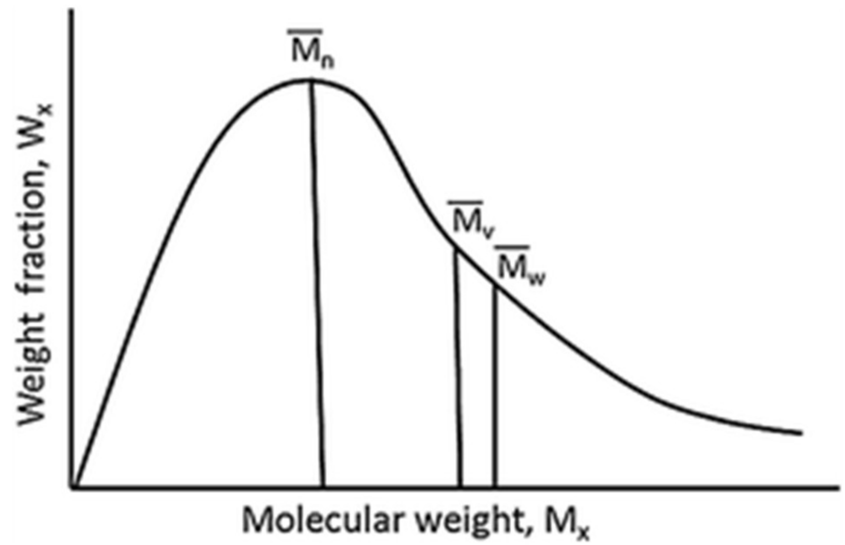
If, t = time for solution
t_o = time for solvent

$\rho = \rho_o$ $\therefore$ dilute solution
ρ_o = solvent density

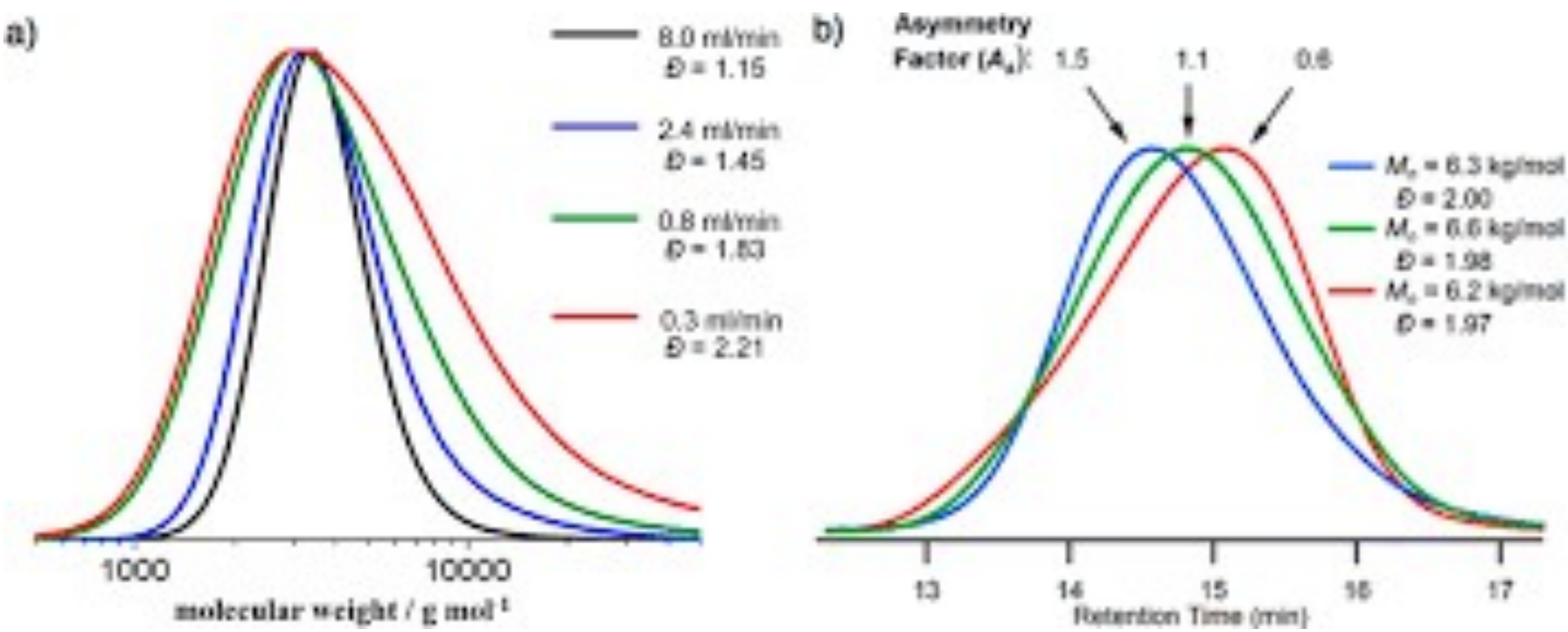
Viscosity Average Molecular Weight (Mv)



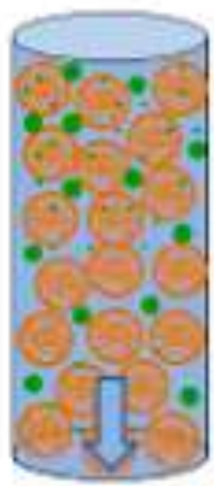
Reduced and inherent viscosity–concentration curves for a polystyrene in benzene (Ewart 1946).

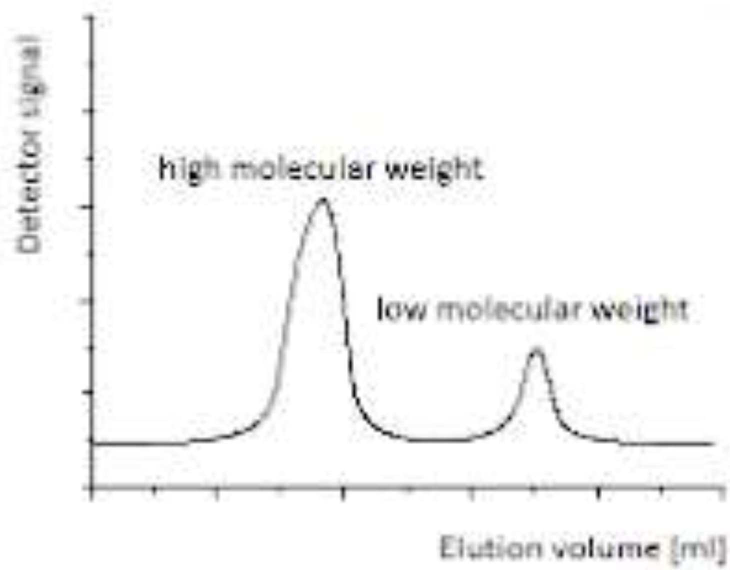


Gel Permeation Chromatography of Polymers



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

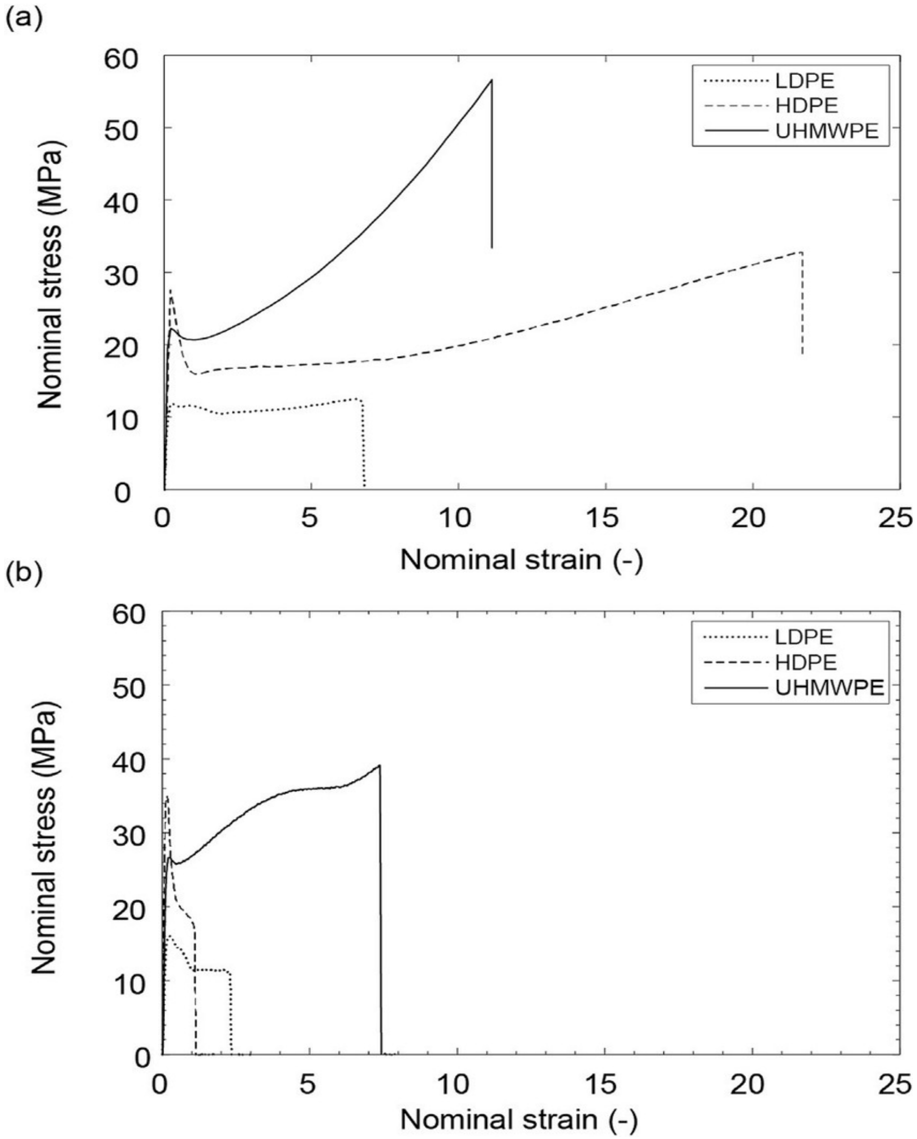
Ultrahigh Molecular Weight Polyethylene

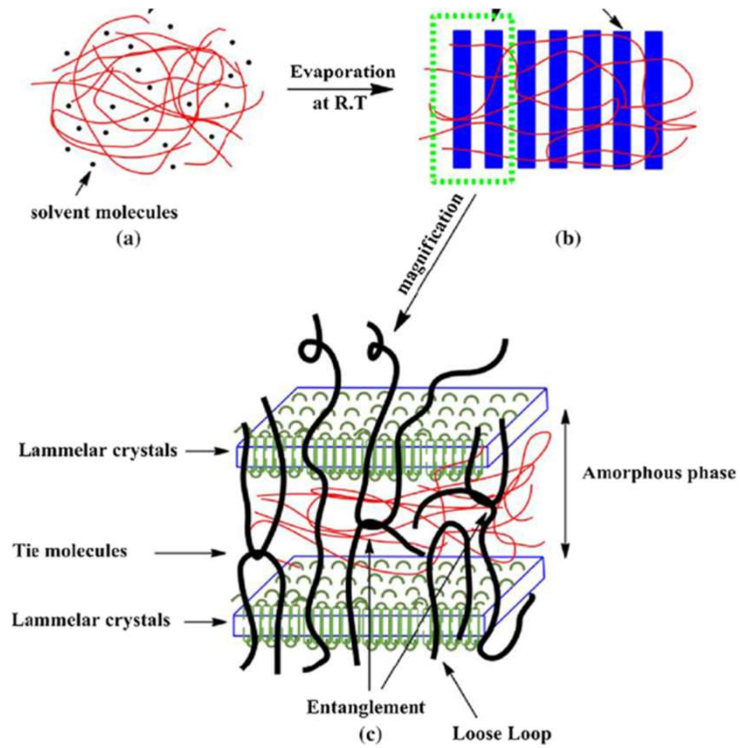
Synthesis

- 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

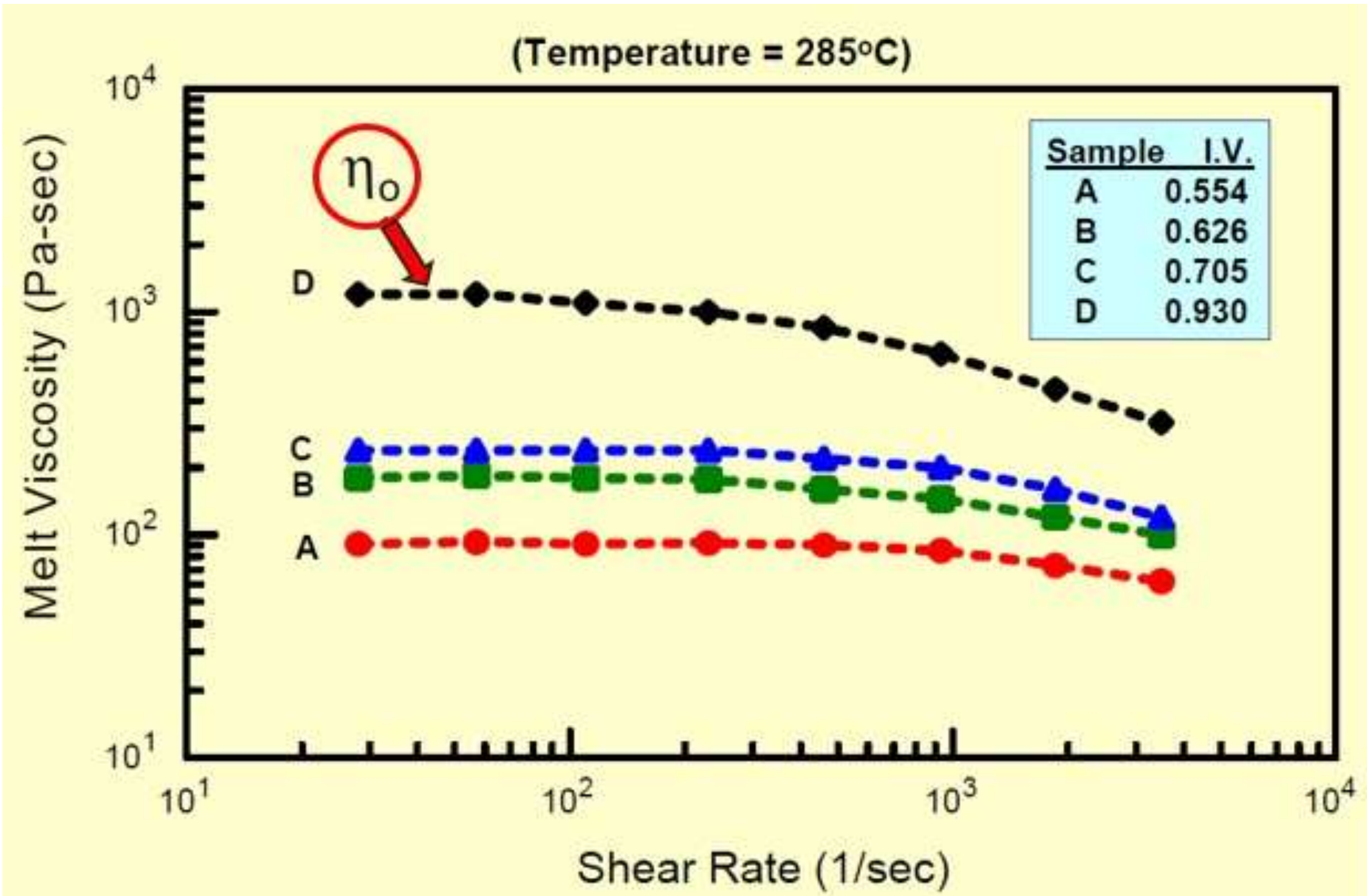
Property	HDPE	UHMWPE
Molecular weight (10^6 g/mole)	0.05 - 0.25	2 - 6
Melting temperature (°C)	130 - 137	125 - 138
Poisson's Ratio	0.40	0.46
Specific gravity	0.952 - 0.965	0.932 - 0.945
Tensile modulus of elasticity* (GPa)	0.4 - 4.0	0.8 – 1.6
Tensile yield strength* (MPa)	26-33	21 – 28
Tensile ultimate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

Mechanical Performance Enhancement with UHMWPE

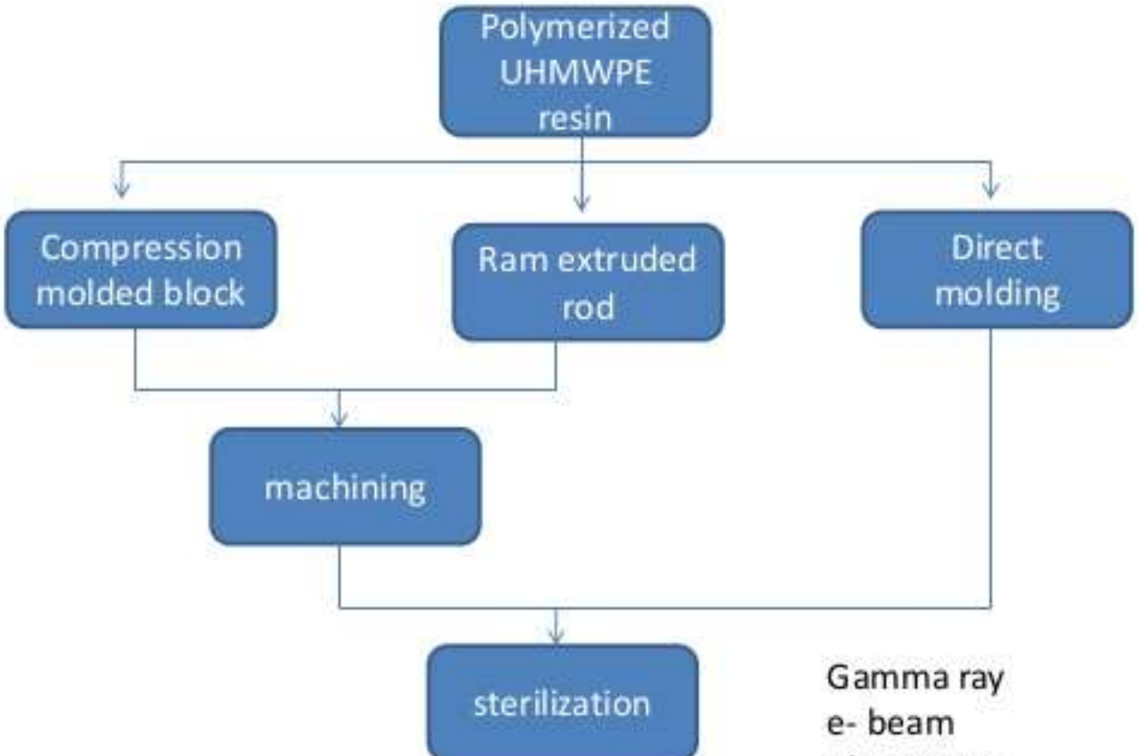




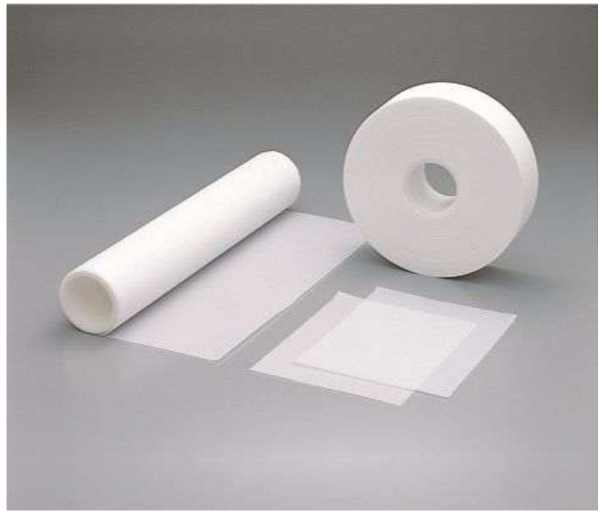
Downside to HMWPE is the Increase in Melt Viscosity and Difficulty to Process on Conventional Equipment



Processing

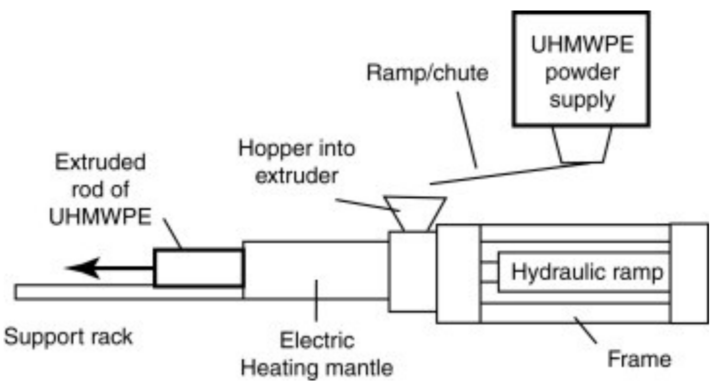


Gamma ray
e- beam
Plasma gas
Et o



Commercial Forms of UHMWPE

UHMWPE has very good abrasion resistance.



ASTM F1473 or the PENT Test

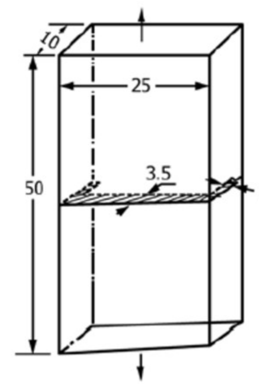
Designation: F1473 – 18

Standard Test Method for Notch Tensile Test to Measure the Resistance to Slow Crack Growth of Polyethylene Pipes and Resins[1]

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

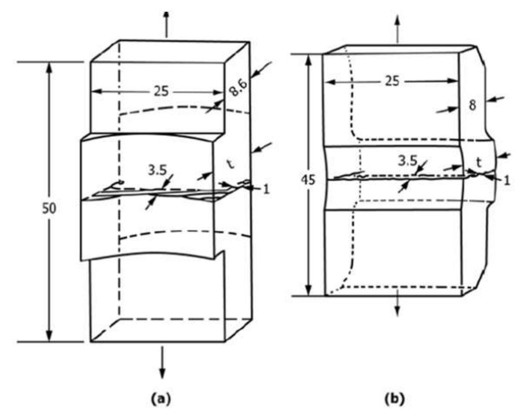
Measures the amount of time for a pre-notched crack to propagate through a polyethylene specimen of a specific dimension.



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.

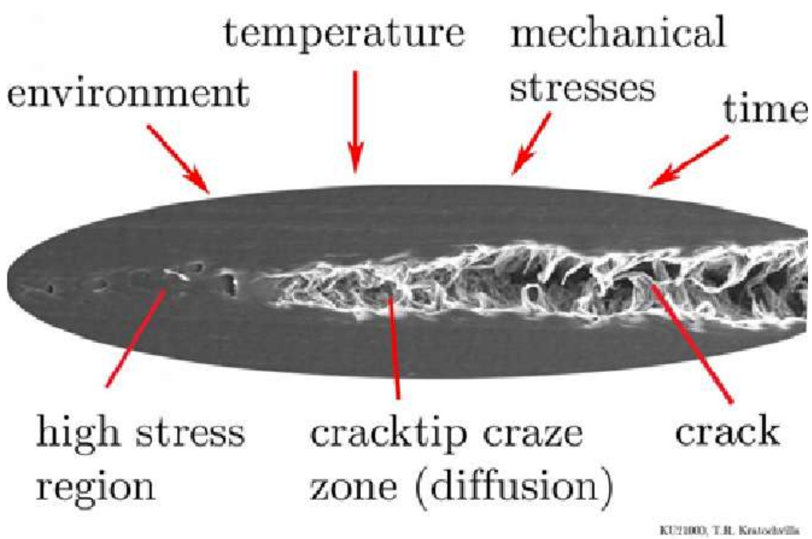


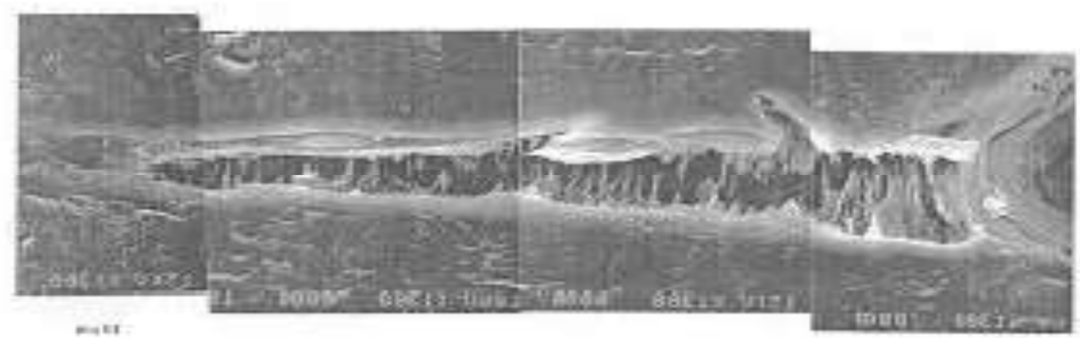
(a) Longitudinal Specimen from 110-mm SDR 11 Pipe with Tensile Axis Parallel to Extrusion Direction

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

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

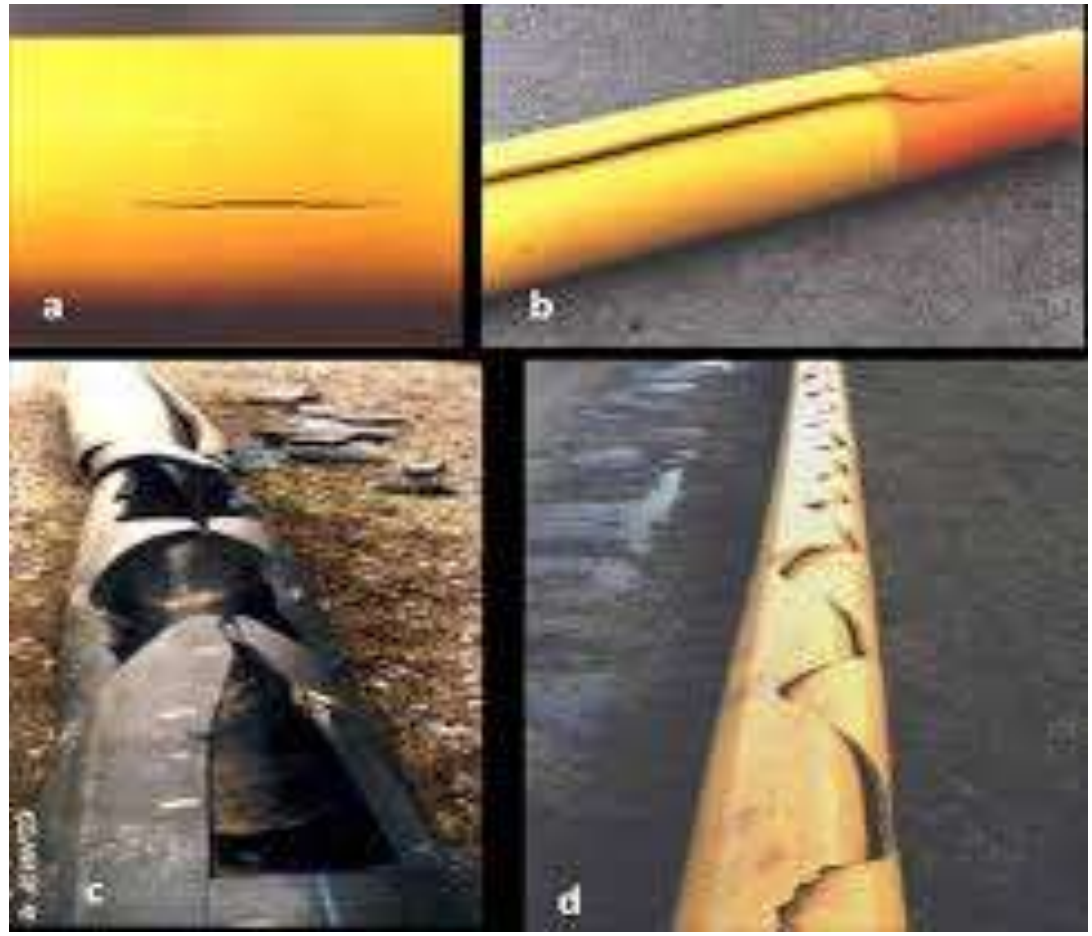
Review of Craze-Crack Propagation





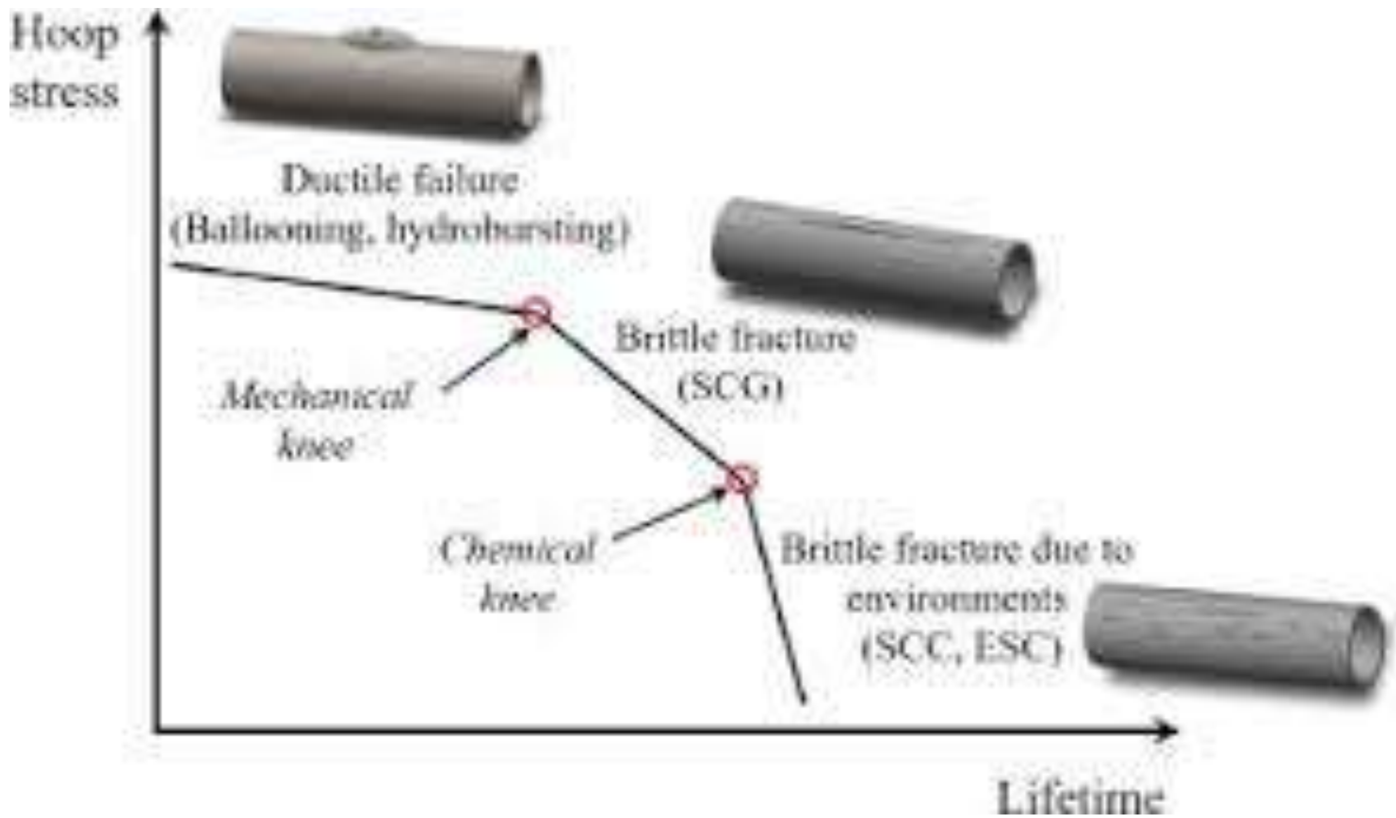
Traditional HDPE and MDPE Polyethylene Pipe Exhibits a Ductile to Brittle Transition at a Specific Stress and Temperature Condition

Ductile Polyethylene Pipe Failure

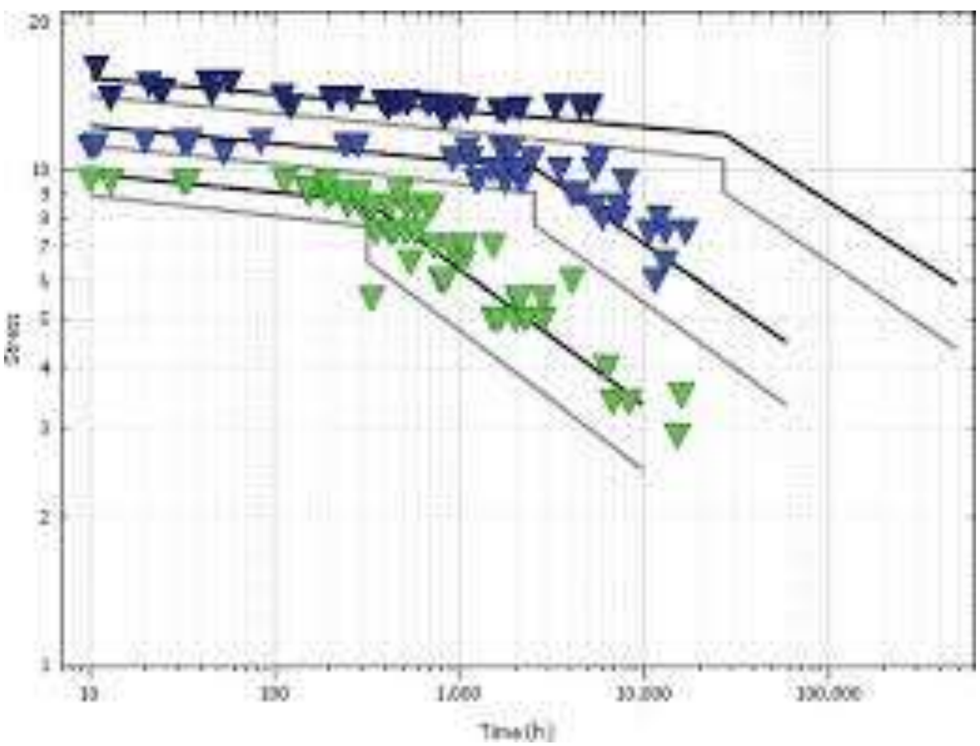


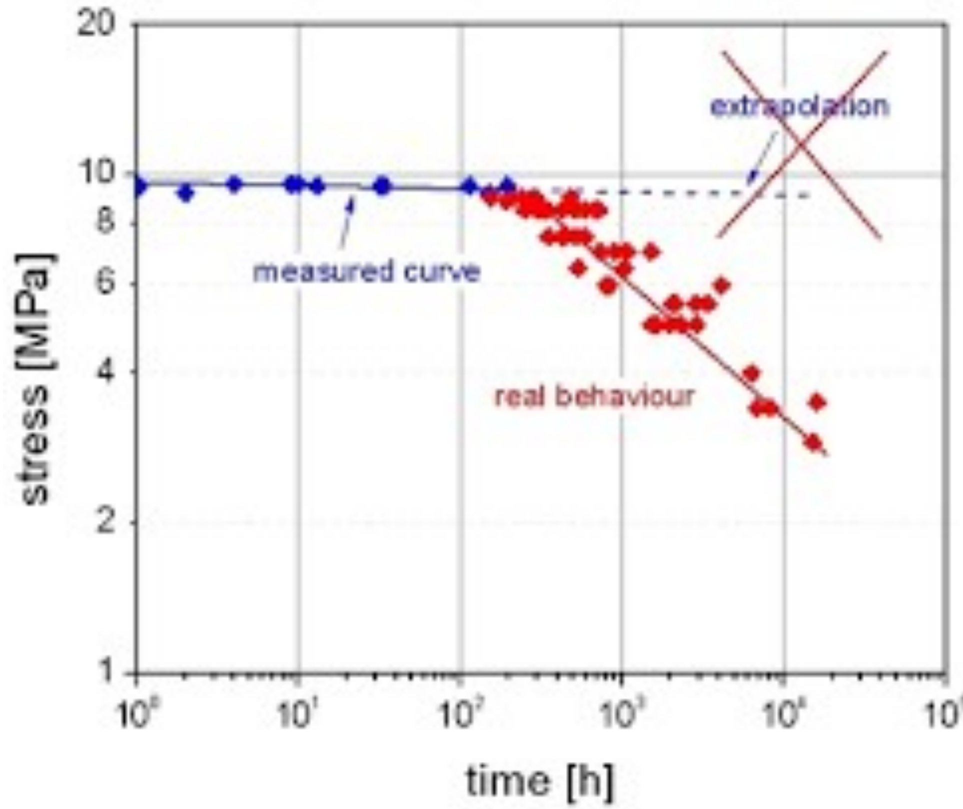
Brittle Polyethylene Pipe Failure

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



Actual Ductile-Brittle Transition for HDPE





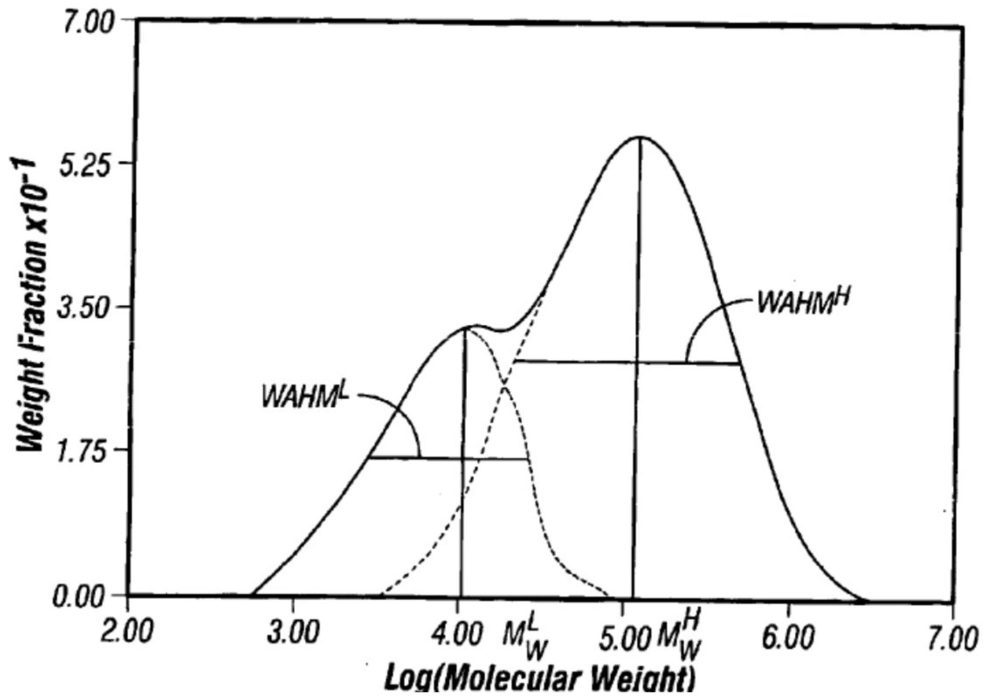
(12) **United States Patent**
VanDun et al.

(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)



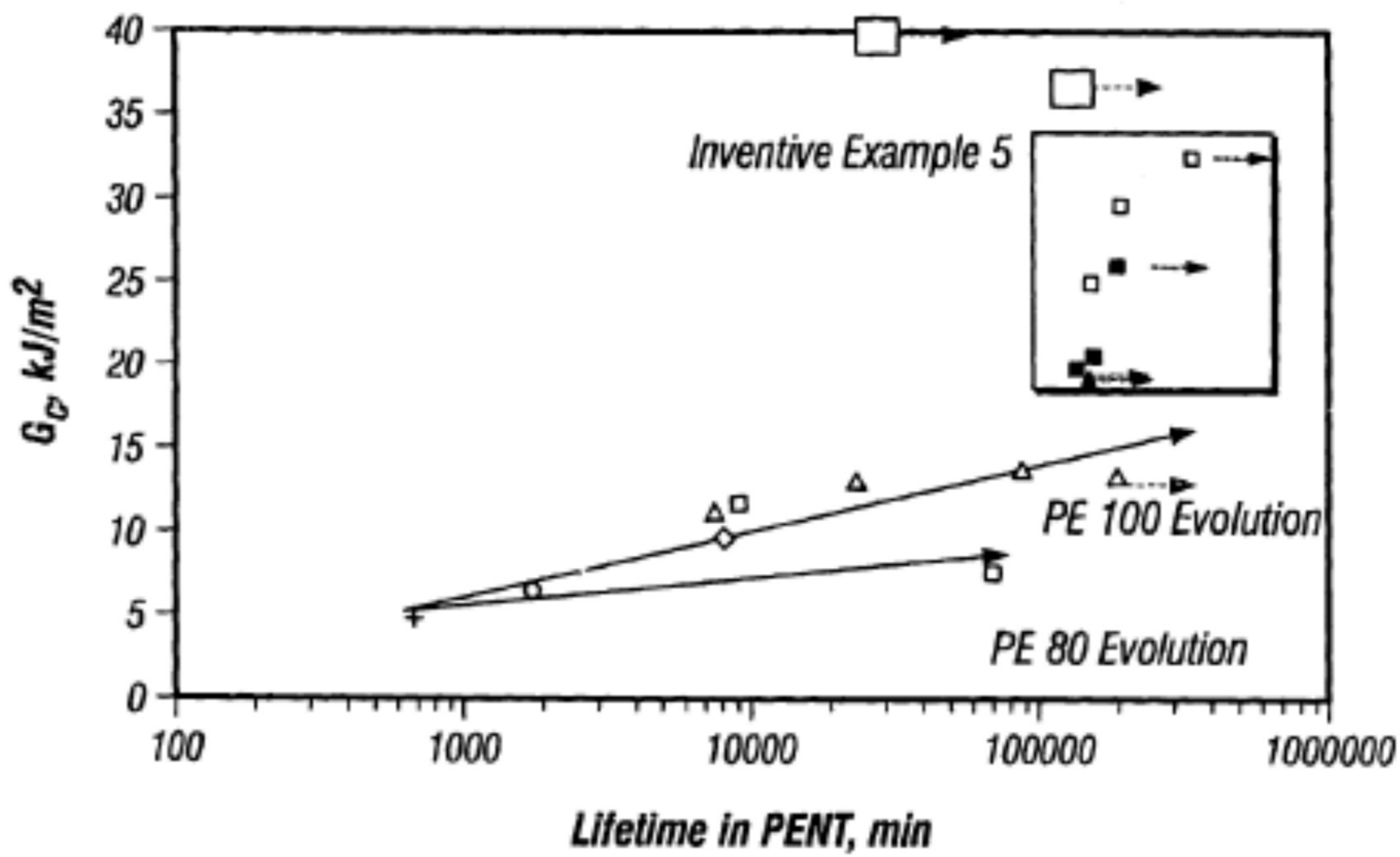
Properties of Dow's Early Investigation into Bimodal PE Materials

TABLE 11

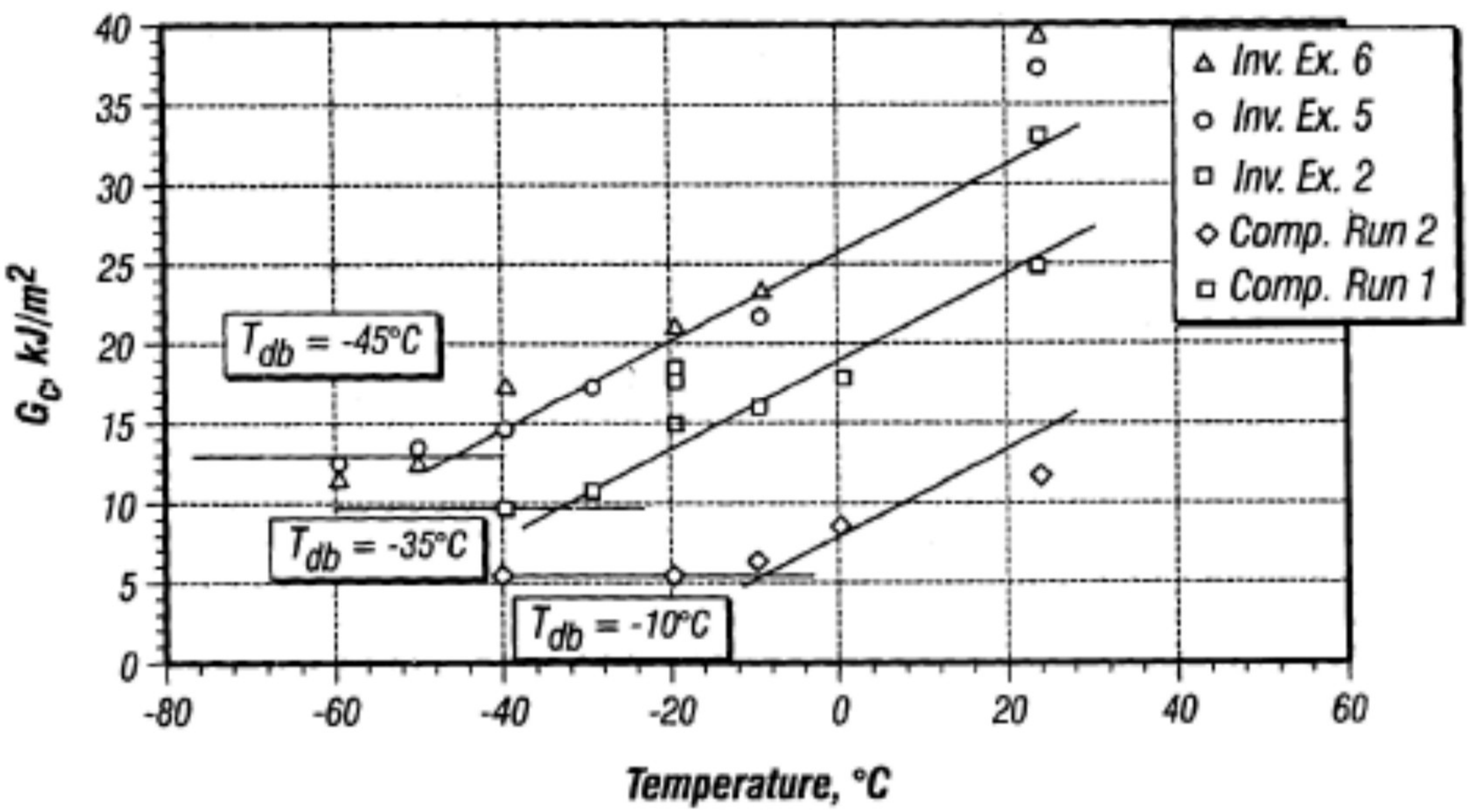
Product and Performance Properties of Inventive Examples

Inventive Example		2	5	6
Density	g/cm^3	0.9511	0.9508	0.9508
GPC				
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
DSC				
T_c	° 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
Tensile properties				
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

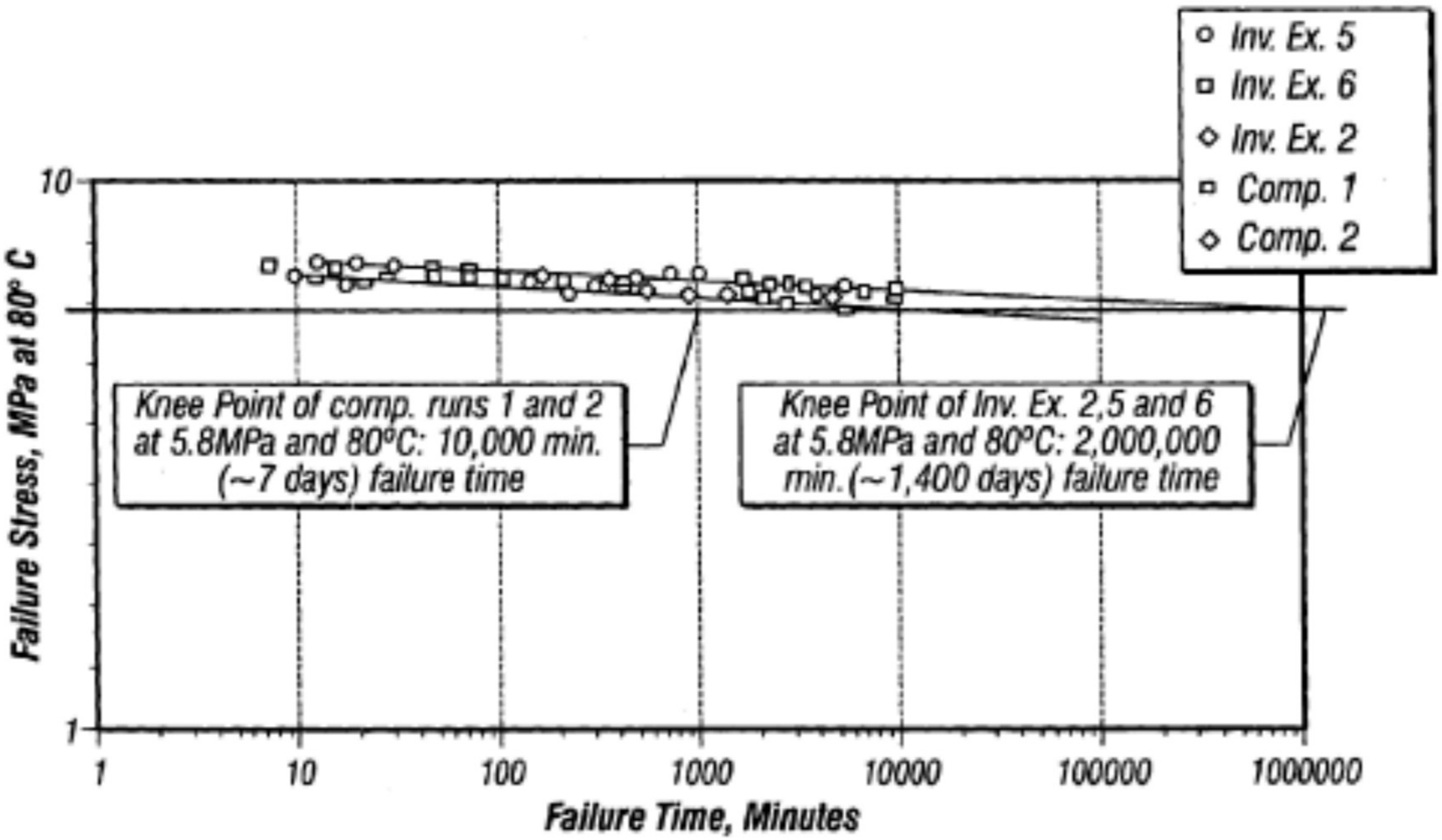
Bimodal PE Enhances the PENT Test Lifetime



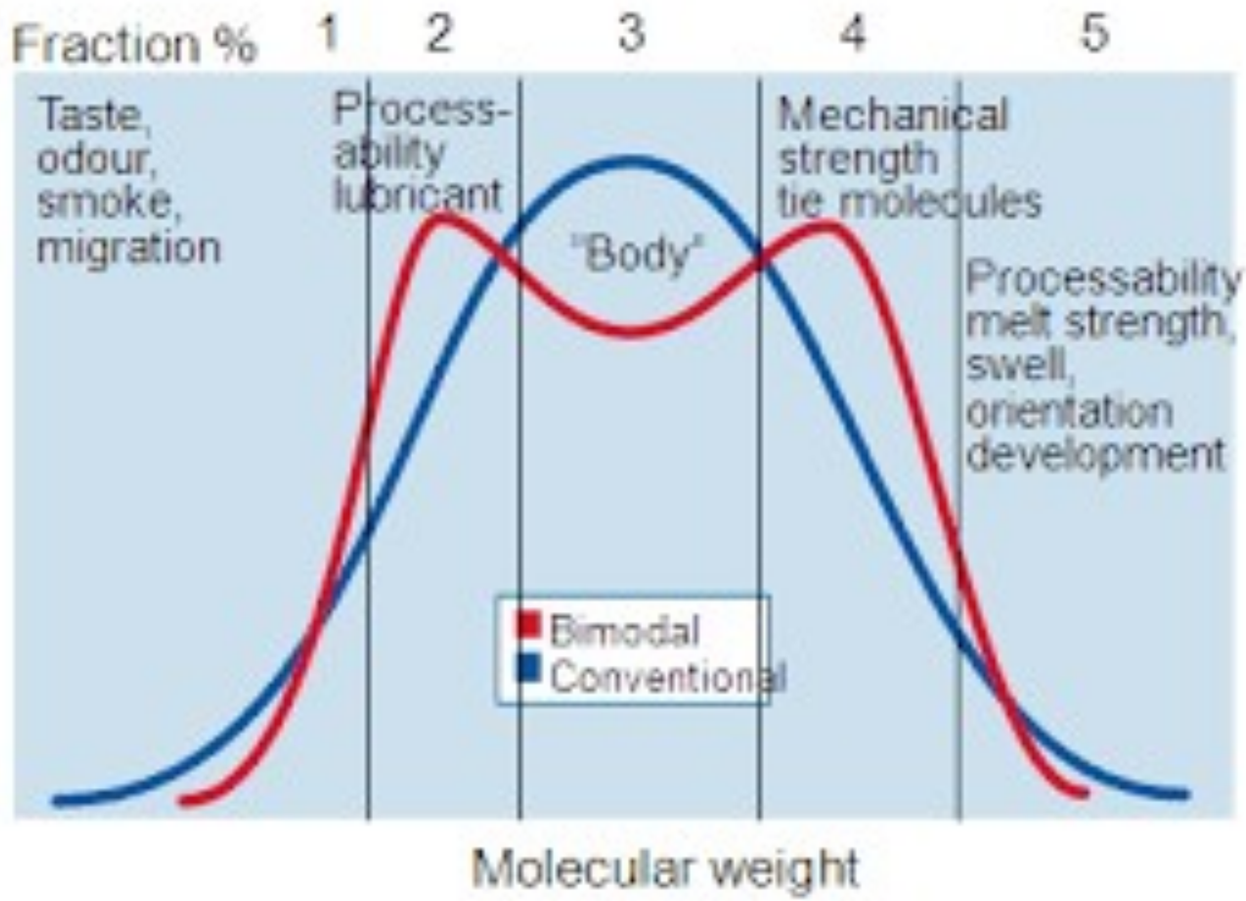
Bimodal PE Extends in Time the Ductile-Brittle Transition



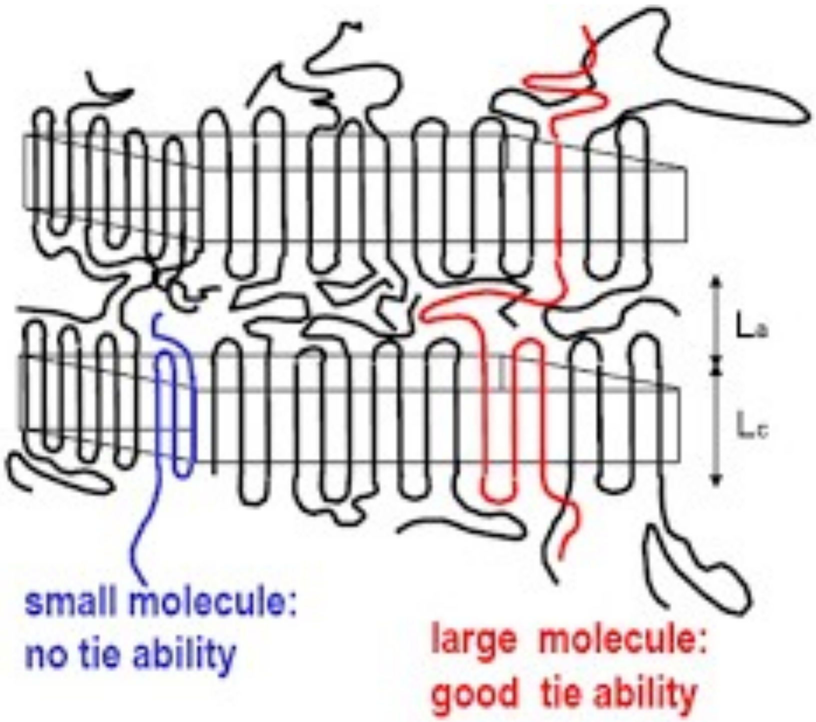
Bimodal PE Extends Improves in the Long-Term Stress Rupture Performance

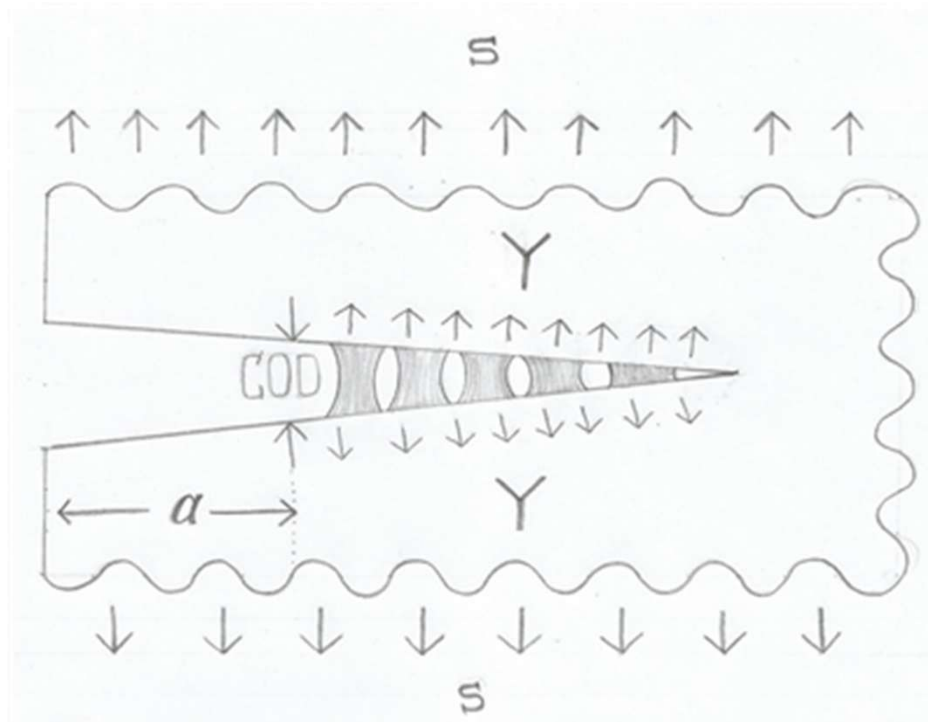


Proposed Performance Mechanism for Bimodal PE Materials



Tie Molecule Influence in Slow Crack Growth



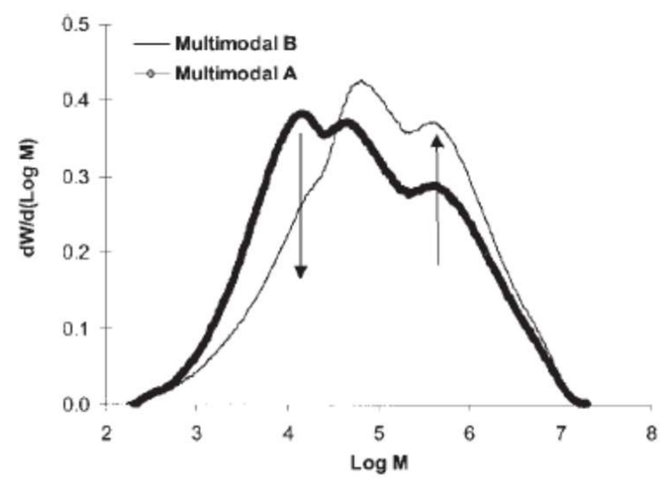


A Comparative Study of Multimodal vs. Bimodal Polyethylene Pipe Resins for PE-100 Applications

Paul J. DesLauriers, Max P. McDaniel, David C. Rohlfing, 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}	MWD
Multimodal A	14.3	9.7	528	3,800	6,830	54
Multimodal B	64.9	13.3	645	3,814	6,864	49

*kg/mol

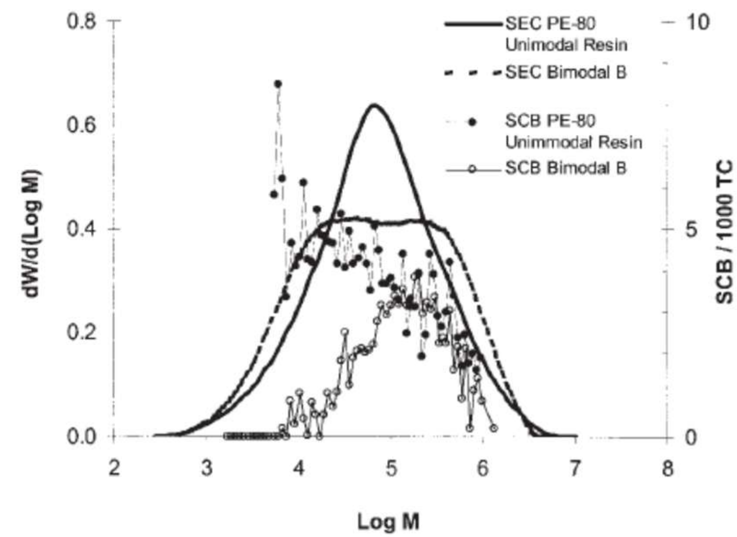


FIG. 11. Comparative SCB profiles across the MWD for a PE-80 sample made using a Cr/silica-titania catalyst and PE-100 Ziegler based bimodal resin (resin B in Table 3).

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

[a]Samples still on test.
[b]Ultra-high MW-PE resins (Ticona) GUR4120 and GUR4150 gave values of 0.006 and 0.0045, respectively.
[c]Values 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.

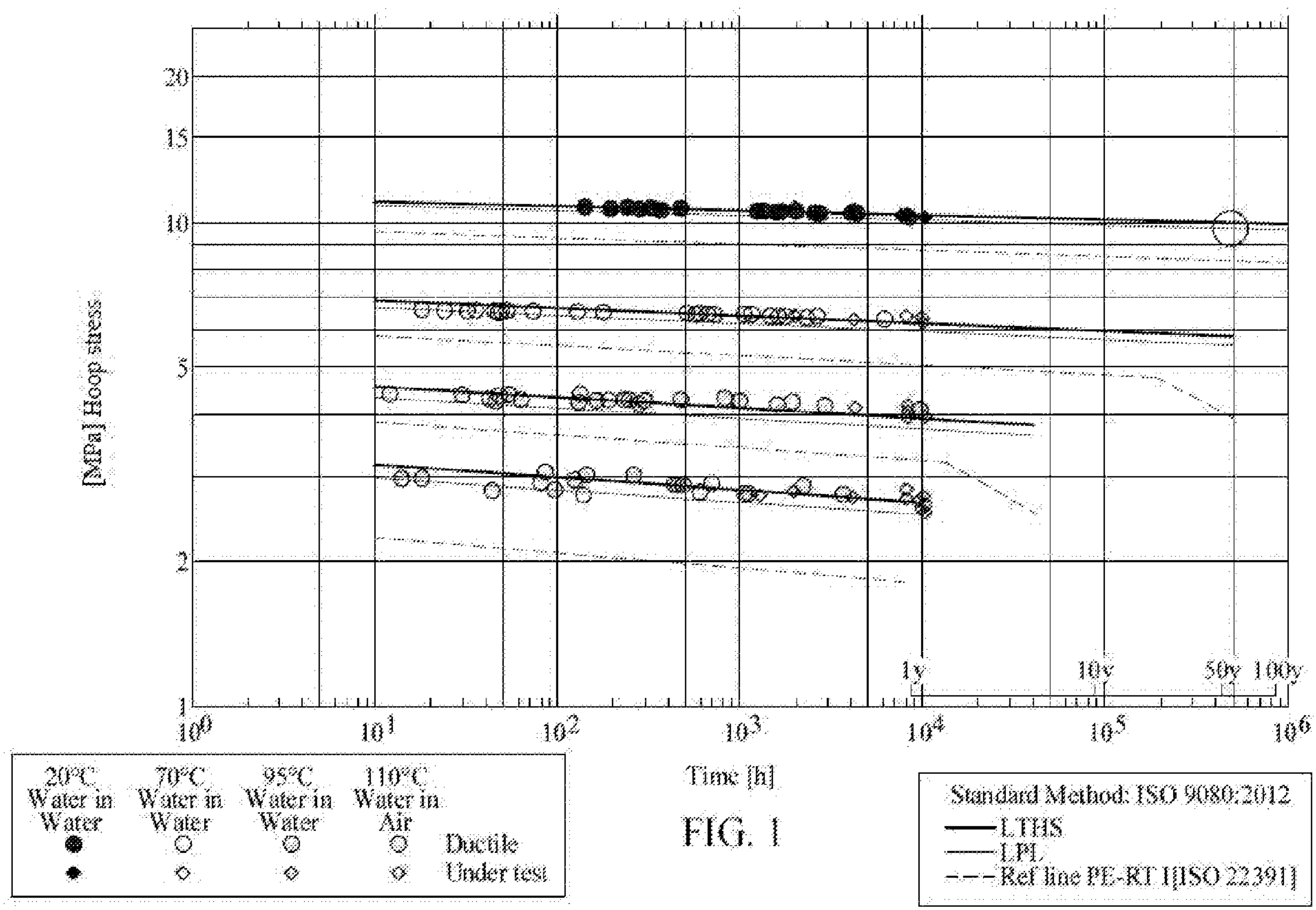


FIG. 1

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."