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

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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.

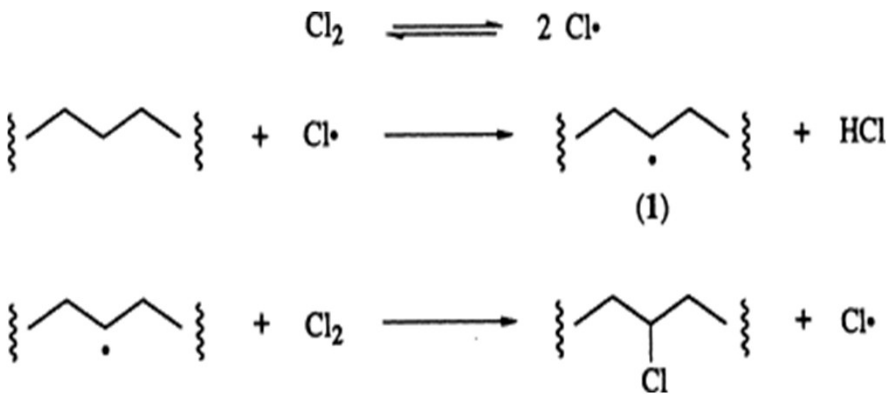
Three fundamental features of polyethylene leading to the diversity of structures and in turn performance are:

a. Short chain and long chain branching.

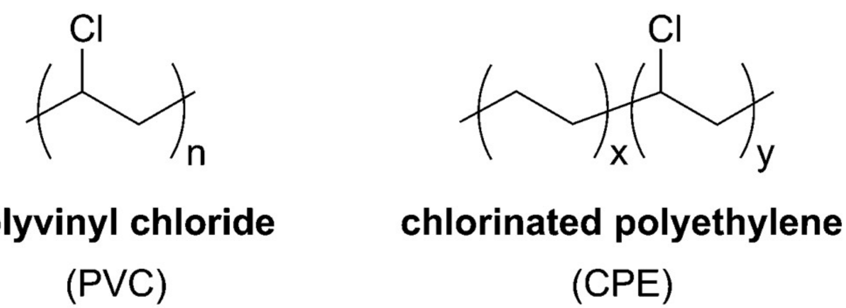
b. Co-monomer content and distribution.

c. Molecular weight and molecular weight distribution.

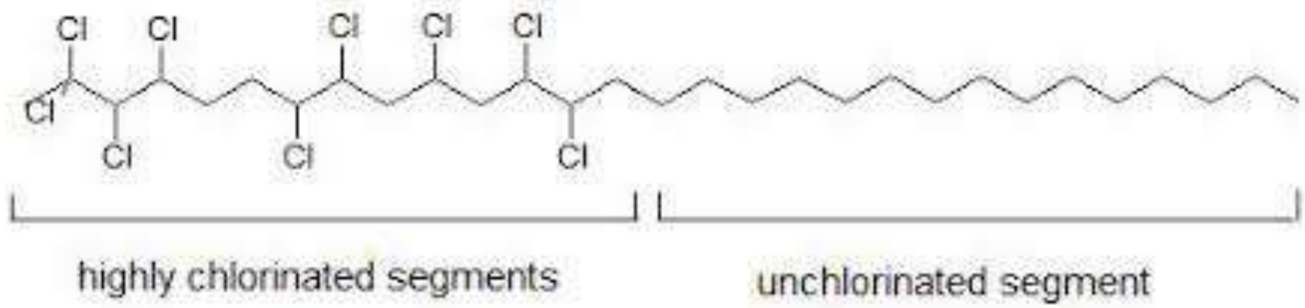
Chlorinated Polyethylene (CPE)



Basic PE Chlorination Reaction



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

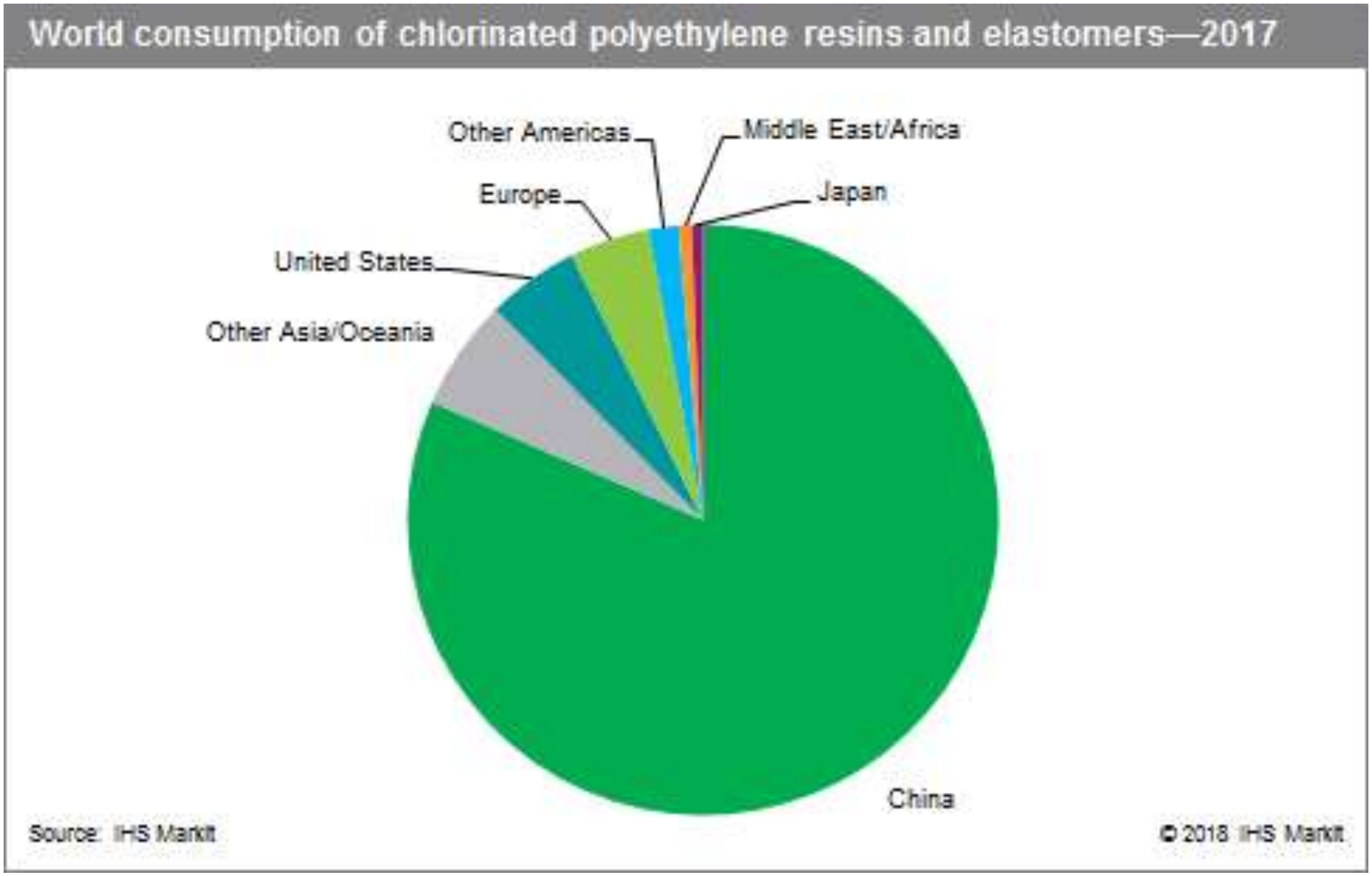
CPE can be divided into two categories: (1) resin-type CPE and (2) elastomer-type CPE.

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

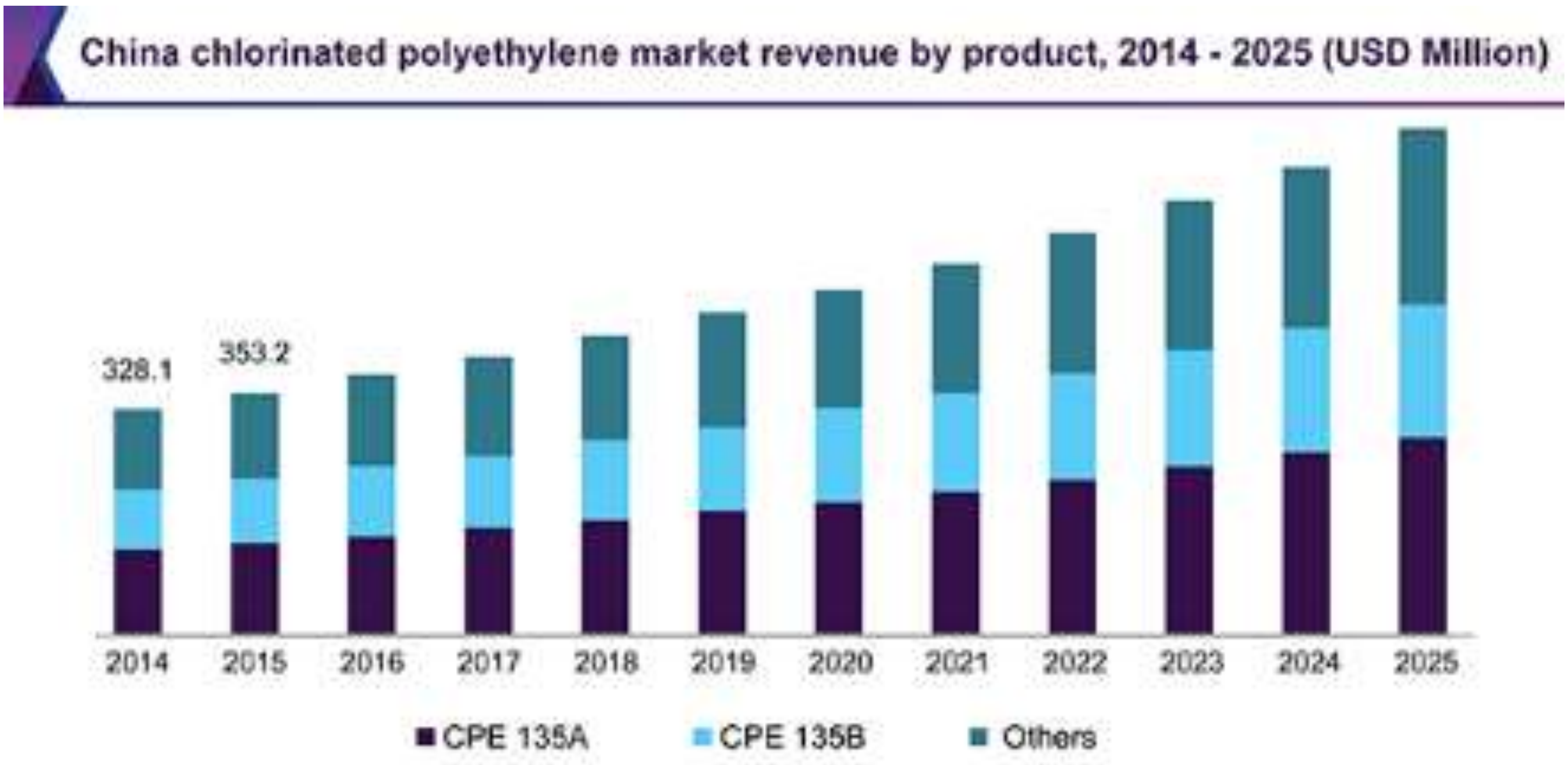
CPE can be used as a high-performance, high-quality rubber and can be applied with ethylene propylene rubber, butyl rubber, nitrile rubber, chlorosulfonated polyethylene.

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.

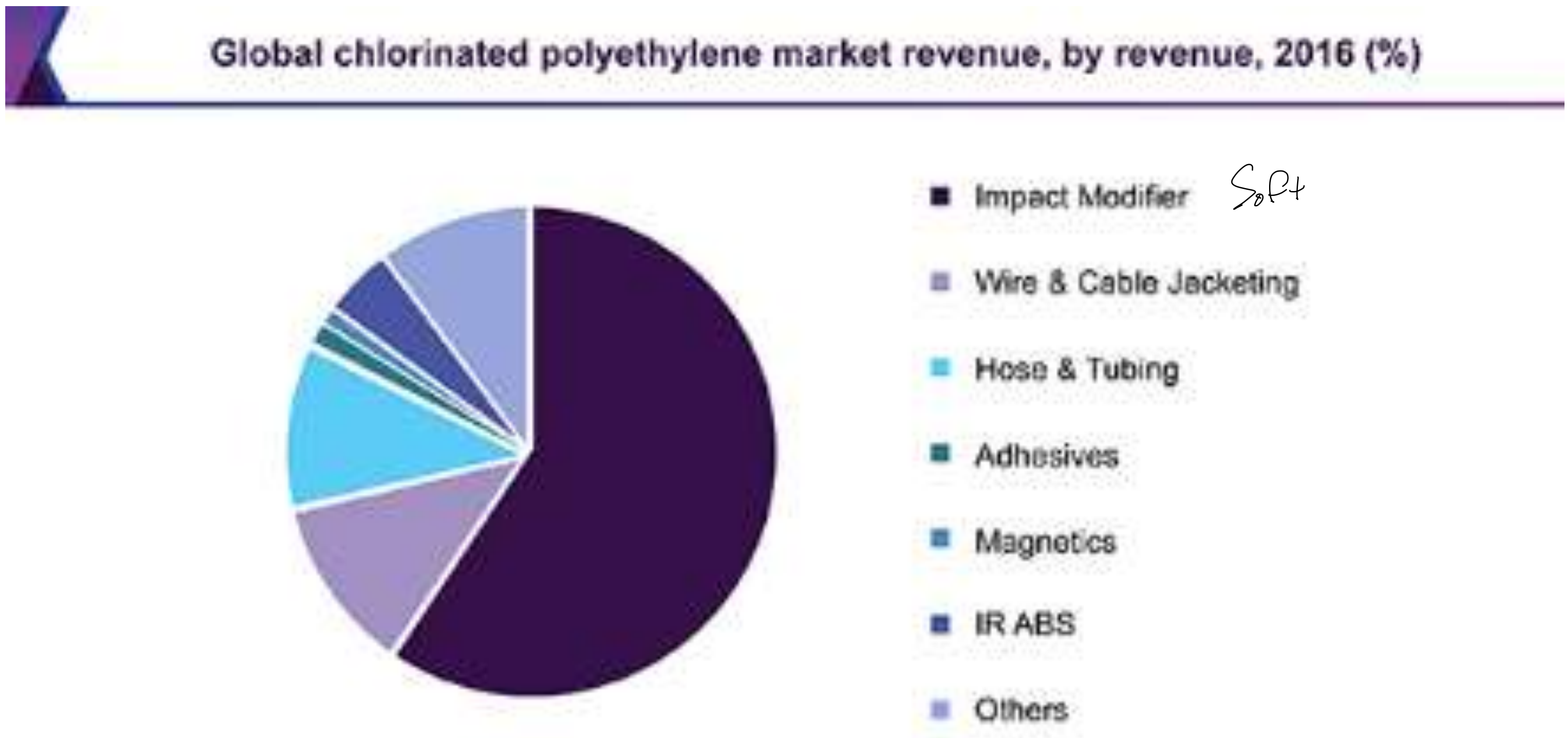
China is the Major Producer of CPE



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

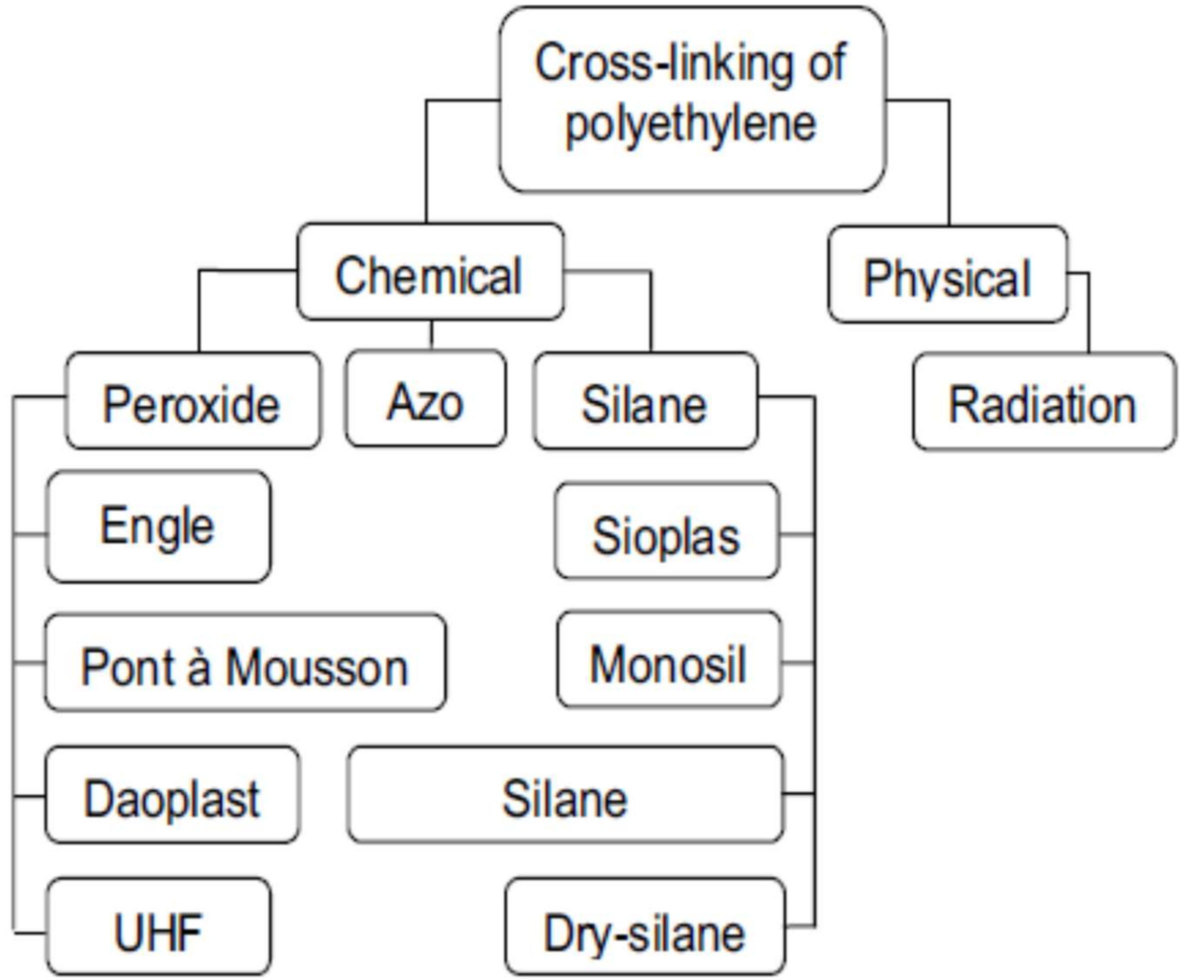


Figure 1. Polyethylene cross-linking methods.

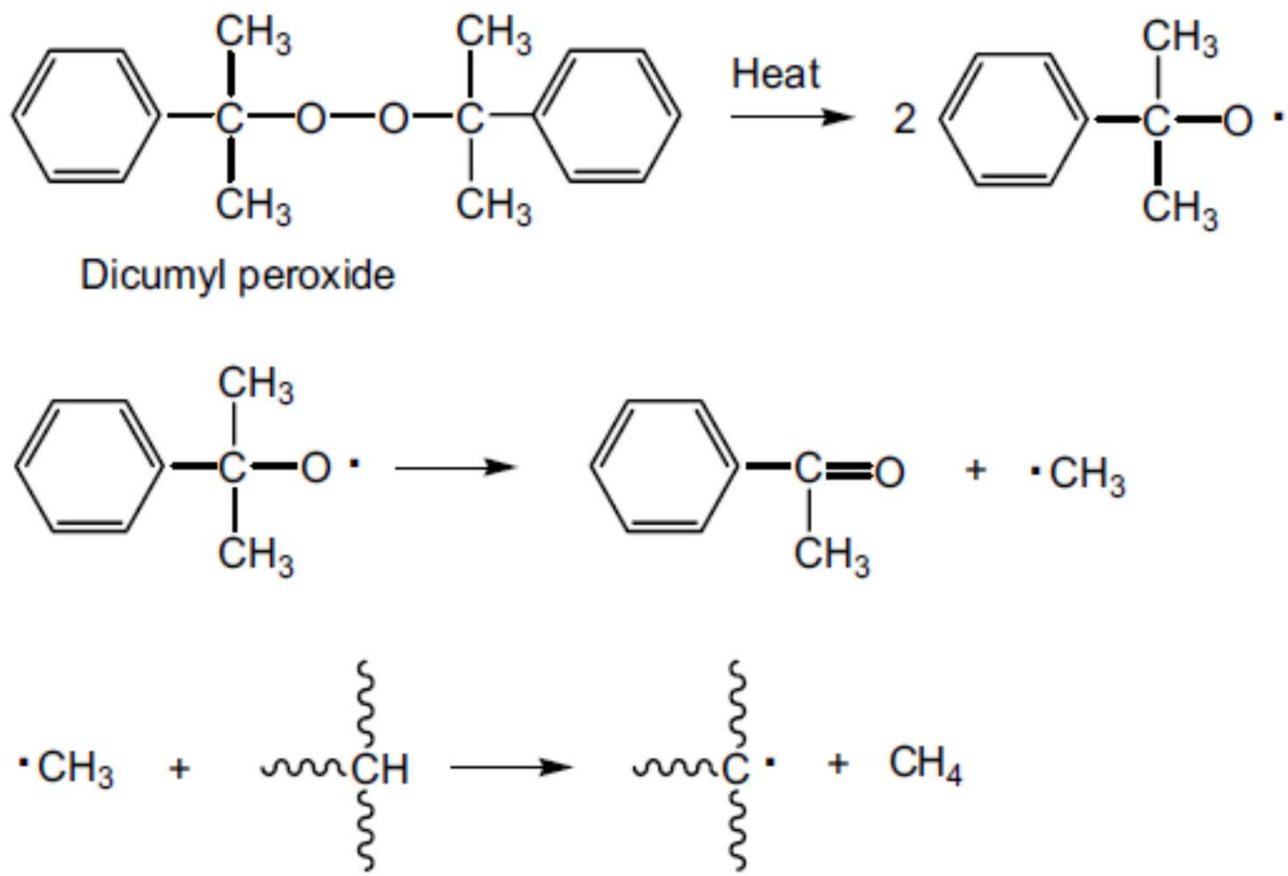
The effects of varying peroxide concentration in crosslinked linear polyethylene

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	% Gel content Toluene (110°C)	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%

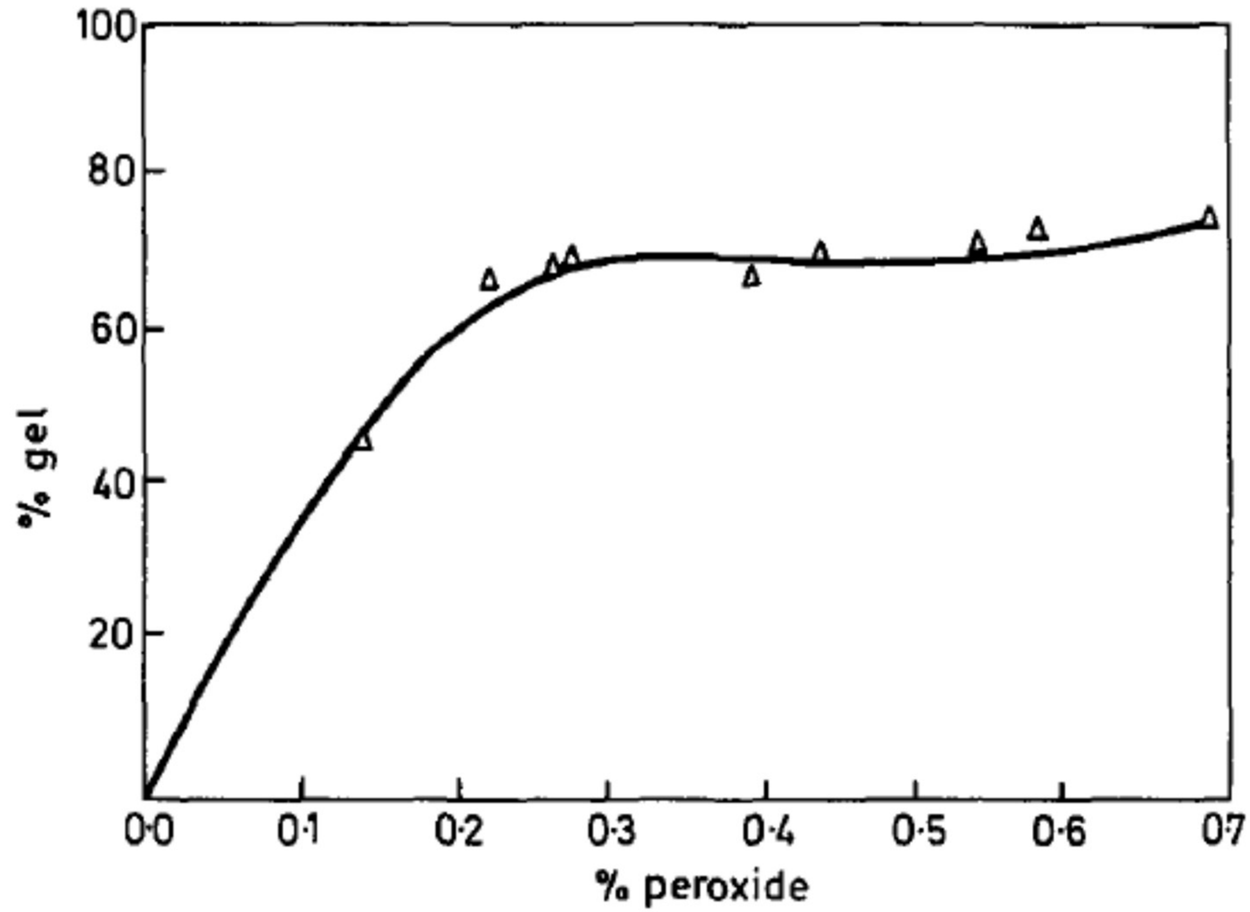


Figure 5 Gel content against peroxide content of crosslinked polyethylene

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

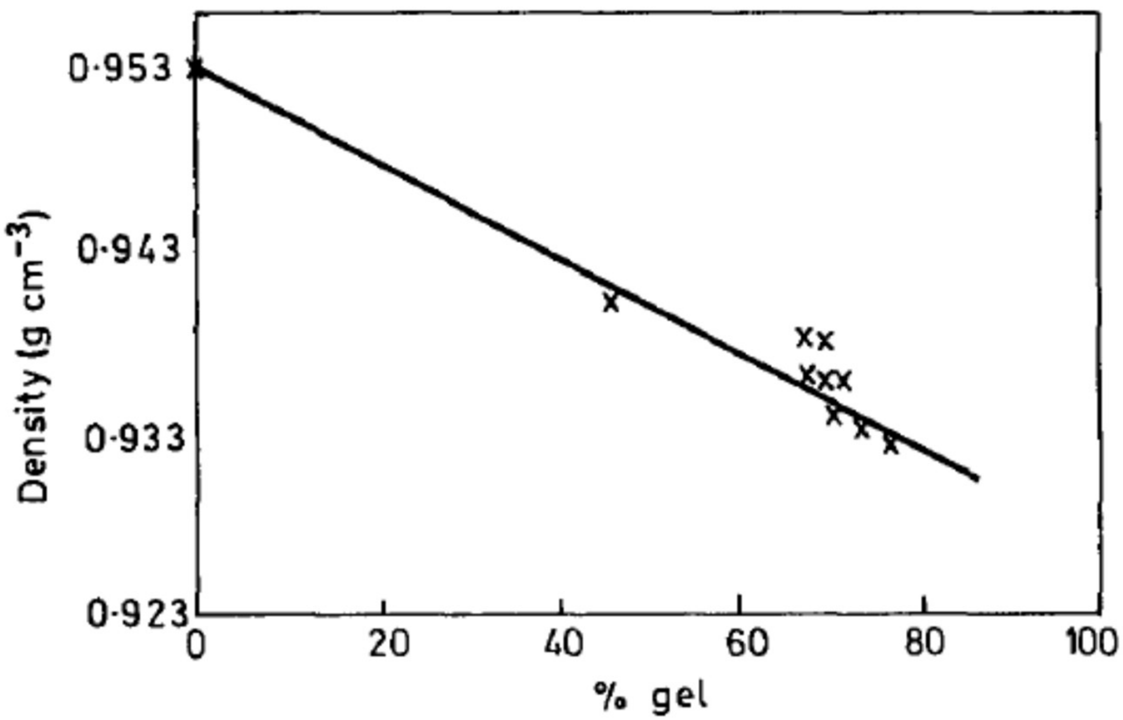
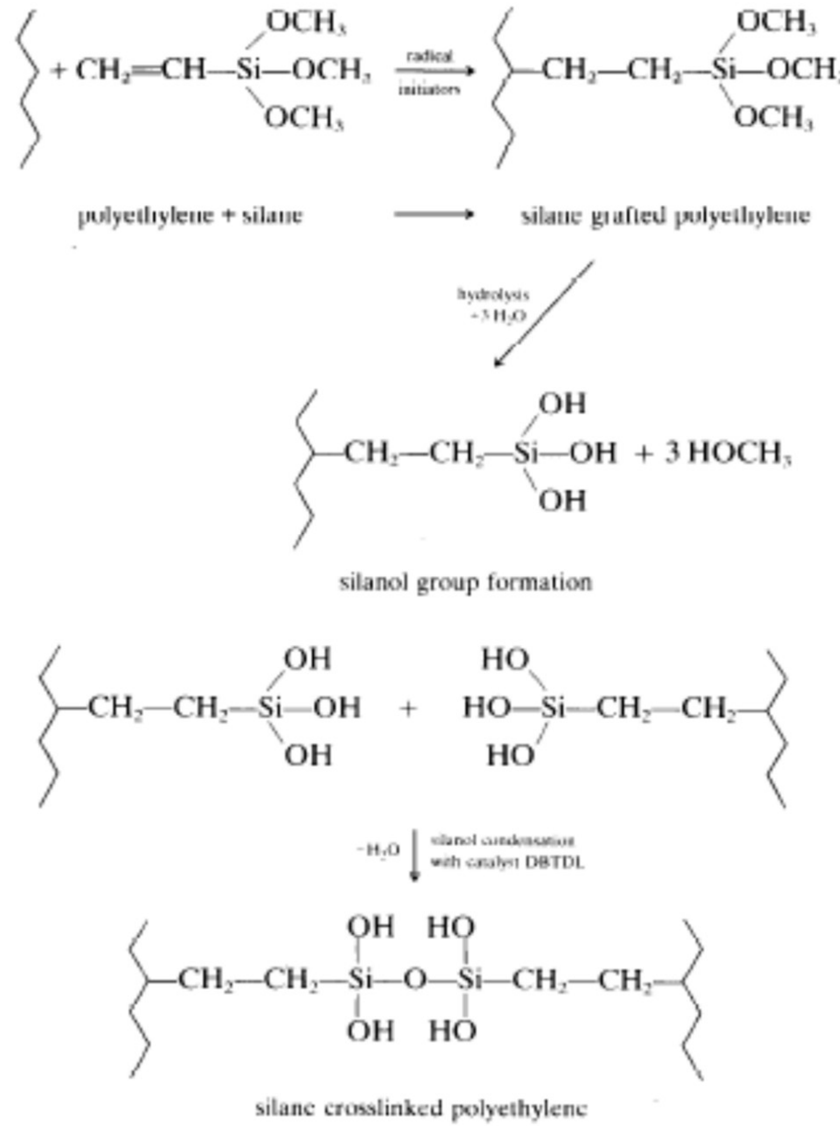


Figure 4 Densities of crosslinked polyethylene against gel content in tetralin

Polyethylene Cross-link Reaction using Silane



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

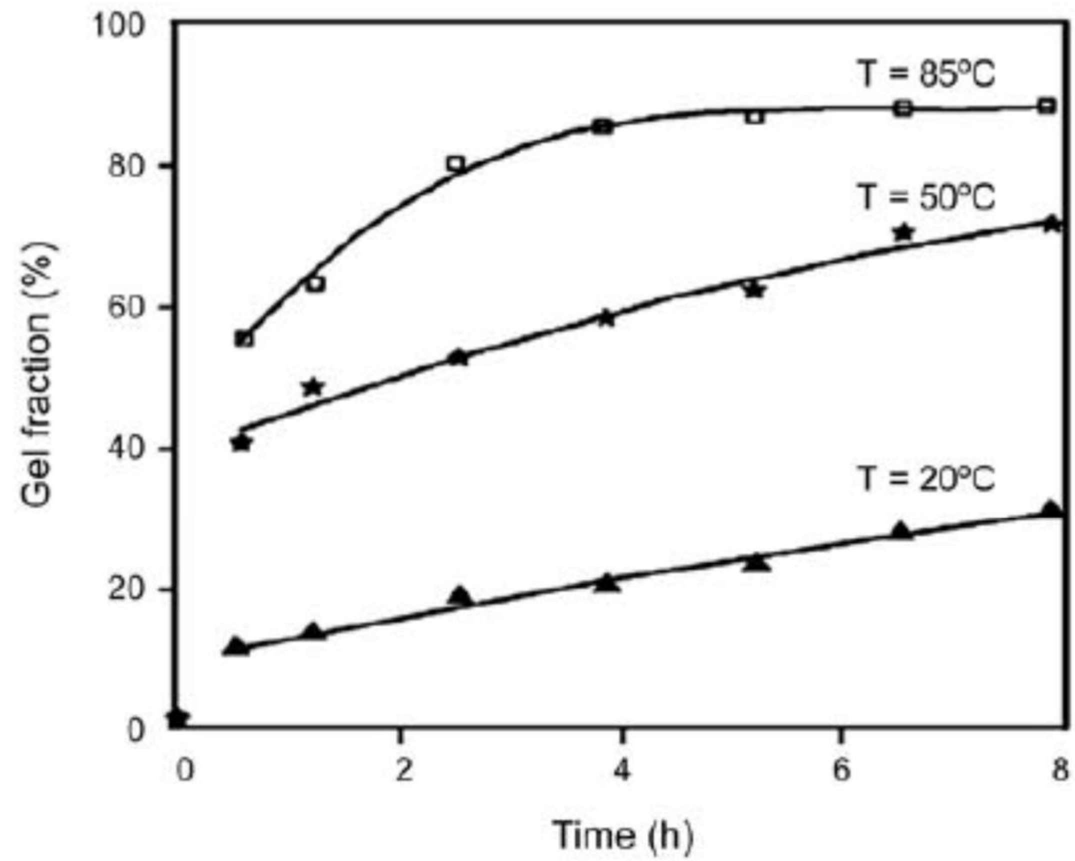


Figure 11. Effect of curing time and water temperature on silane cross-linking of LDPE [84].

Comparison of Peroxide and Silane PEX Tensile Properties

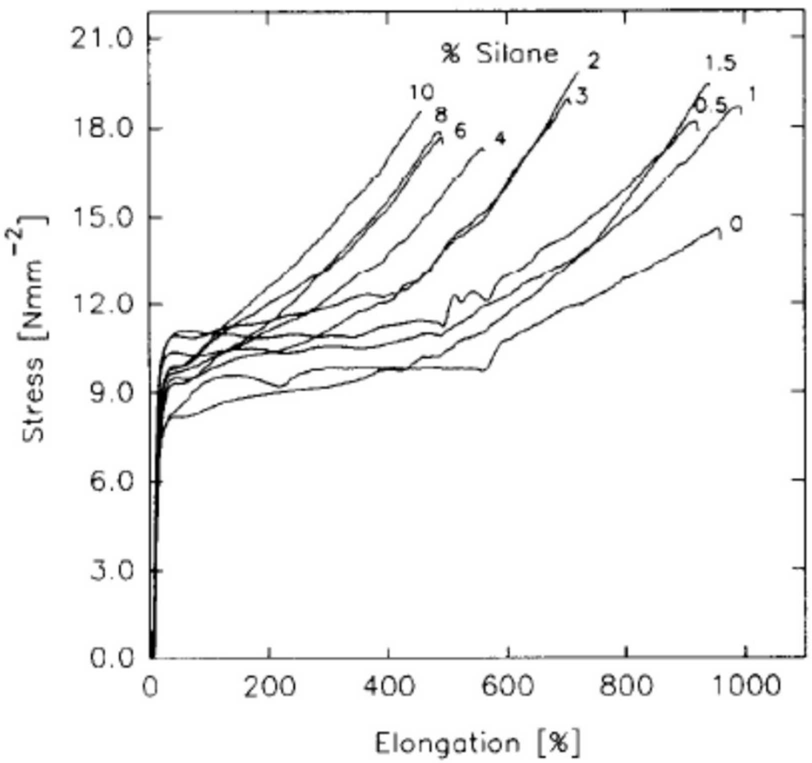


Fig. 6. Typical tensile testing results of silane XLPE samples.

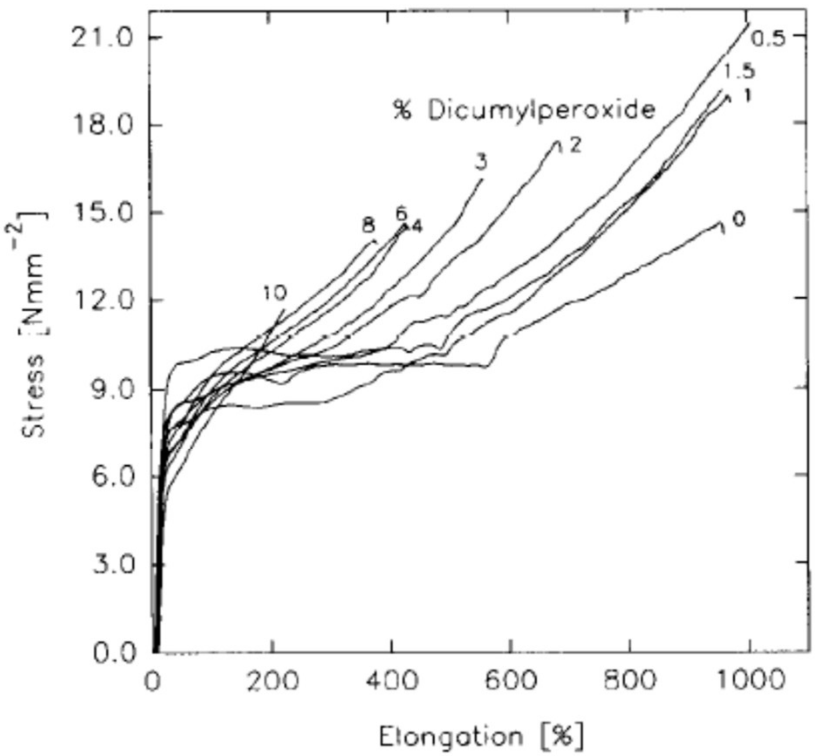


Fig. 5. Typical tensile testing results of peroxide XLPE samples.

Comparison of PEX Cross-linking Methods

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

Aspect / Method	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

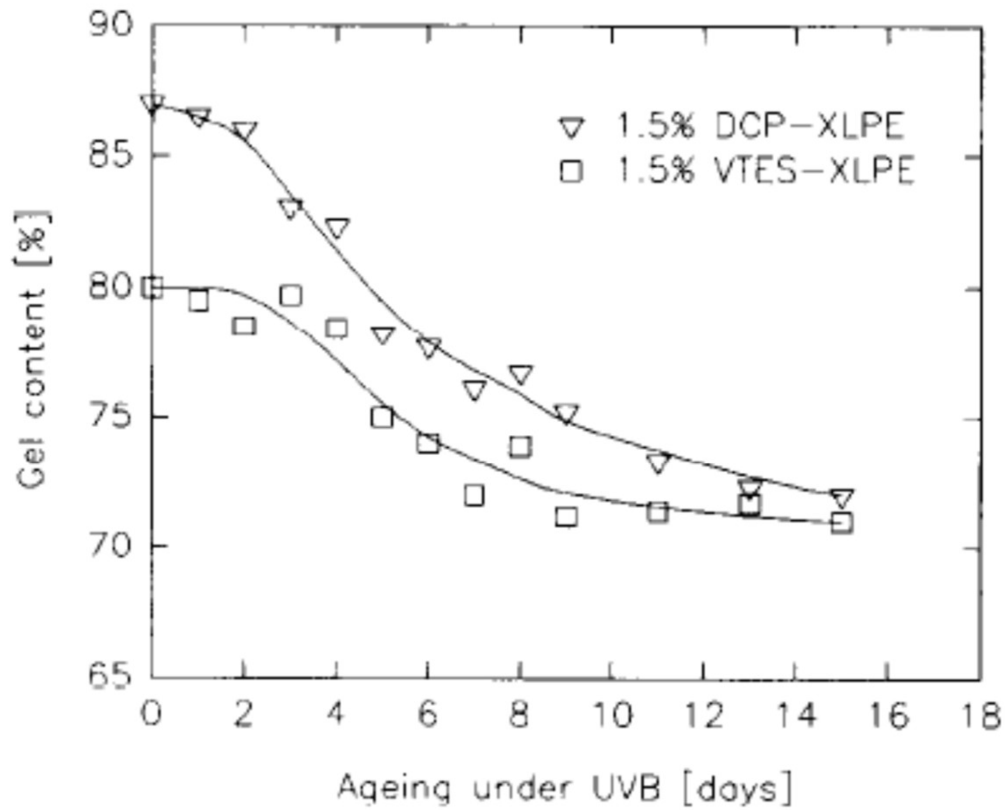


Fig. 16. Changes in the gel content of peroxide and silane XLPE during accelerated UVB exposure.

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

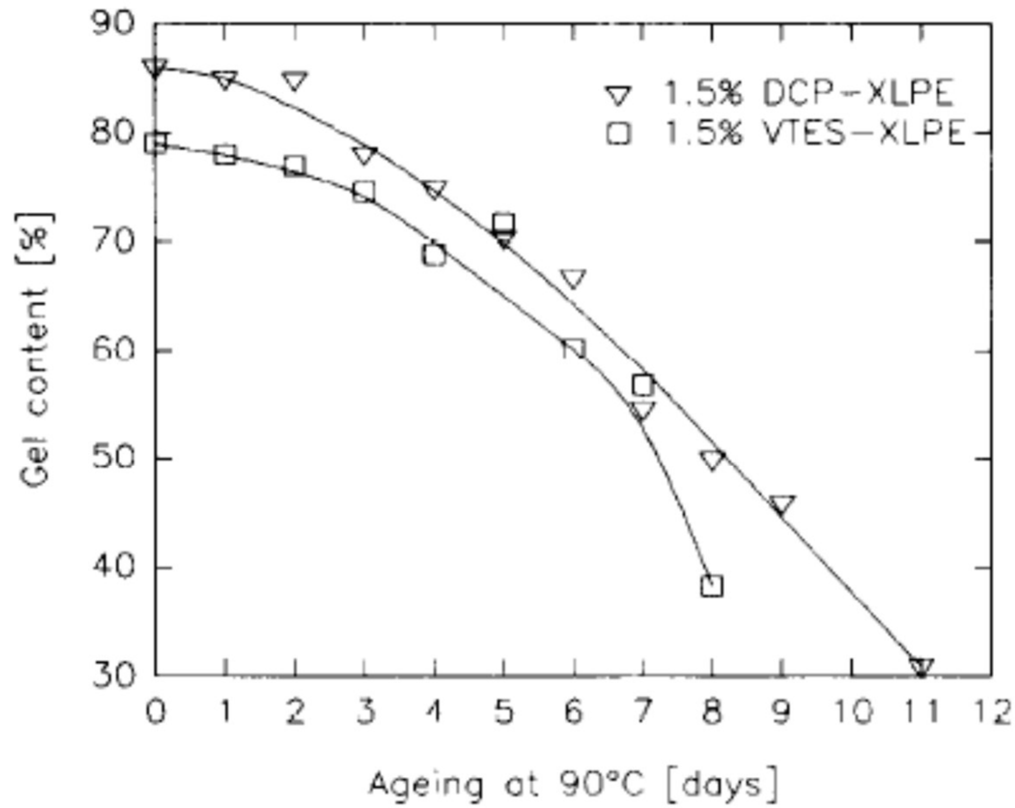


Fig. 14. Changes in the gel content of peroxide and silane XLPE during thermal ageing at 90°C under oxygen.

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

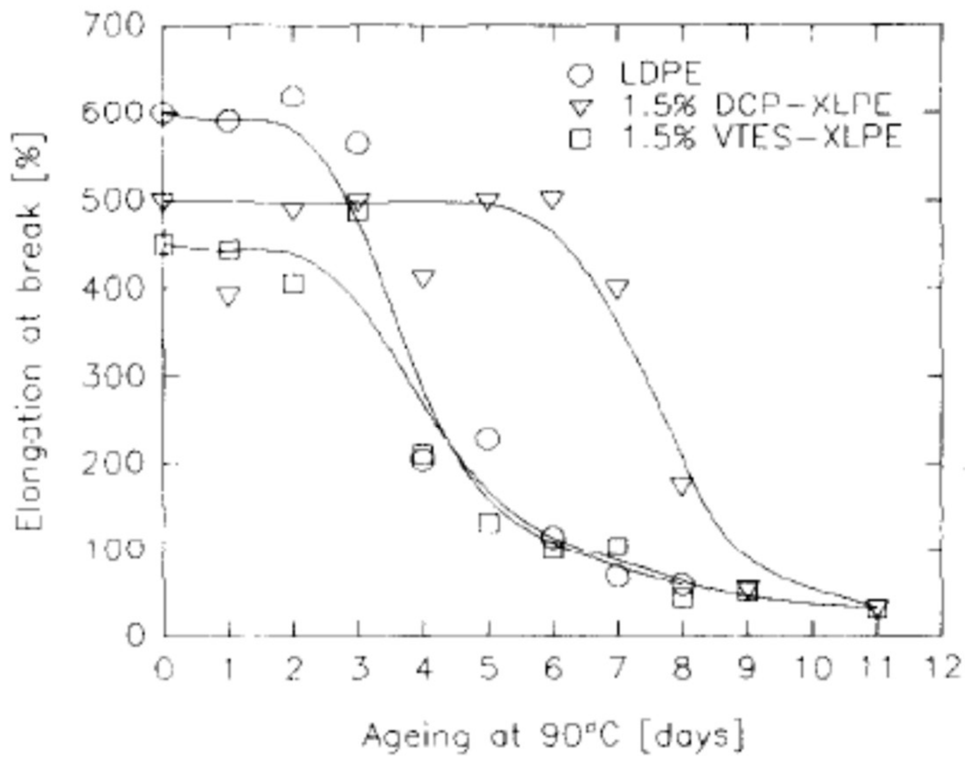
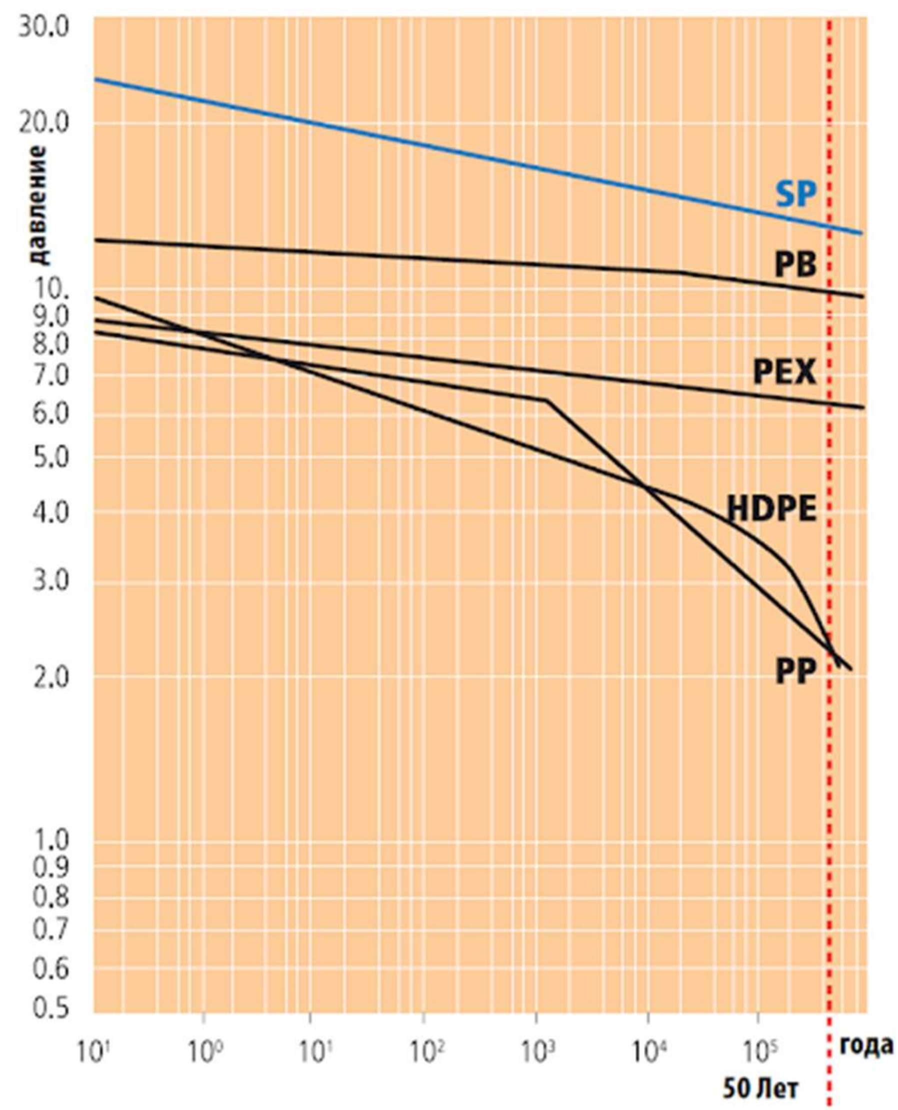


Fig. 13. Changes in the mechanical properties of LDPE and XLPE samples during thermal ageing at 90°C under oxygen.

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



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

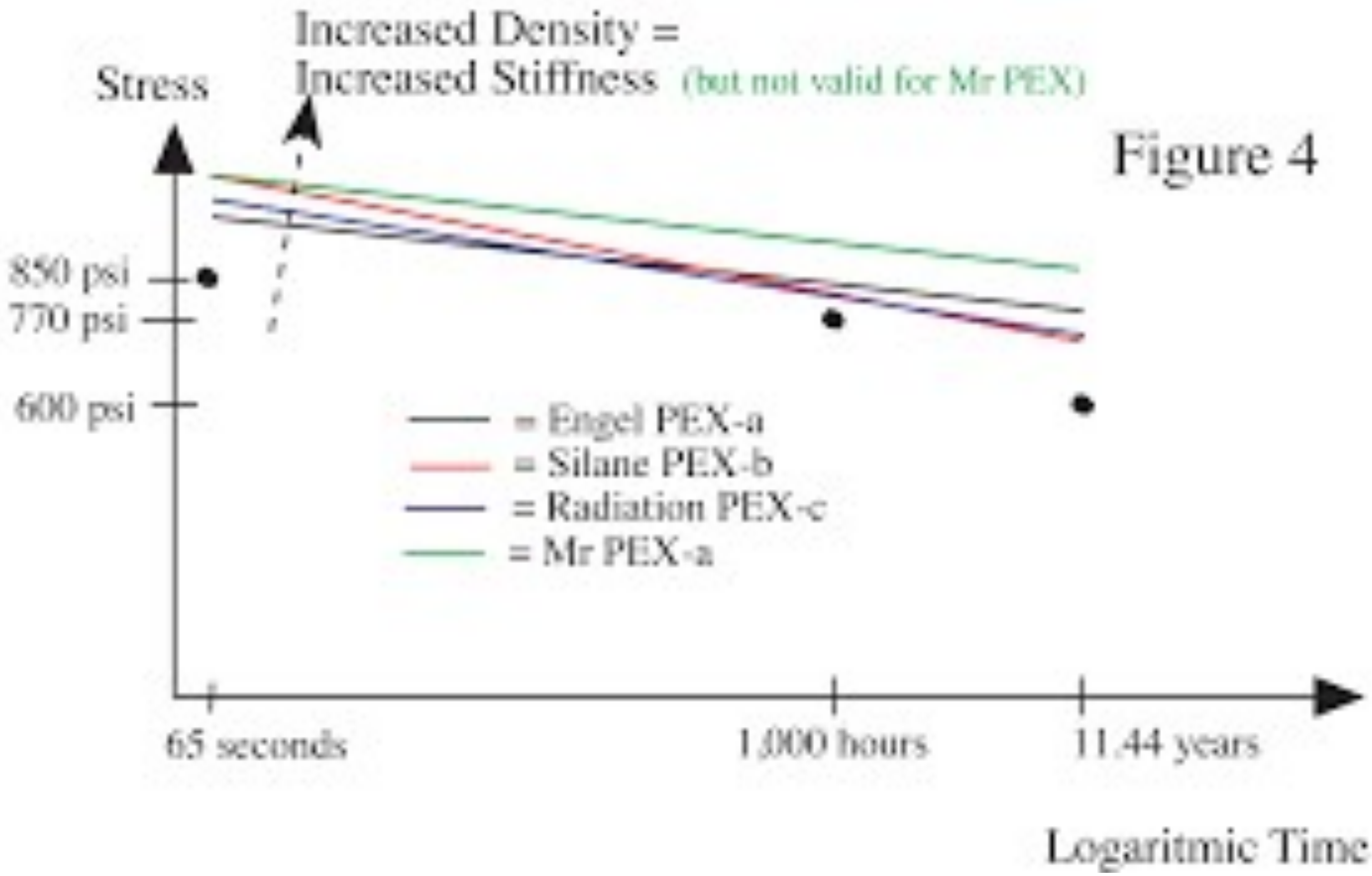
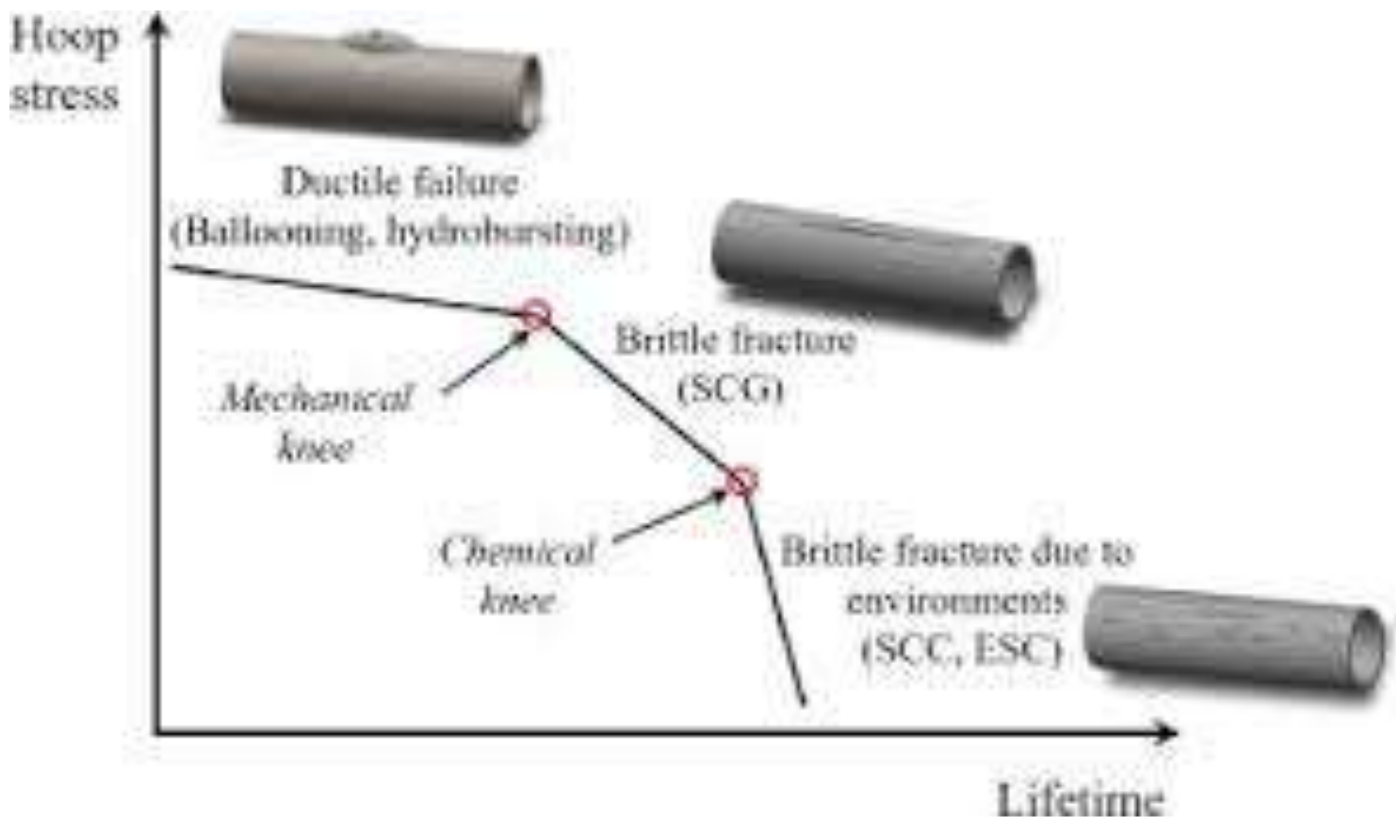


Illustration of the Environmental Degradation Failure on a Hoop Stress vs Failure Time Plot



Environmental Degradation Failure of PEX Plumbing Pipe

1.A: 10% of Pipe Lifetime

1.B: 50% of Pipe Lifetime

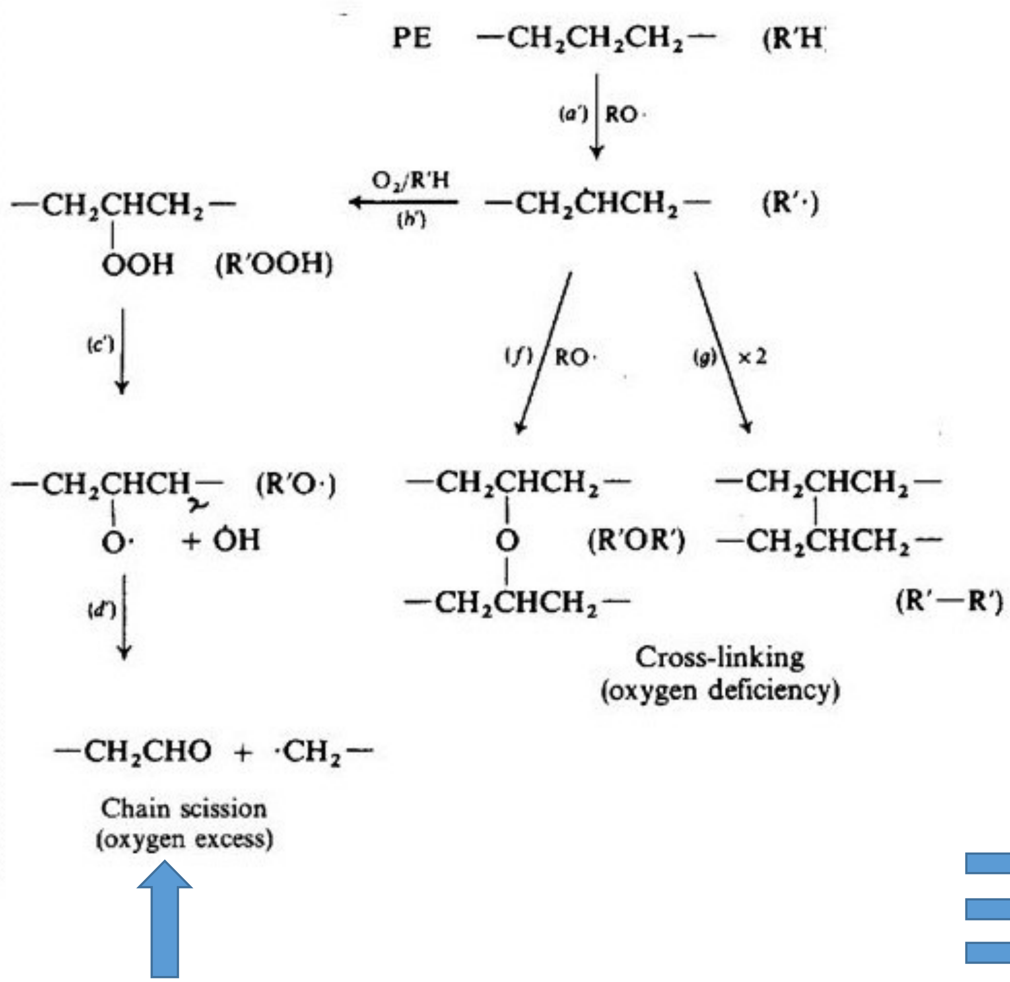
1.C: At Failure

2.A: 10% of Pipe Lifetime

2.B: 50% of Pipe Lifetime

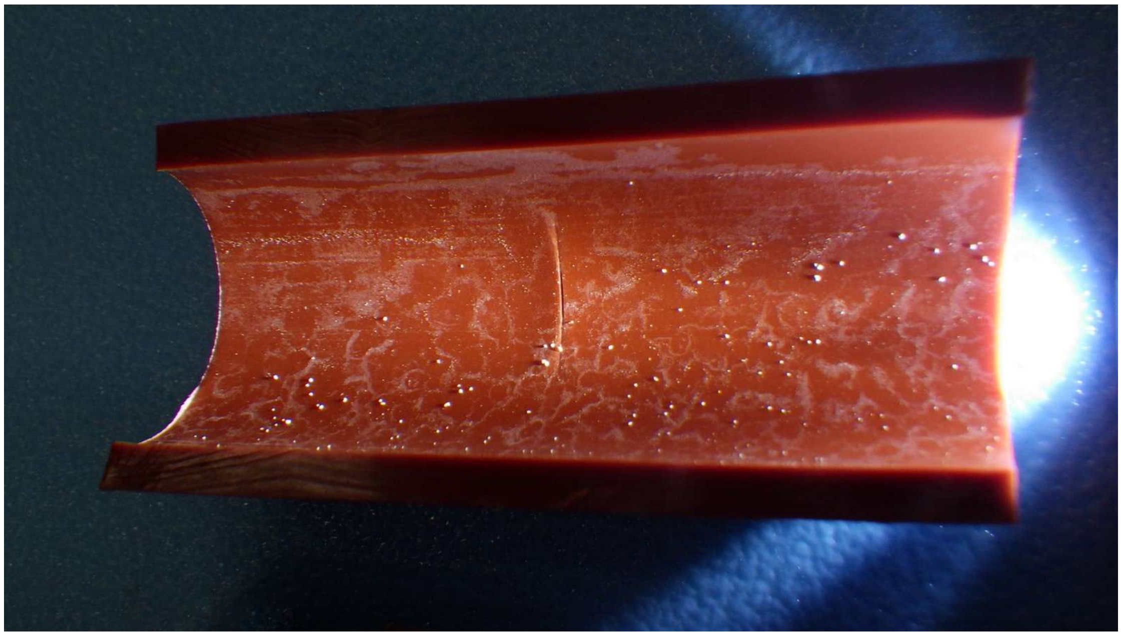
2.C: At Failure

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."