EMAC 276

Lecture 19: Environmental Stress Cracking (ESC)

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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 Reagents[1]

Traditional Solvent-Polymer Tests only Looked at the Interactions Under Static (Unstressed) Conditions

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.

12. Procedure II—Mechanical Property Changes

12.2 Determine the mechanical properties of identical nonimmersed 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**."

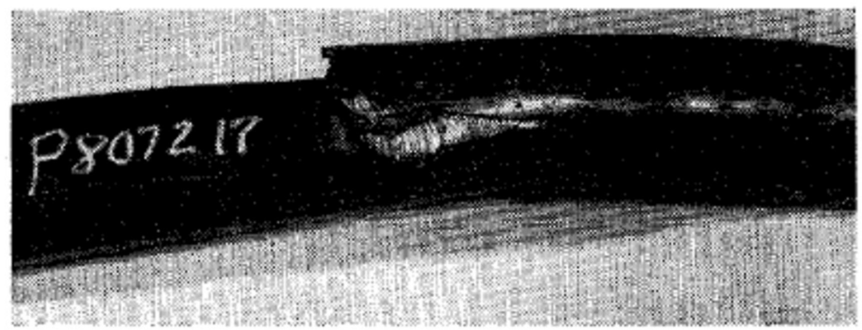


Figure 1. Environmental Stress Crack in Polyethylene Cable Sheath

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

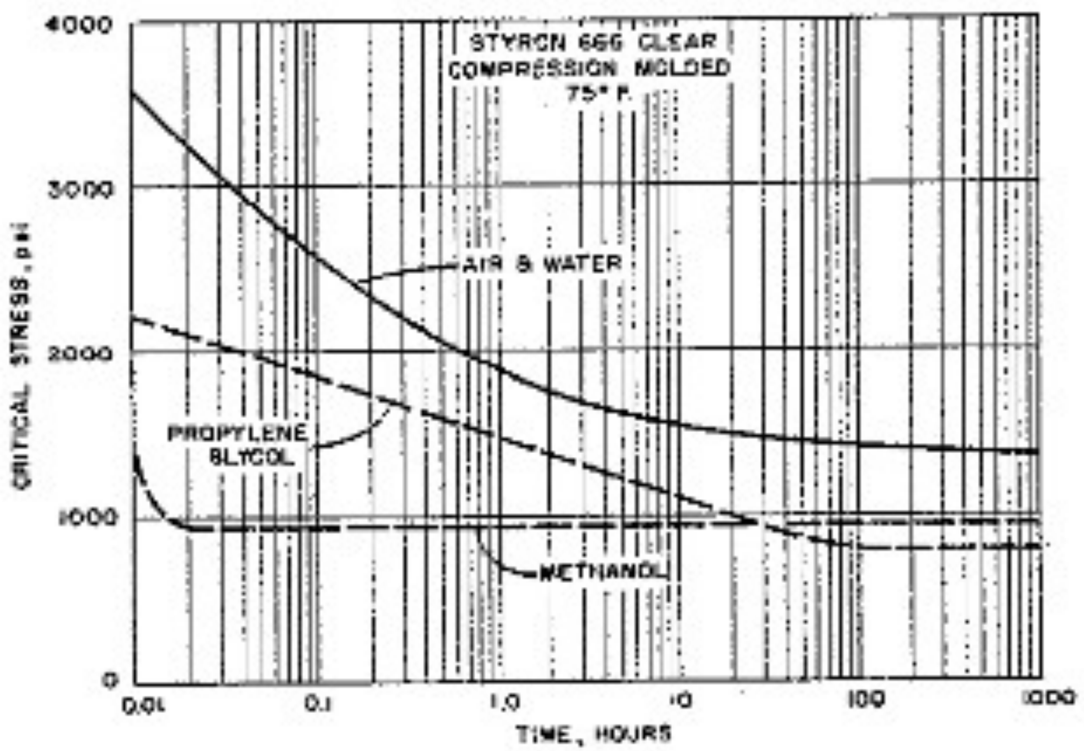
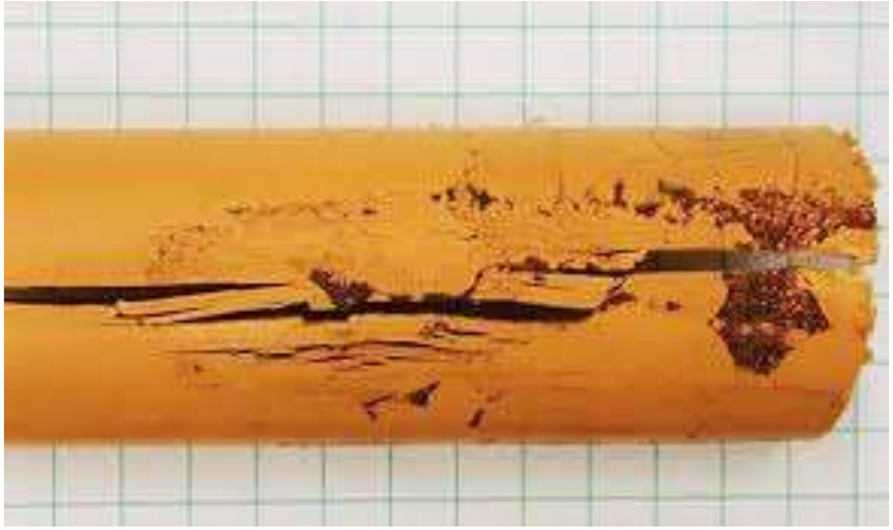


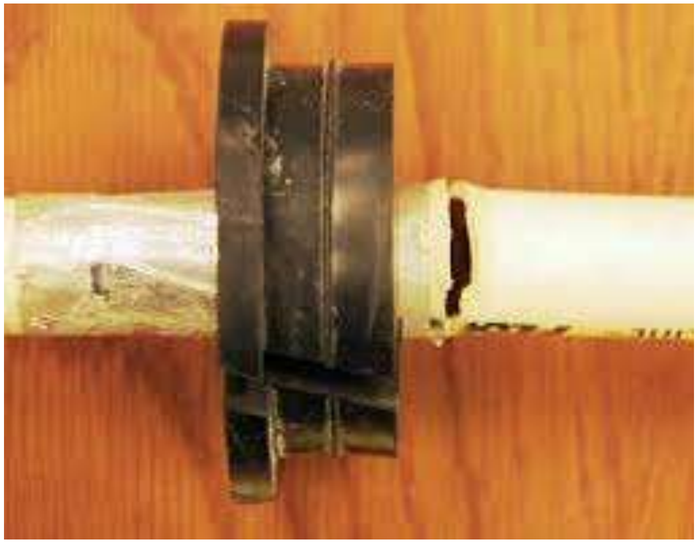
Table 4. Effect of Dairy Products on Stress Cracking of Styron 666 and Q-767 at 75° F.

	Equilibrium Critical Stress, Psi.	
Reagent	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 believe 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.

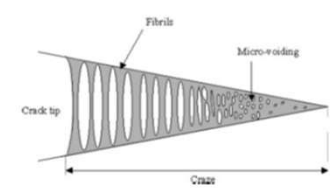


FIG. 1. Schematic diagram of the craze structure in polyethylene.

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

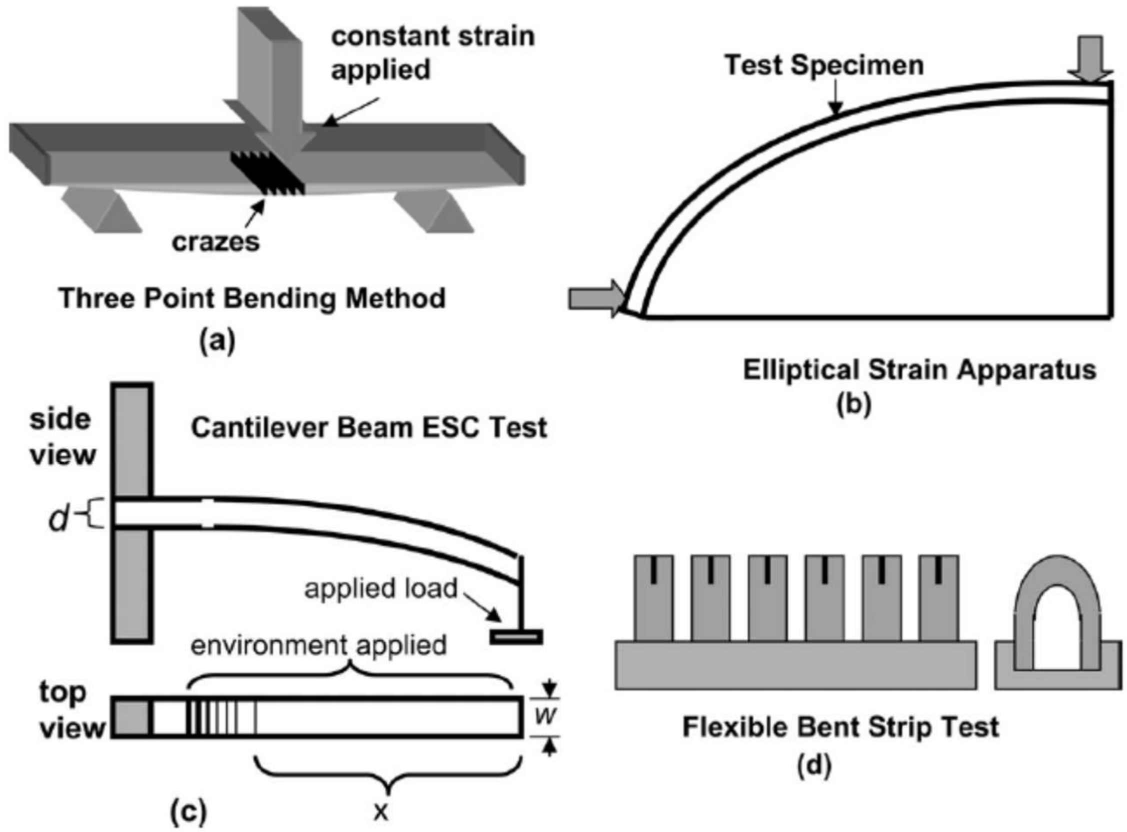
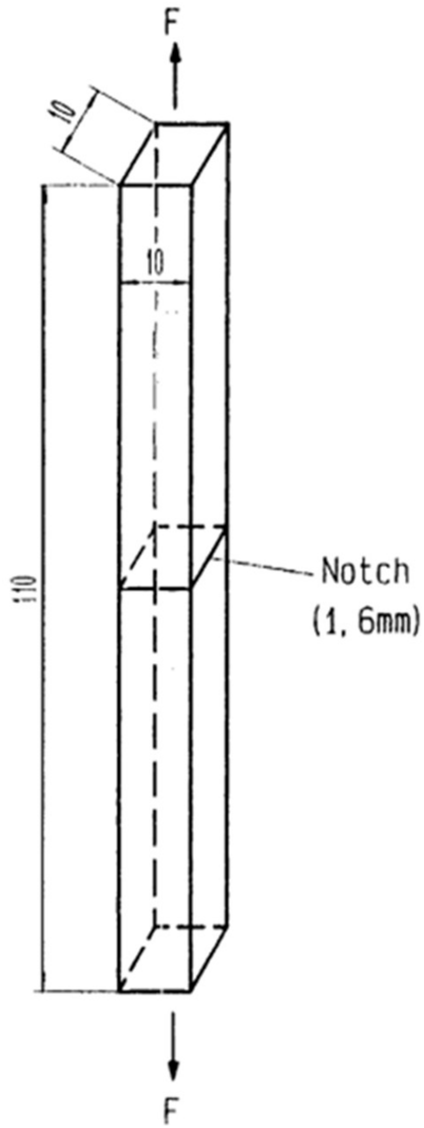
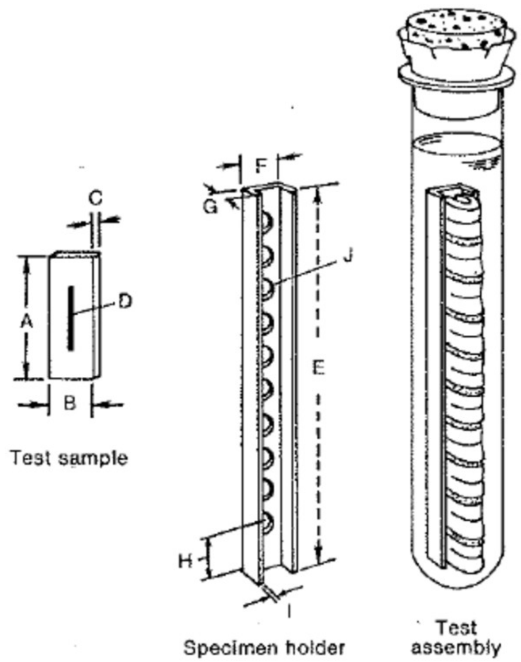
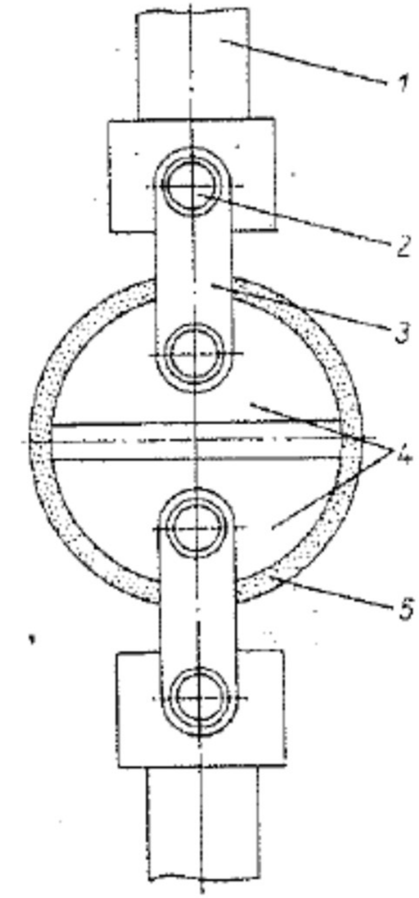


FIG. 5. (a–d) Illustration of various test methods to access environmental stress crazing/cracking.

Other ESC Test Devices







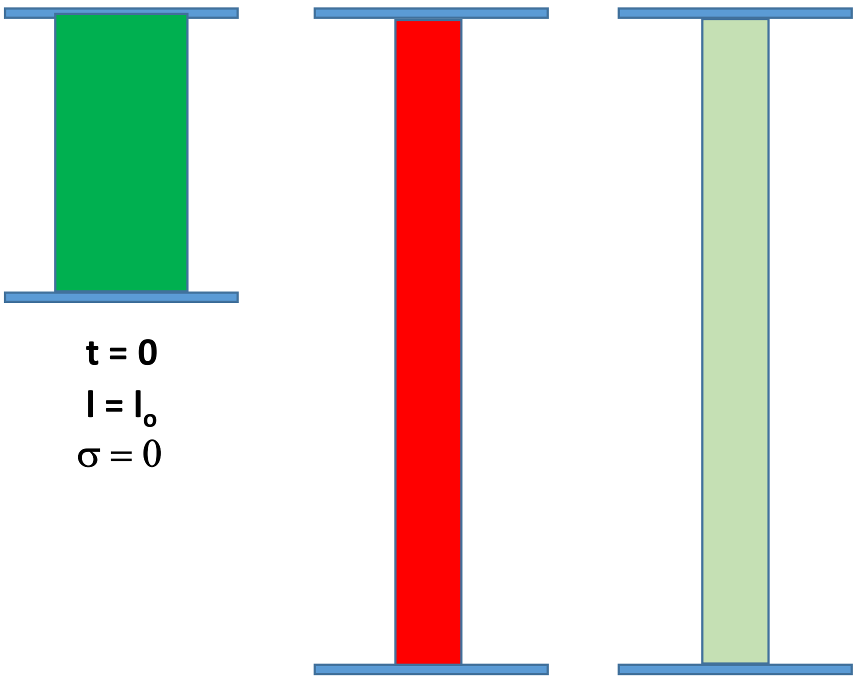
Viscoelastic Performance of Polymeric Materials

- 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.

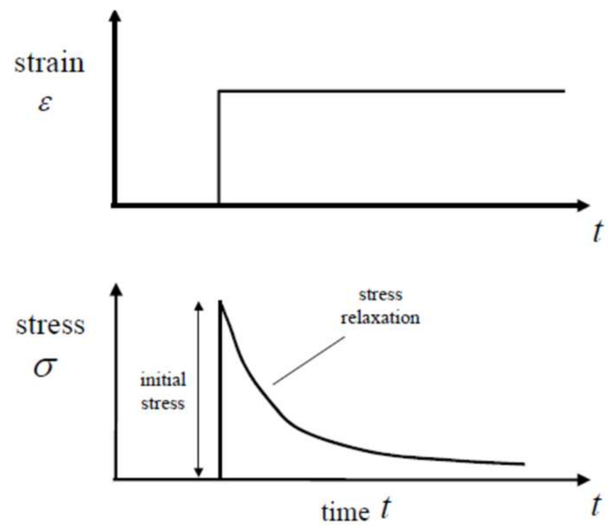
Stress Relaxation



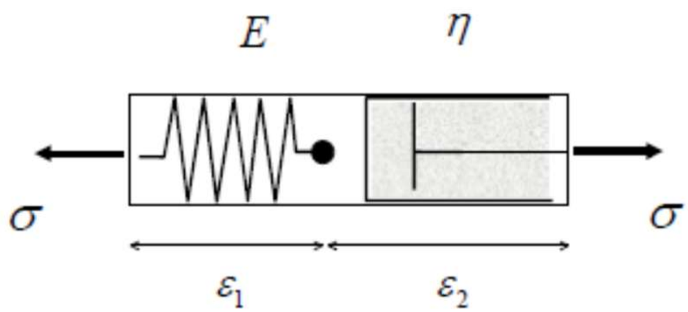
$t = 0$
$l = l_o$
$\sigma = 0$

$t = t_1$
$l = l_1$
$\sigma = \sigma_1$

$t = t_2$
$l = l_1$
$\sigma = \sigma_2 < \sigma_1$



Stress Relaxation



$$\varepsilon_1 = \frac{1}{E}\sigma$$

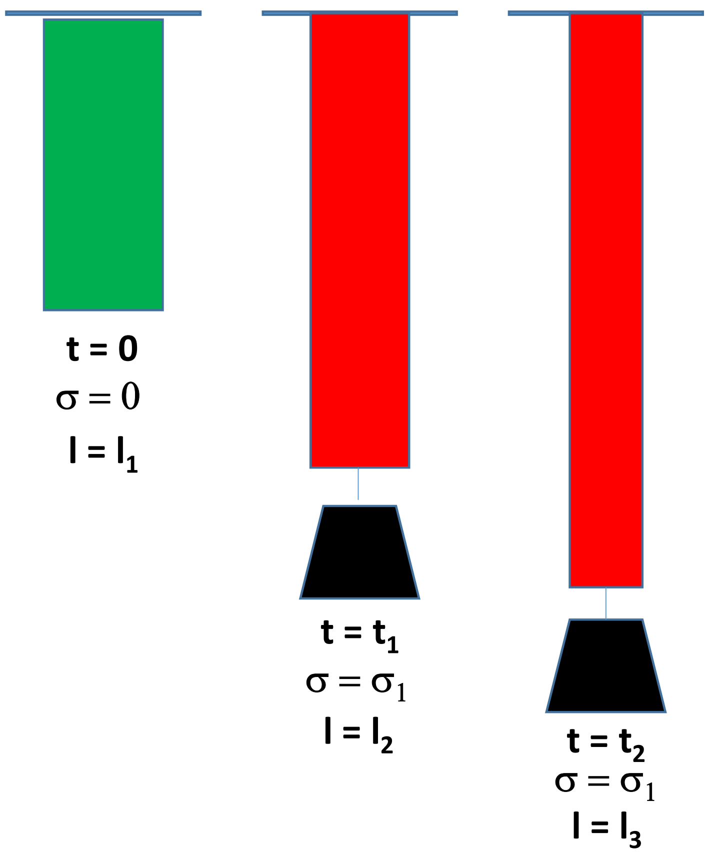
$$\dot{\varepsilon}_2 = \frac{1}{\eta}\sigma$$

$$\varepsilon = \varepsilon_1 + \varepsilon_2$$

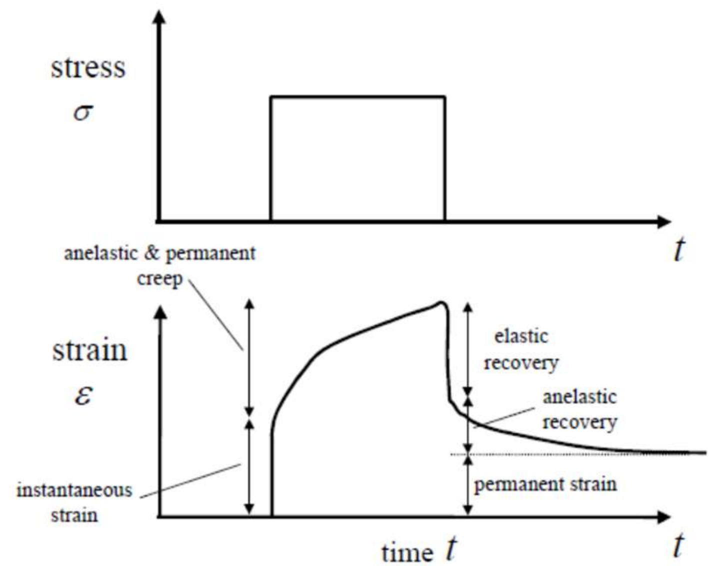
$$\dot{\varepsilon} = \frac{1}{E}\dot{\sigma} + \frac{1}{\eta}\sigma \qquad \sigma + \frac{\eta}{E}\dot{\sigma} = \eta\dot{\varepsilon}$$

$$\frac{\sigma(t)}{\epsilon_0} = E_{\mathrm{rl}}(t) = E_0 \exp(-t/\Theta_{\mathrm{rl}})$$

Creep

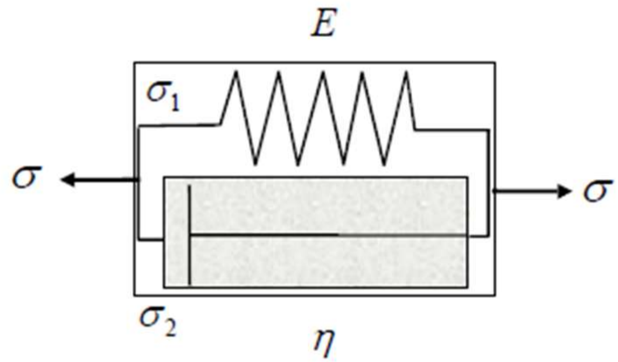


t = 0
σ = 0
l = l₁
t = t₁
σ = σ₁
l = l₂
t = t₂
σ = σ₁
l = l₃



stress
σ
t
anelastic & permanent creep
strain
ε
elastic recovery
anelastic recovery
instantaneous strain
permanent strain
time t
t

Creep



$$\varepsilon = \frac{1}{E}\sigma_1$$

$$\sigma = \sigma_1 + \sigma_2$$

$$\sigma = E\varepsilon + \eta\dot{\varepsilon}$$

$$\dot{\varepsilon} = \frac{1}{\eta}\sigma_2$$

$$\frac{\epsilon(t)}{\sigma_0} \equiv D_{\mathrm{rt}}(t) = D_0\{1 - \exp(-t/\Theta_{\mathrm{rt}})\}$$

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.

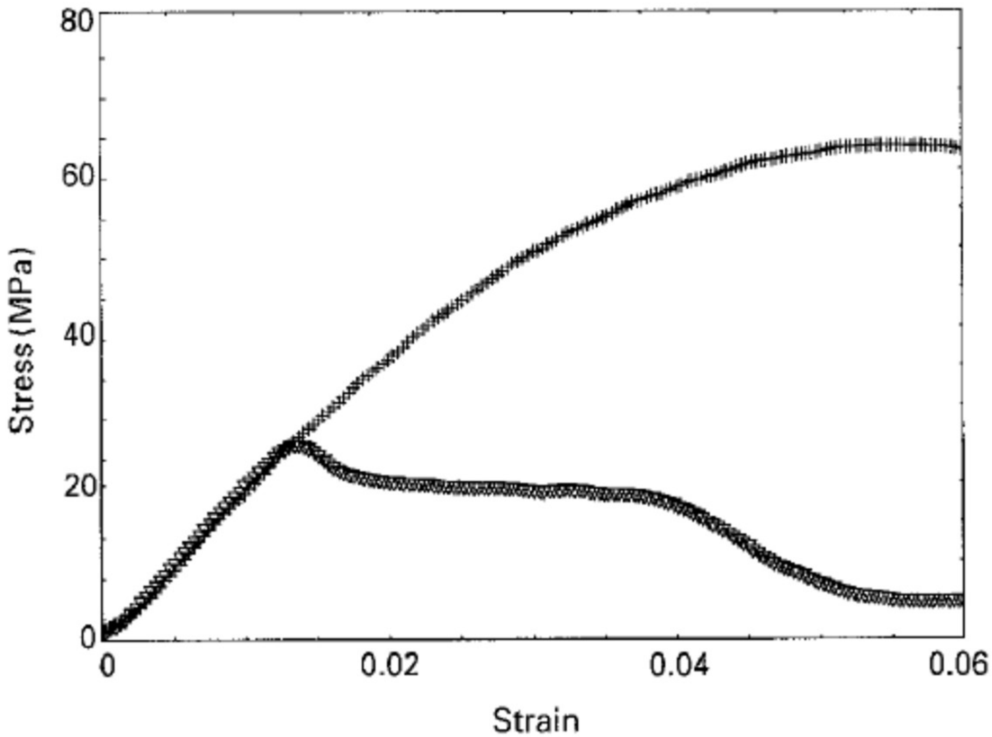
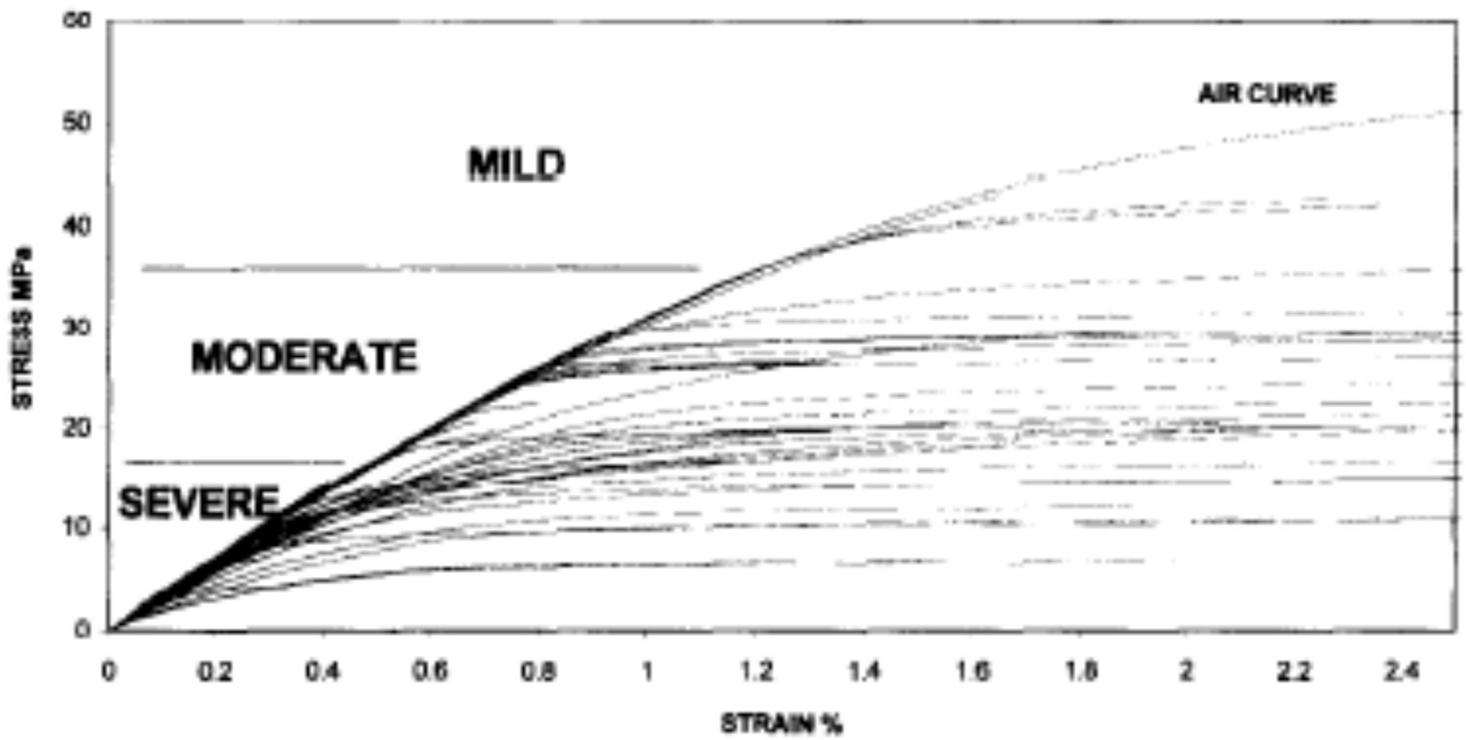


Figure 2 The variation of stress with strain for samples tested in (+) air and (▽) ethanol at a strain rate of 9.2×10^{-6} s^{-1}.

Test Methods for Assessing Environmental Stress Cracking of Amorphous Thermoplastics

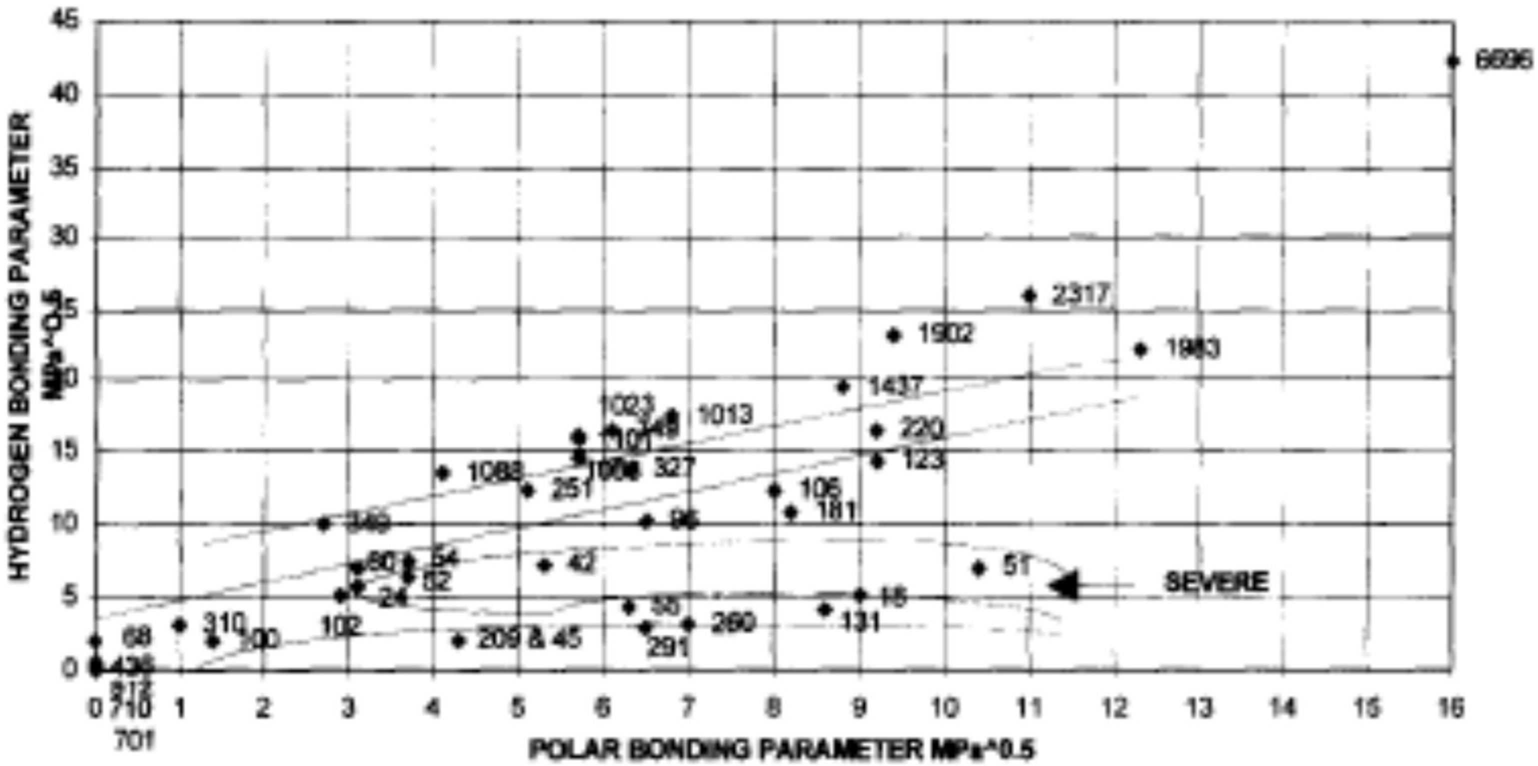
Hough and Wright, Polymer Testing, 15 (1996) 407 - 421



Monotonic 4 MPa/h stress-strain characteristics of UPVC in air and 41 fluids at 20 ^{o}C.

Test Methods for Assessing Environmental Stress Cracking of Amorphous Thermoplastics

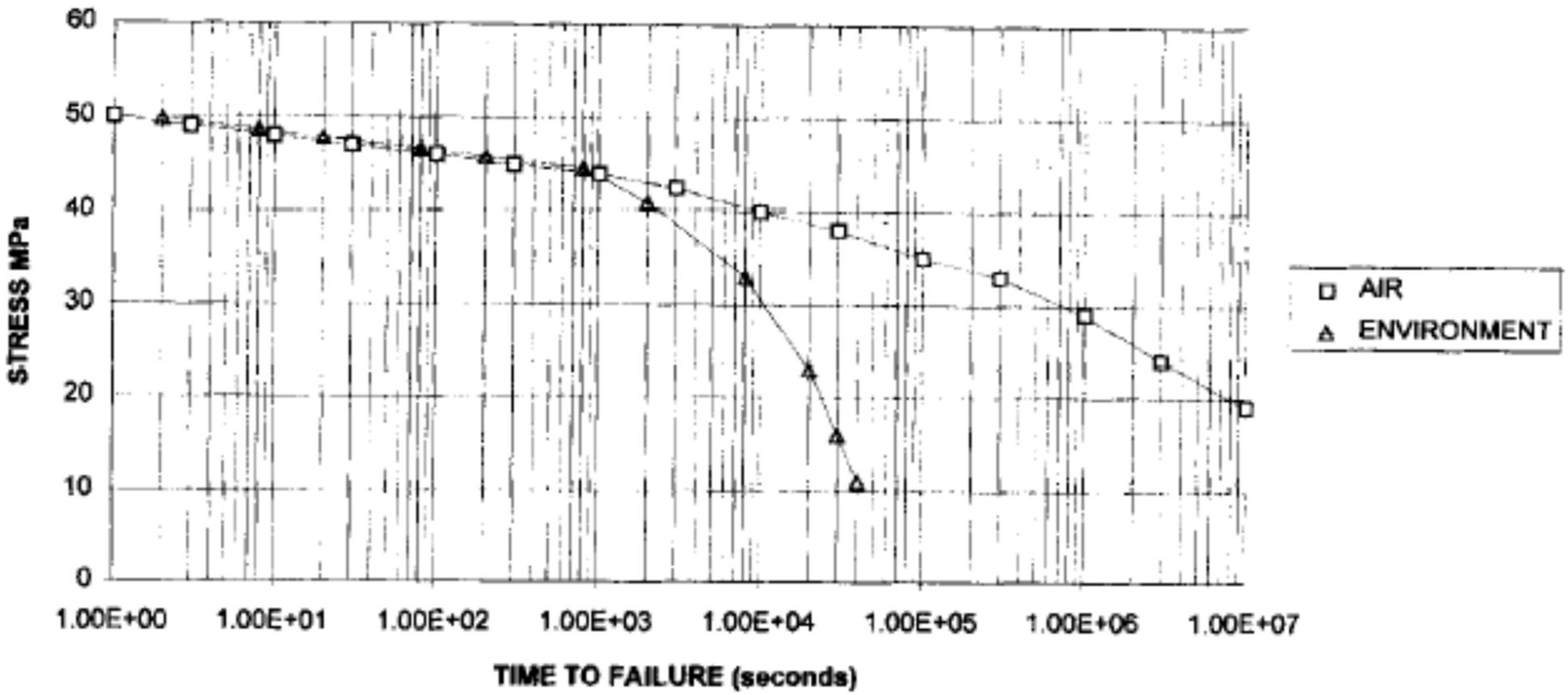
Hough and Wright, Polymer Testing, 15 (1996) 407 - 421



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

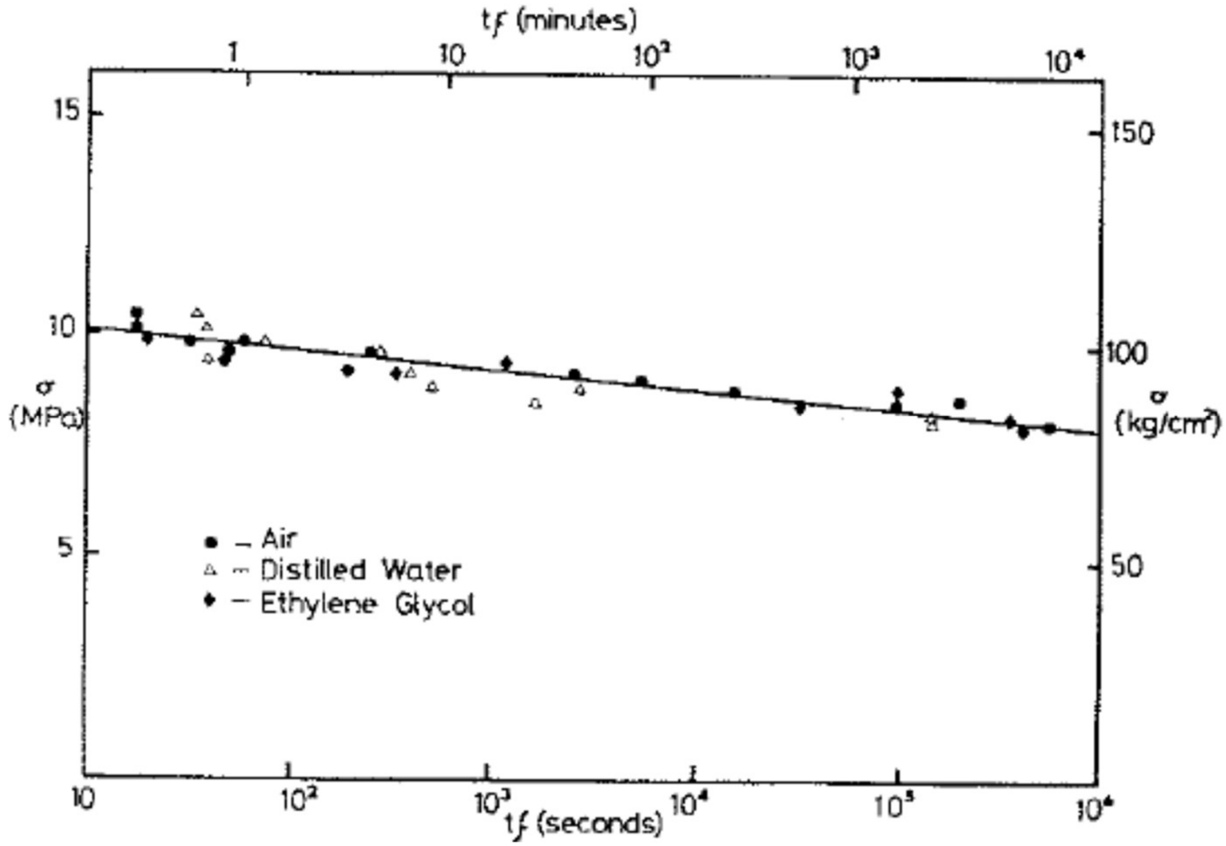


Hough, M.C., Wright, D.C., Polymer Testing, 15, 407-421, 1996

Environmental Stress Cracking of Polyethylene: Criteria for Liquid Efficiency

Shanahan and Schultz,

Journal of Polymer Science, Polymer Physics 17, (1979), 705 – 710.



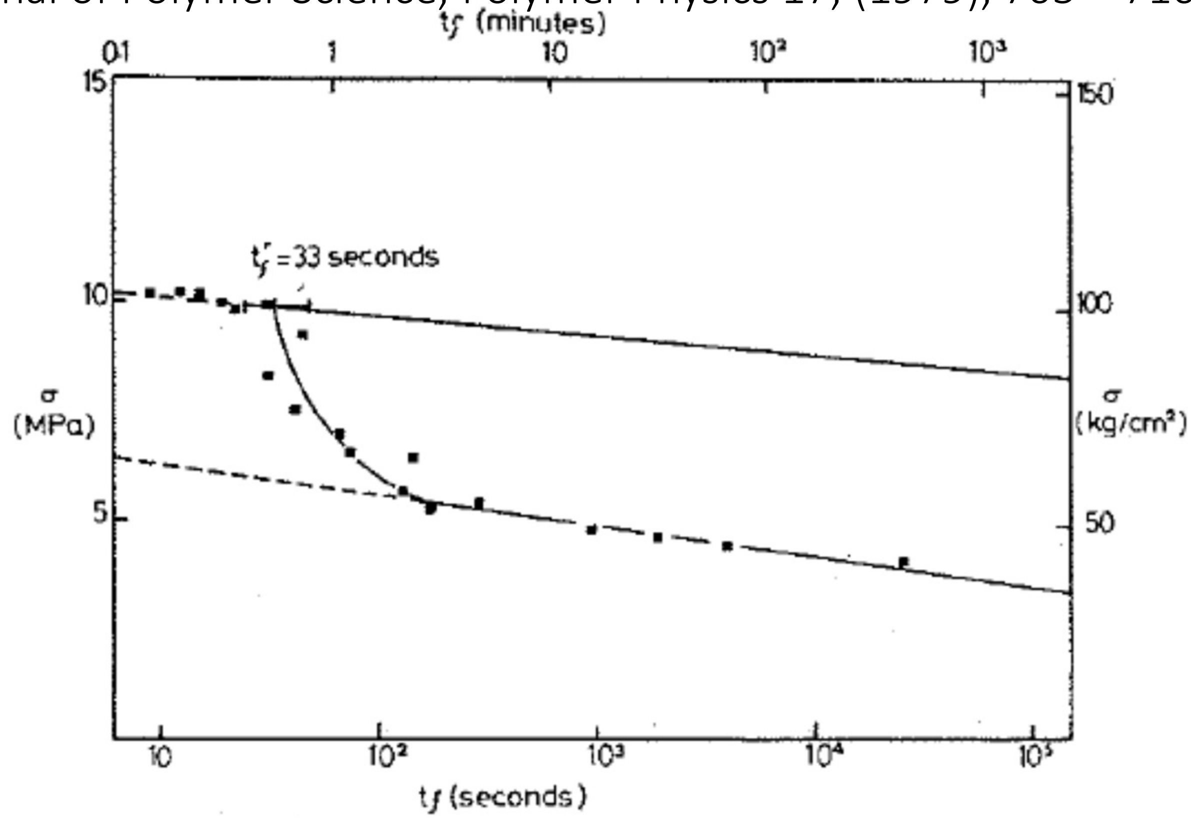
FYI: 10^6 seconds = 277 days

Stress versus failure time for air, distilled water, and ethylene glycol at 25 ^oC

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 (η = 340)	33	48	24	340	13.7
PDMS (η = 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.

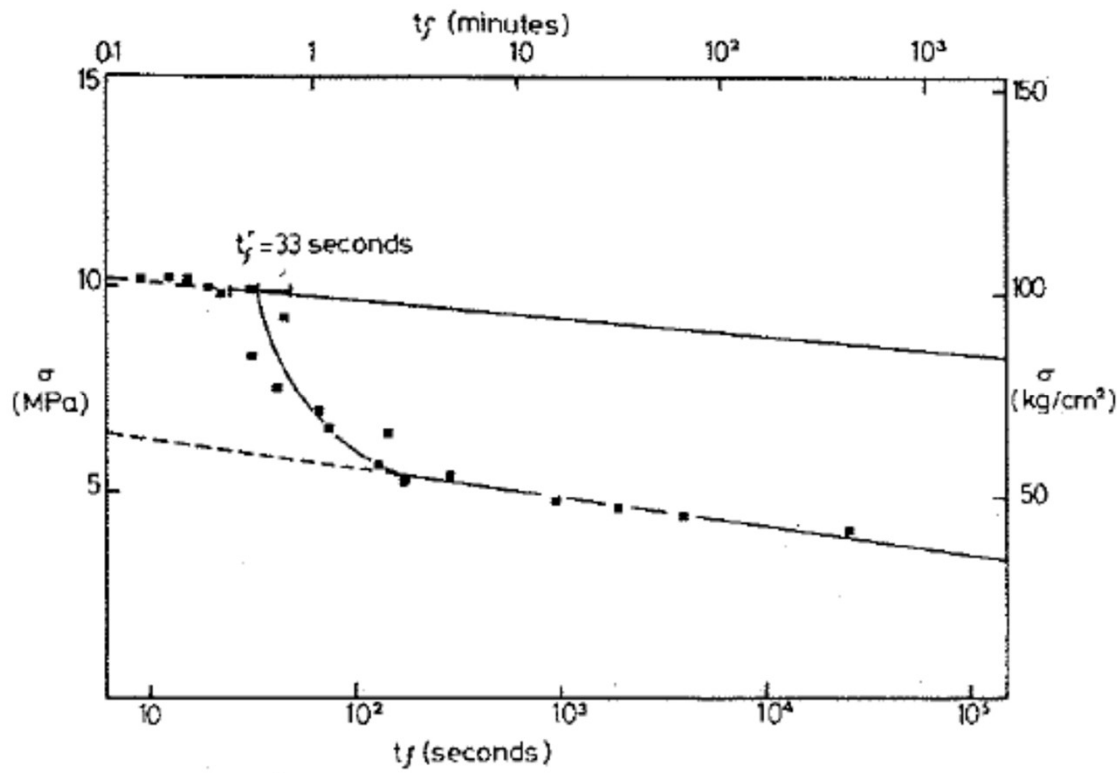
2. **Intermediate Stress Regime** – depending upon the liquid environment a transition region is encountered. The speed of penetration of the liquid within a growing crack largely controls overall time to failure.

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

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- Historical Perspective
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- Test Methods
- Macro Characterization of ESC Mechanism
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- Future Opportunities

Microstructure of Different Polyethylene Materials

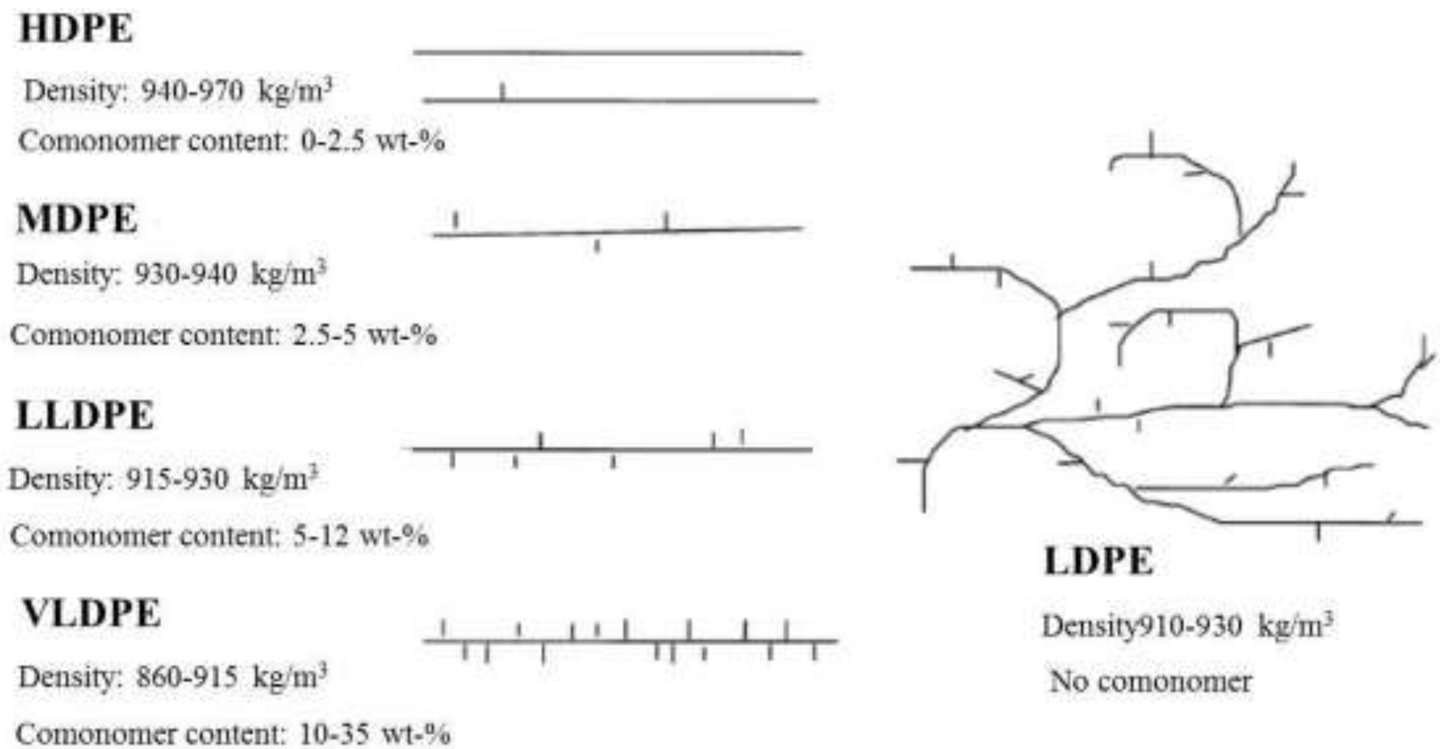


Figure 2.1: Molecular structure of different type of polyethylene (1)

Morphology of Polyethylene - A Semicrystalline Polymer

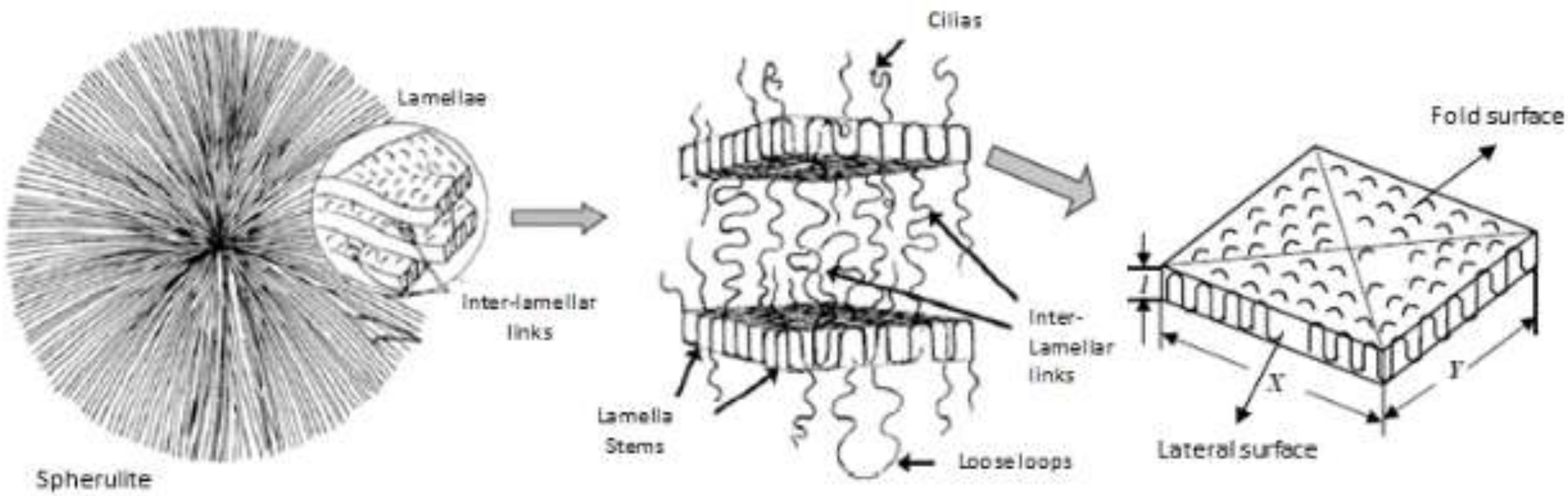


Figure 6.6: Spherulitic and lamellar structure of melt crystallized PE, adapted from (7, 26)

Influence of Uniaxial Stress upon Polyethylene Morphology

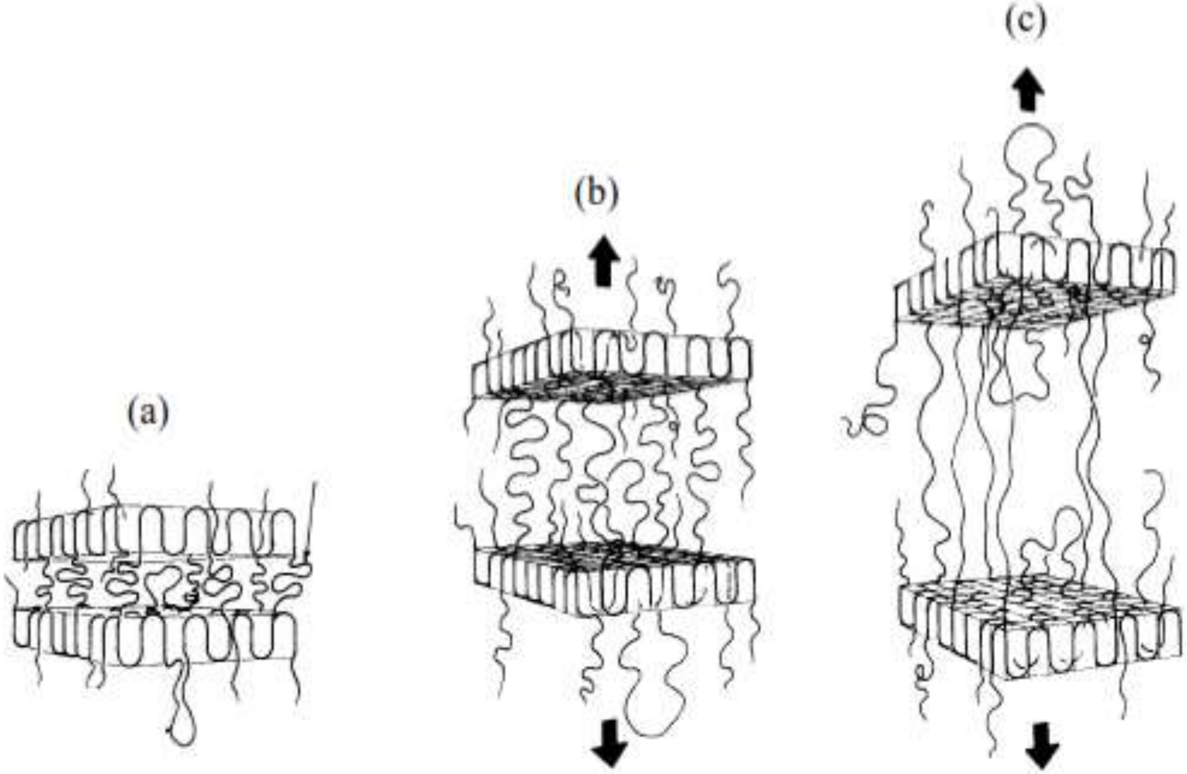


Figure 2.3: Brittle fracture of polyethylene; (a) Unstressed lamella structure (b) Stretch and break of tie-molecules (c) Seperation of lamellae (17)

Morphology and Terminology for Crazing, Cracking and ESC

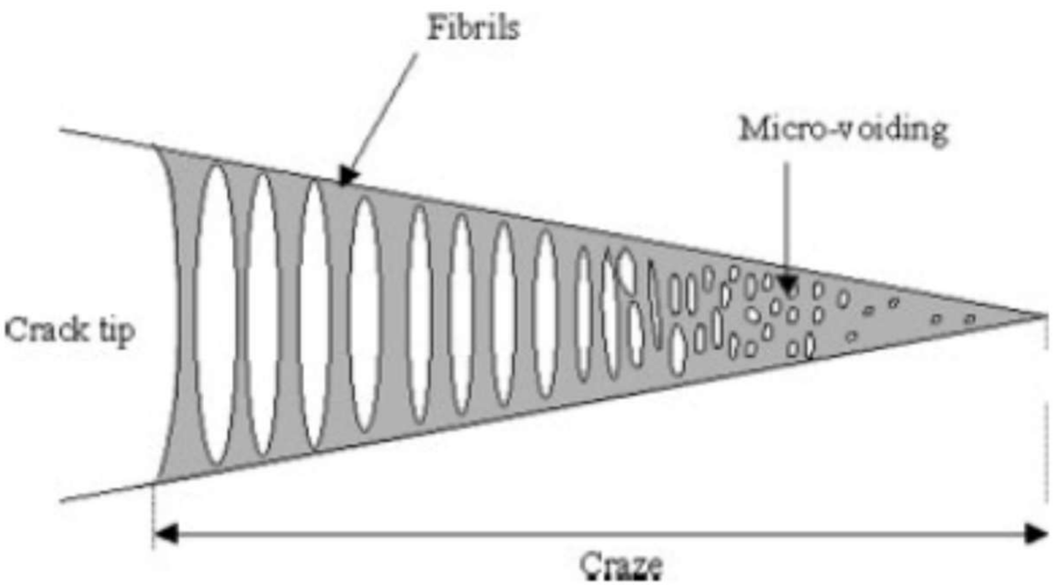
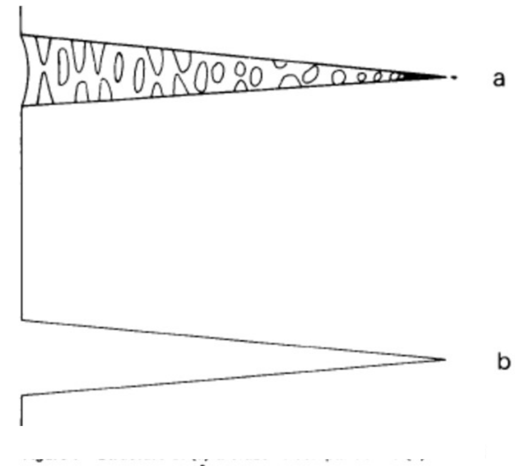
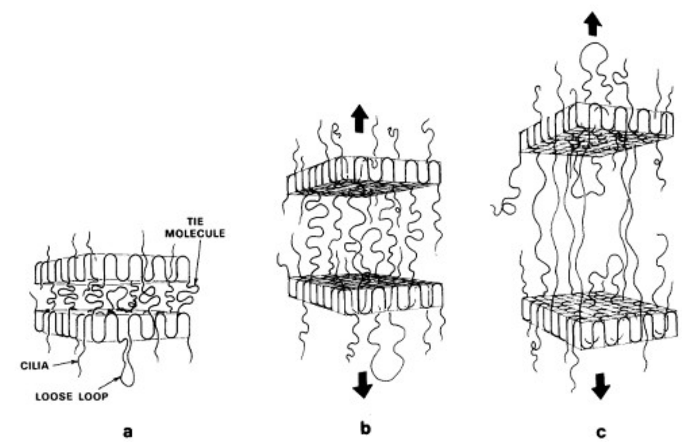
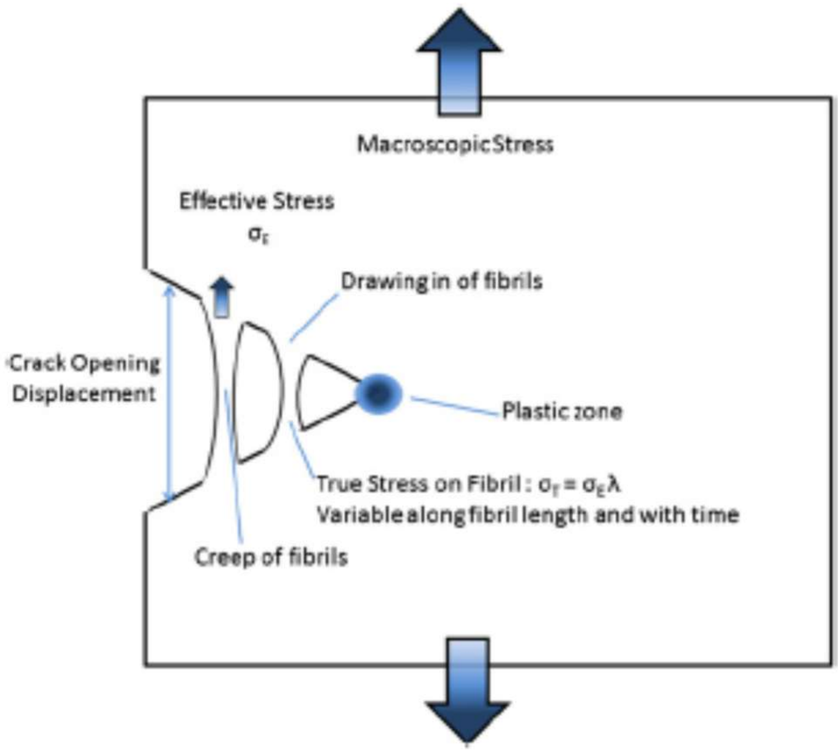


FIG. 1. Schematic diagram of the craze structure in polyethylene.

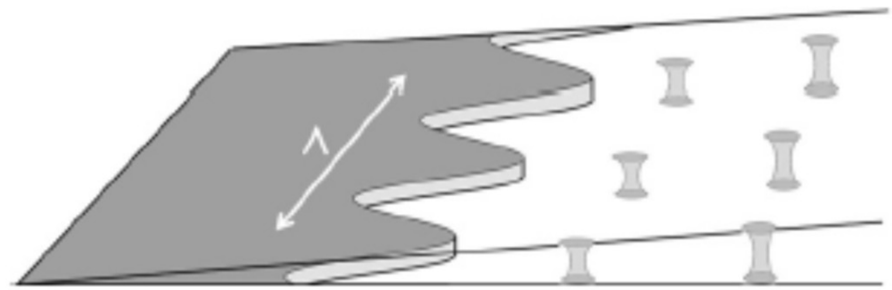




Deblieck, van Beek, Remerie, Ward, Polymer, 52 (2011) 2979 - 2990

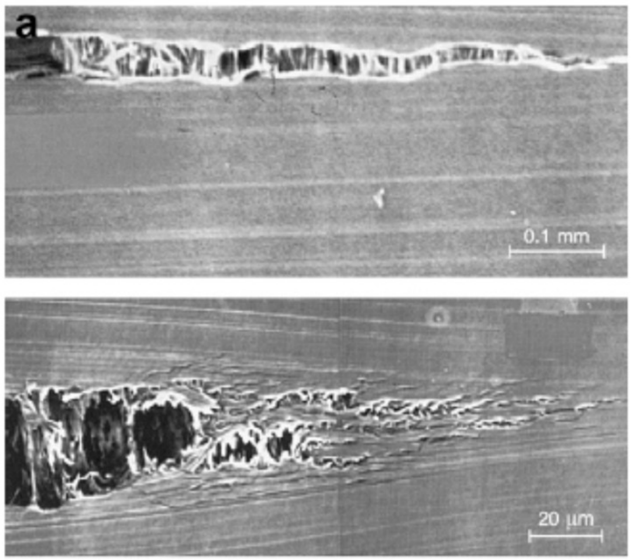


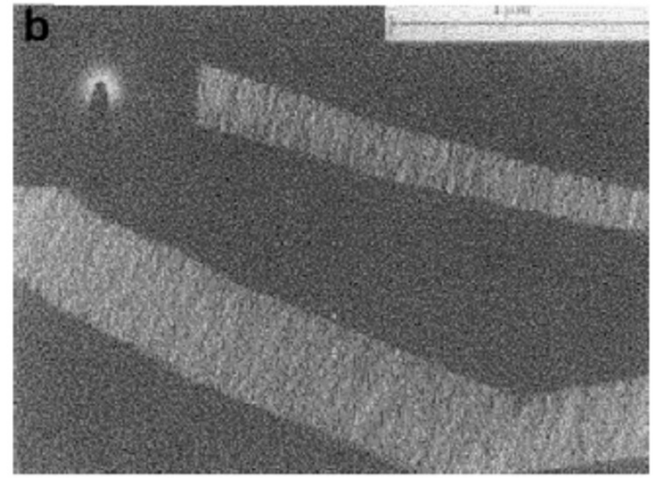
Craze-crack and craze propagation represented schematically. The propagation goes from left to right. The principal stress acts in the up-down direction.

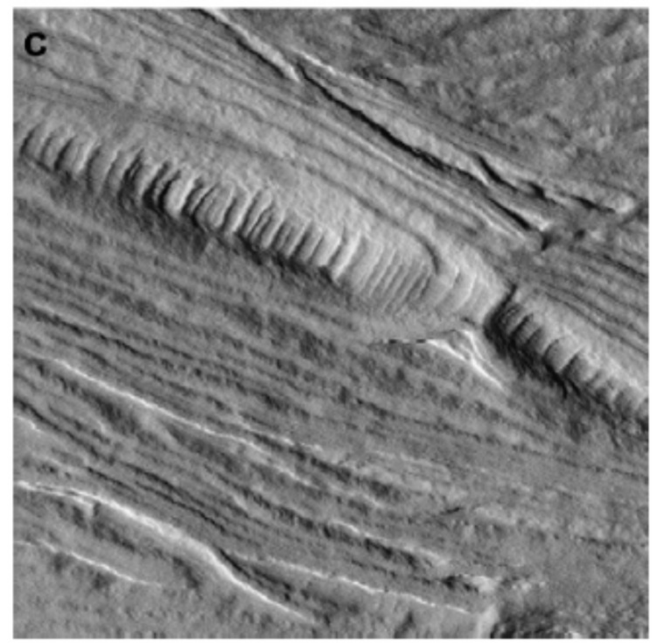


Stress induced melt at a craze tip transforms into fibrils via a surface tension driven Taylor meniscus instability.

Deblieck, van Beek, Remerie, Ward, Polymer, 52 (2011) 2979 - 2990

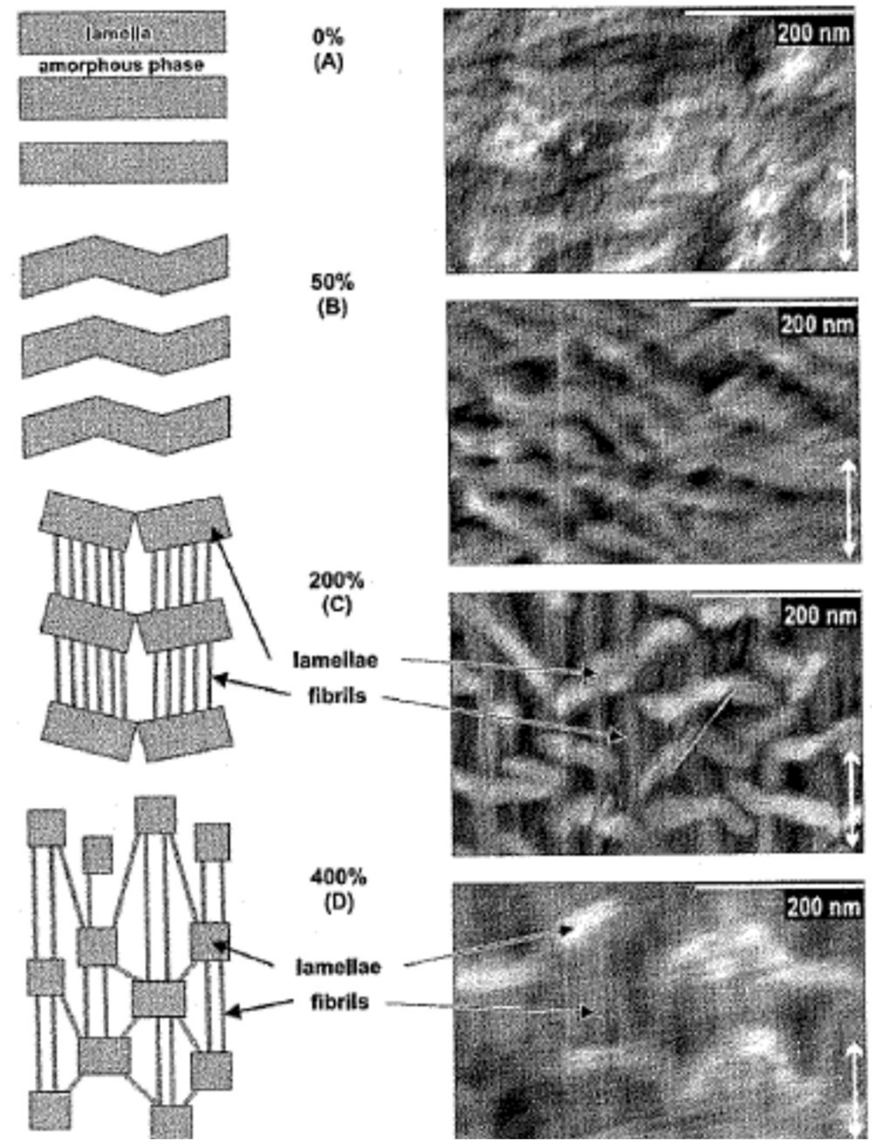






a) Craze fibrillar network and the craze-crack transition in PE (upper) in addition multiple crazing around the craze tip is revealed (lower).
b) Crazing as observed by TEM in a thin film of spherulitic isotactic polystyrene at room temperature
c) Crazing and coalescence of crazes as observed by tapping 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.

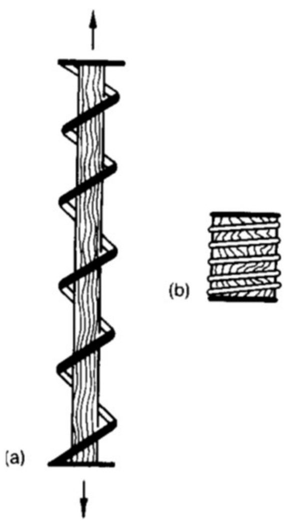


FIG. 11. Schematic illustration of possible coexistence of surface forces (spring) together with conformational property of the fibrillar mass so that the fibril is always in an extended state; (a) loaded or (b) unloaded.

Fiber Strength Contribution - $F_E = \frac{\pi D^2}{4} E\varepsilon$

Surface Strength Contribution - $F_S = \pi D \gamma$

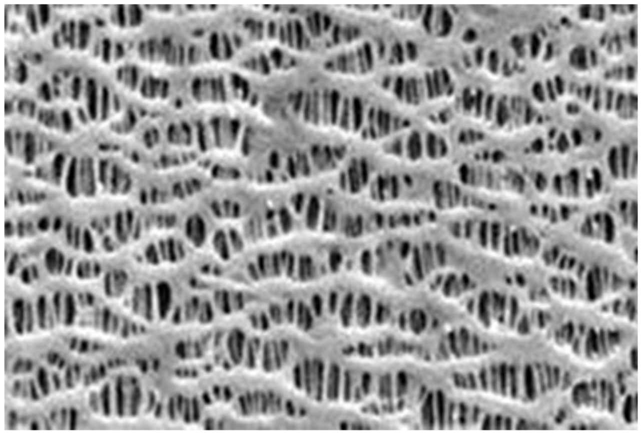
$$F_T = F_E + F_S = \frac{\pi D^2}{4} E\varepsilon + \pi D \gamma$$

$$\Delta\sigma_f = \sigma_{SA} - \sigma_{SL} = \frac{4}{D}(\gamma_{SA} - \gamma_{SL})$$

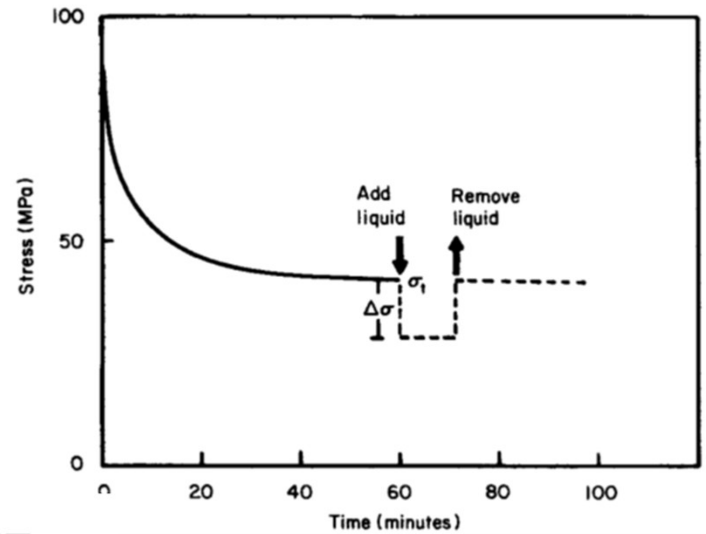
$$\Delta\sigma = \frac{4 A_f \gamma_{LA} \cos\theta}{\bar{D}}$$

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®



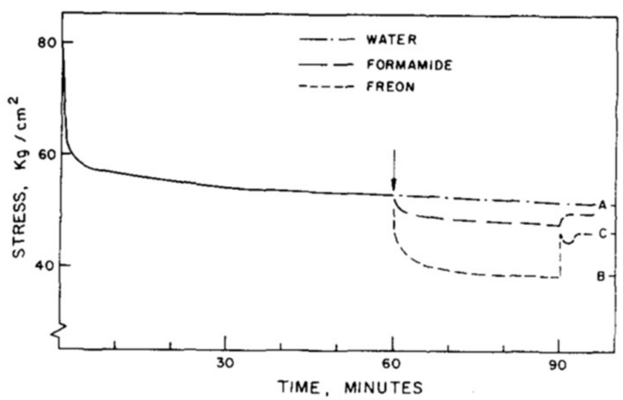


FIG. 9. Stress-relaxation behavior of hard-elastic HIPS in air for 1 h and then in liquid (arrow) for 30 min, after which the liquid is removed.

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)	Depression of retractive stress 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	19.8	...
			to		
Silicone oil	8.3	19.7	5.9	21.4	...
Silicone oil	1.7	19.2		30.5	13.7
n-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

[a] Polydimethylsiloxane.
[b] Fluorocarbon liquid (DuPont Co.).
[c] Estimated from heat of vaporization.

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

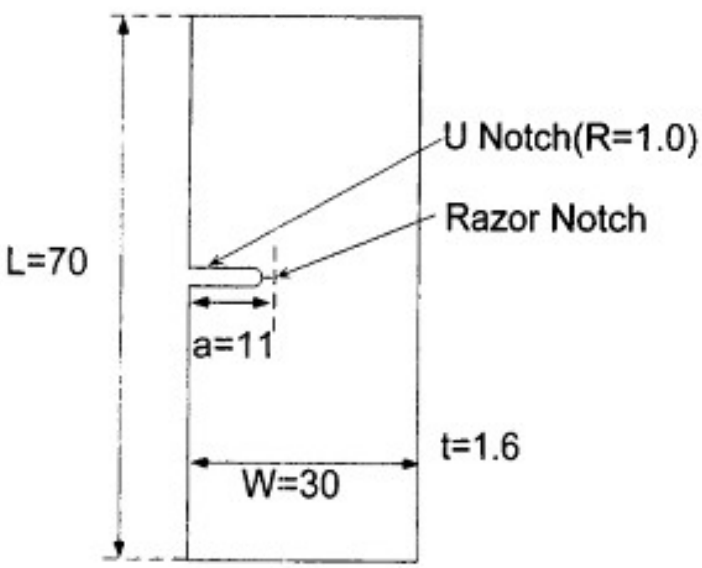
Molecular Mechanisms **for** Reducing the Effects of ESC

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

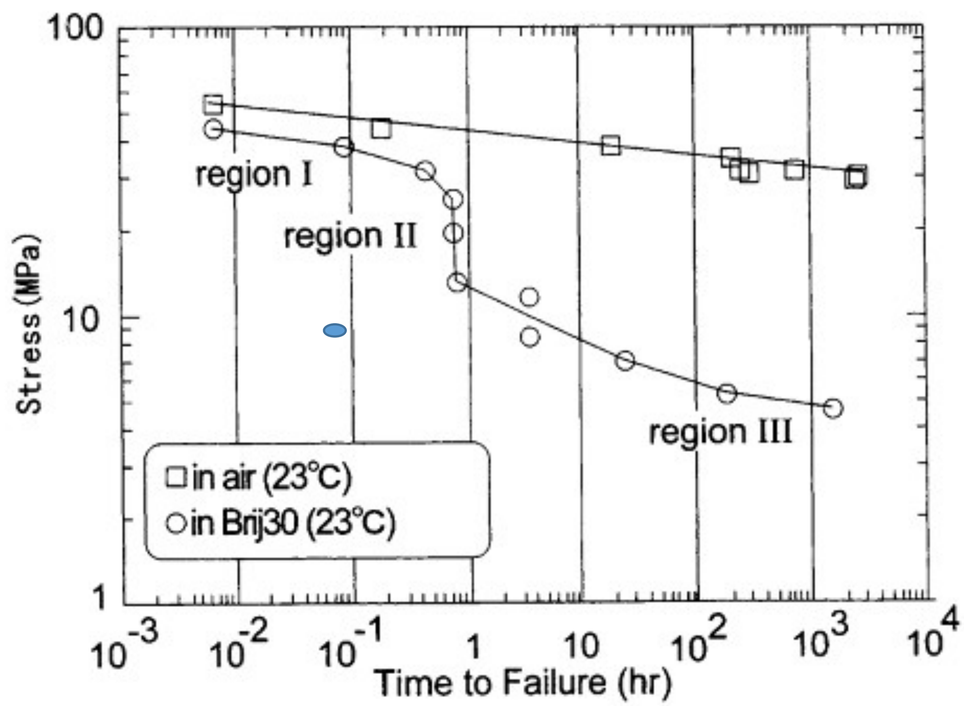
Environmental Stress Cracking of Poly(Acronitrile-Butadiene-Styrene)

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(Acronitrile-Butadiene-Styrene)

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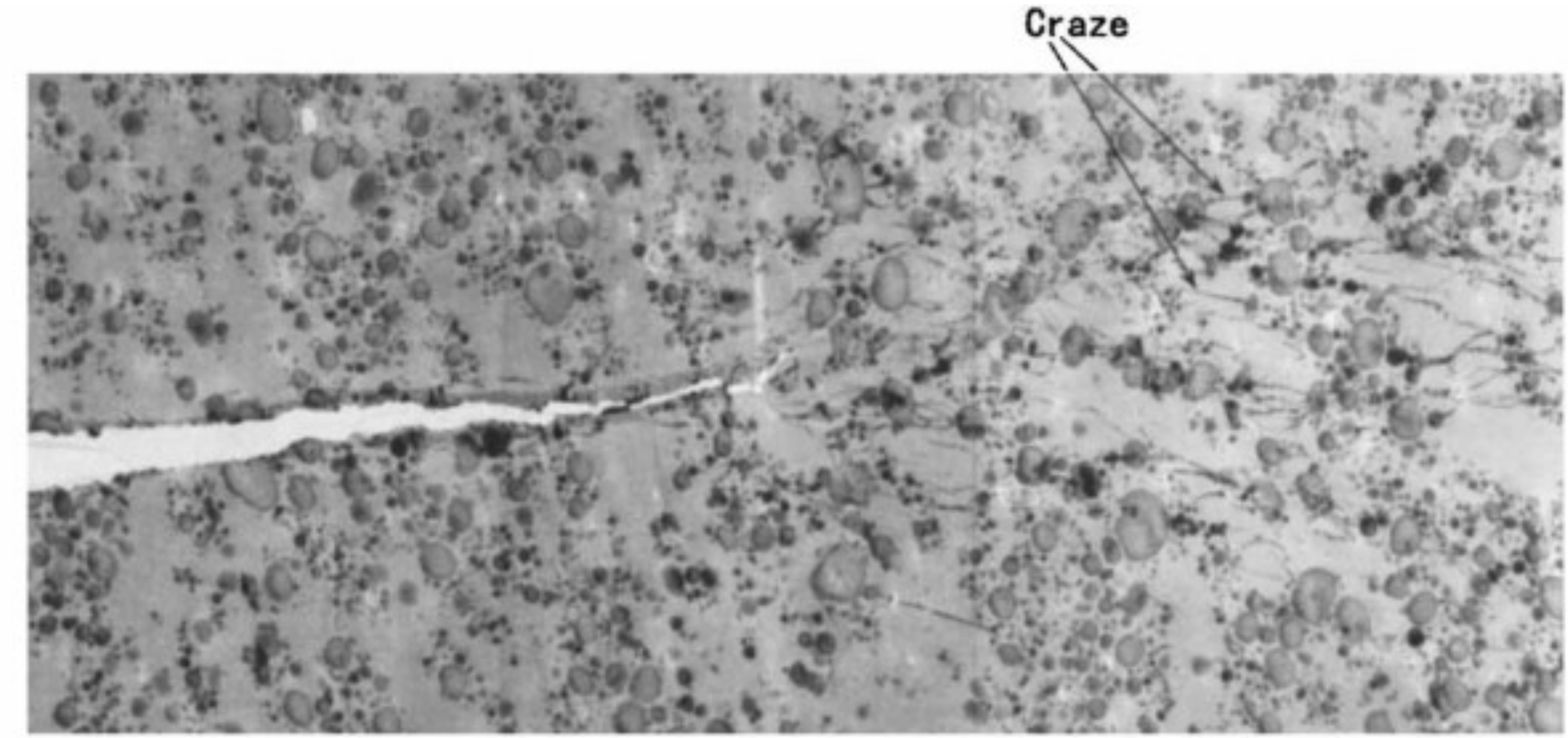

TEM image of the crack tip in an ECT test.

Environmental Stress Cracking of Poly(Acronitrile-Butadiene-Styrene)

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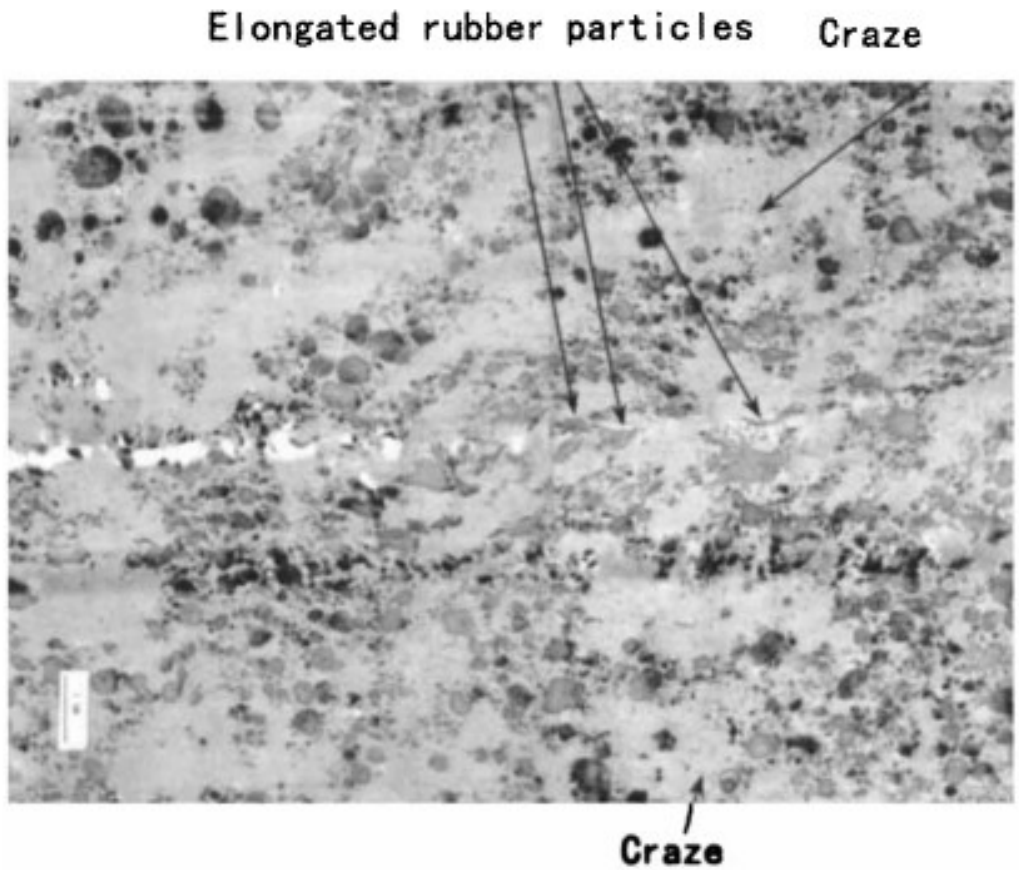
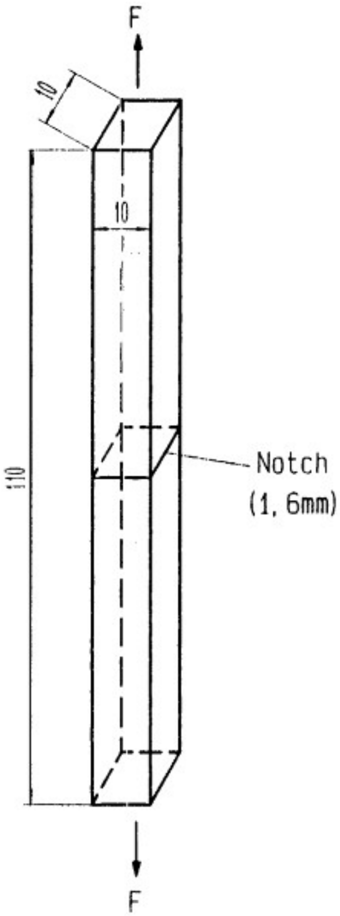


TEM image of the crack tip.

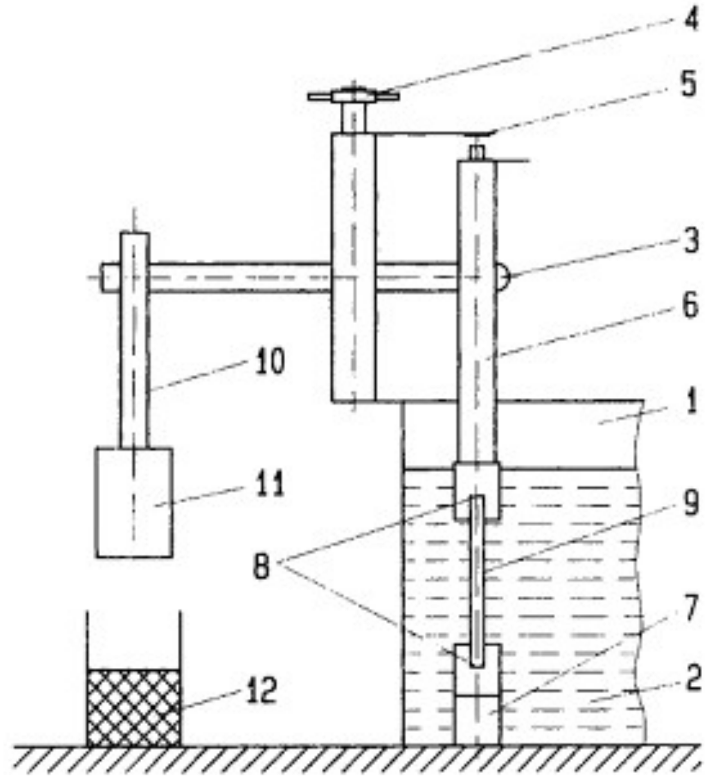
Environmental Stress Cracking Resistance of Blends of High-Density Polyethylene with Other Polyethylenes

Schellenberg, Feinhold, Polymer Eng. & Sci., 38(9), (1998), 1413 – 1419.

Test piece geometry



Test configuration



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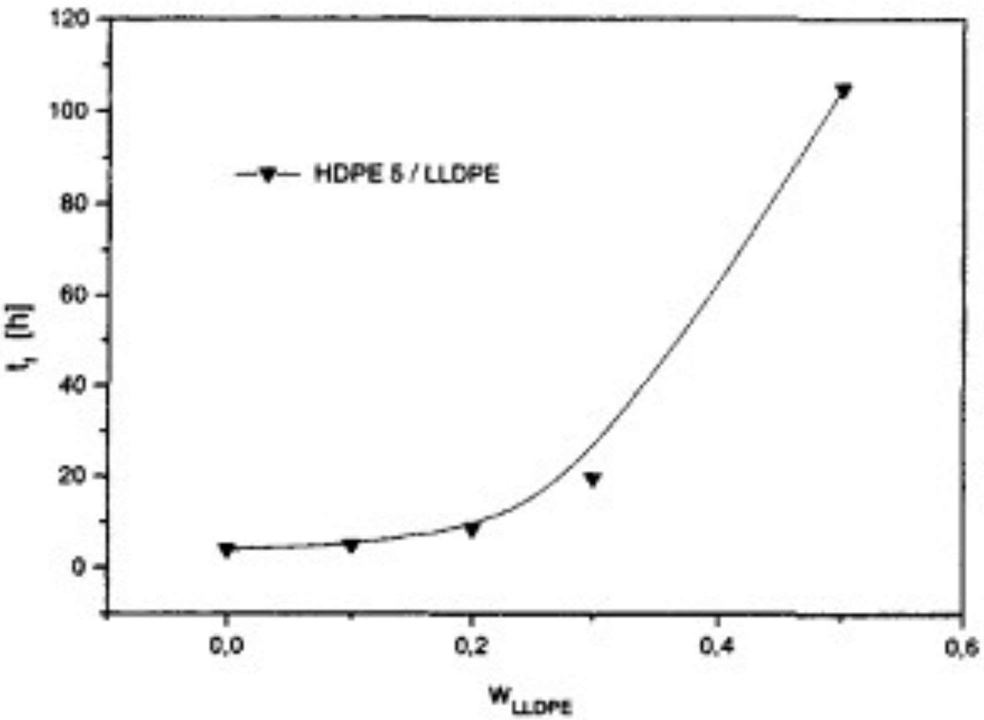
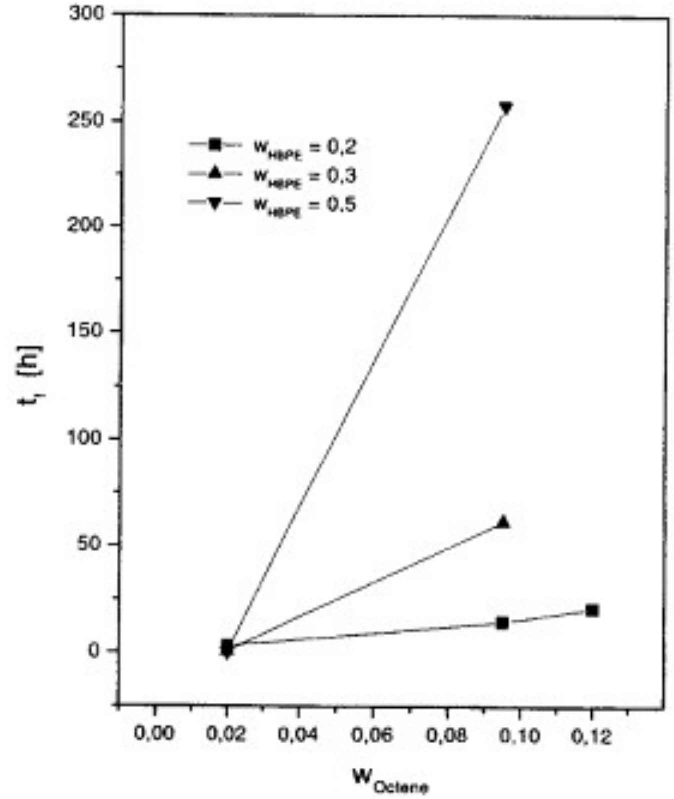


Dependence of failure time t_f on weight fraction of LLDPE (W_{LLDPE}) in HDPE/LLDPE blends (test load 6 Mpa).



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.

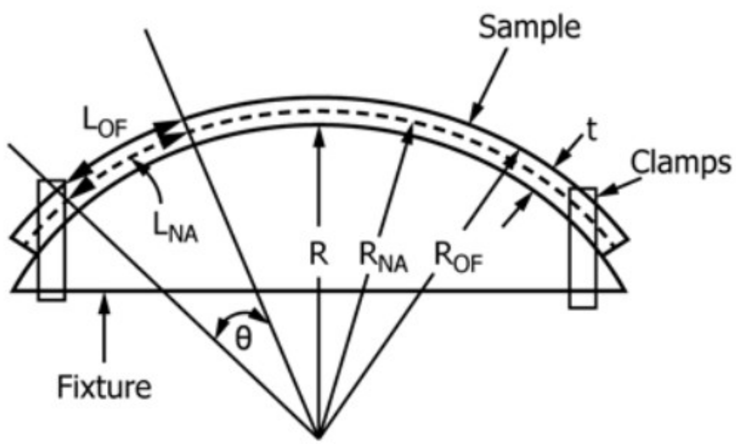
- Until testing standardization has been introduced, the correlation of data from different laboratories will be difficult.

- 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 Reagents[1]



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?

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.