# **Environmental Stress Crazing**

Arnold Lustiger, AT&T Bell Laboratories

THE UBIQUITY OF THERMOPLAS-TICS in everyday life attests to the tailorability of their material properties for specific end-uses. However, these materials also display a tendency that limits their use in many of these same applications: Under certain stress and environmental conditions, they can form crazes.

Crazing can be described as the formation of regions of plastic deformation normal to the local tensile strain. In glassy thermoplastics, crazes appear as whitened areas that are visually indistinguishable from cracks. Figure 1 illustrates the phenomenon on a sample of polycarbonate. Viewed microscopically, however, it is evident (Fig. 2) that fibrous material bridges these regions, which means that crazes can be load bearing.

Although crazing is generally the precursor to cracking, the distinction between a craze and a crack is far from an academic issue. The concept of rubber toughening of thermoplastic materials is based on using the crazing phenomenon to advantage so that fracture energy can be absorbed over a wide area of the structure rather than localized at a single area of weakness. In addition, the appearance of a craze at the tip of a preexisting crack can have significant implications, from a fracture mechanics standpoint, in predicting crack growth rates under stable crack growth conditions, and thus is critical in determining the service life of a given thermoplastic system.

As engineering plastics find their way into new and more demanding applications, their resistance to failure in specific chemical environments becomes a critical consideration. Often, environmental stress crazing (ESC) is the life-limiting mode of failure. For example, polyethylene, which could hardly be considered an engineering plastic because of its wide acceptance in items such as milk containers, is now finding its way into more demanding areas, such as in-ground liners for solid and hazardous waste disposal. These liners are placed under landfills to prevent groundwater contamination, an application which requires a service life of at least 30 years. Resistance to cracking due to the combined effects of stress and chemicals leaching from the waste essentially determines whether the service life objective is met.

The engineer who wishes to work with thermoplastics in a given environment needs to consider particular questions and problems:

- · Why certain environments promote crazing in polymers under stress
- · How to identify environments that promote crazing in specific polymer systems
- What, if anything, can be done to optimize materials to improve resistance to environmentally induced crazing
- How to identify appropriate tests to determine the susceptibility of polymers to this mode of failure in specific environments

The phenomenon of ESC in glassy amorphous thermoplastics has been recognized for almost 40 years. Direct evidence of crazing by ESC of semicrystalline polyte-



trafluoroethylene was observed as early as 1973 and then later in polyethylene and nylon (Ref 2-5); thus, craze growth and breakdown in these materials also will be described in this article.





150 µm



(c)





Environmental stress crazing in a sample of polycarbonate under three-point bending. (a) Sample before Fig. 1 exposure to acetone. (b) Sample after exposure to acetone (on cotton swab)

Fig. 2 Electron microscope views of crazes. (a) In polyphenylene oxide. Source: Ref 1. (b) In polyethylene. (c) In nylon. Source: Ref 2

(a)

# Environmental Stress Crazing / 797



Fig. 3 Steps in the interlamellar failure of polyethylene. Source: Ref 7

## Molecular Mechanism

For glassy thermoplastics, the crazing phenomenon is manifest as linear regions of local plastic deformation forming perpendicular to the applied stress. The craze itself is a highly voided, spongy structure of material oriented across its width.

For a craze to form from a previously undisturbed glassy matrix, considerable molecular mobility must somehow be introduced into a structure in which the polymer chains are essentially stiff. A possible scenario for introducing this mobility has been suggested in Ref 6: During the process of intrinsic crazing, which is crazing in the absence of an accelerating environmental effect, increased free volume can open up in local regions of the polymer under stress. This occurs because the intermolecular forces between adjacent polymer chains are low relative to the vield point of the material. As the local free volume in the vicinity of these chains increases, molecular mobility likewise increases. Subsequent cavitation and drawing take place within this

softened material. Although the same intermolecular forces are overcome during yielding, the important point about crazes is that they initiate at defects where the stress is concentrated.

When a specific environment acts as a crazing agent, it tends to weaken these intermolecular forces even further. The environment thus acts as a solvent or plasticizer, essentially lubricating the polymer chains so they can move past each other. The overall effect of a plasticizer is to lower the glass transition temperature of the polymer. When the  $T_{\rho}$  decreases to below room temperature in the region of the craze, the material ceases to behave as a glass, and hence significant flow processes can occur as material is drawn across the craze width. As a result, environmentally induced crazes tend to be much longer and more extensive than intrinsic crazes (Ref 1).

**Polyethylenes.** Although ESC of polyethylene takes place in environments in which the plasticization effects are not as obvious, the same mechanism as that mentioned above generally becomes pertinent. However, because polyethylene is semicrystalline, the action of the environment is limited to the amorphous regions.

Figures 3 to 5 are simplified views of what is generally believed to occur during the ESC of polyethylene. If a tensile load is applied normal to the face of the semicrystalline lamellae, it can be seen that the tie molecules in the amorphous regions that connect adjacent lamellae will stretch. At a certain point, however, they can be stretched no farther. Under a long-term low-level load, tie molecules begin to disentangle under the effect of a plasticizing environment, and interlamellar failure begins to take place (Ref 7, 9-13). However, as adjacent regions in the polymer undergo interlamellar failure (thereby acting as voids), material that is in between experiences much higher stresses (Fig. 4). Ductile deformation can occur at these high stresses, resulting in fiber formation as the lamellae break up into smaller units (Fig. 5). Aligned fibers therefore form across the craze (Fig. 2b), although not nearly to the elongations typical of ductile deformation.



Fig. 4 Void formation due to interlamellar failure. Source: Ref 8

#### 798 / Failure Analysis



Fig. 5 Fiber formation within craze due to interlamellar deformation between adjacent voids. Source: Ref 7

It should be mentioned, however, that under much longer-term lower-level loads, Chan and Williams found a totally fiber-free fracture surface (Ref 13). They suggested that under these conditions interlamellar failure occurs exclusively, without the ductile deformation in between. In such a situation, crazes presumably do not form; only cracking takes place.

**Crazing in nylons** is found to occur in the presence of inorganic salts of various metals, such as zinc and cobalt chloride. It has been well demonstrated (Ref 14, 15) that cracking occurs because of the disruption of





hydrogen bonding in the plastic as the environment becomes attracted to the dipolar amide groups. The amide N–H protons then bond with either water in the environment or with hydrated metal halide molecules. Other types of metal halides, such as lithium and magnesium chlorides, form protondonating solvated constituents that act as solvents for the plastic. In the latter case, the typical mechanism associated with glassy plastics, described above, becomes pertinent.

# **Environmental Criteria**

**Glassy Thermoplastics.** As explained earlier, ESC agents tend to weaken intermolecular forces between polymer chains. A measure of the strength of these forces is given by the cohesive energy density, CED, (Ref 16):

$$CED + \frac{\Delta E_v}{V_1}$$

where  $\Delta E_{v}$  is the molar energy of vaporization and  $V_{1}$  is the molar volume of the liquid. The square root of the CED parameter, called the solubility parameter,  $\delta$ , is particularly useful. A liquid with a solubility parameter,  $\delta_{0}$ , close to that of a given polymer,  $\delta_{p}$ , generally dissolves the polymer. Similarly, such environments in contact with polymers under stress result in craze formation. Figure 6 clearly shows such a correlation between the critical strain to craze and the solubility parameter of polyphenylene oxide. Similar correlations exist for polysulfone and polystyrene (Ref 18, 19).

Although correlating  $\delta_0$  with  $\delta_p$  provides an excellent rule of thumb for defining possible crazing agents, its sole use is frequently insufficient. Figure 7(a) shows that no simple correlation between  $\delta_0$  and  $\delta_p$  exists for various aliphatic hydrocarbons in polycarbonate (Ref 20), as was shown above for polyphenylene oxide. The  $\delta_p$  for polycarbonate is about 42 (J/cm<sup>3</sup>)<sup>1/2</sup> (10 (cal/cm<sup>3</sup>)<sup>1/2</sup>).

One of the parameters that must be taken into account, in addition to  $\delta$ , is the molar volume of the solvent,  $V_0$  (Ref 20). The larger the molar volume, the more difficult it is to enter between adjacent polymer chains, despite increasingly compatible solubility parameters. Figure 7(b) displays the same data as Fig. 6, except the data are normalized for differences in molar volume, displaying excellent correlation with critical strain to craze,  $\epsilon_c$ .

Other complications arise when the environment is a polar liquid. When this is the case, it has been found that by separating the solubility parameter of the liquids into polar,  $\delta_a$ , and nonpolar,  $\delta_d$ , components, two-dimensional ESC maps can be developed to adequately describe  $\epsilon_c$  (Ref 20). It should be emphasized, however, that this



Fig. 7 Critical strain for environmental craze initiation in polycarbonate. (a) Versus solubility parameter of the solvent,  $\delta_0$ . (b) Versus molar volume times the square of the solvent,  $\delta_0$ . (b) Versus molar volume times the square of the solvent. Source: Ref 20

approach has been applied only to polycarbonates, although conceptually there is no reason to expect that it would not apply to other glassy thermoplastics. As shown in Fig. 8, plastics with both polar and nonpolar solubility parameters near those of the solvent (that is, with data points near the origin of the plot) tend to have low values of critical strain to craze. Solubility parameters, as well as their various components, are listed in Ref 21 for a variety of plastics and solvents.

Finally, there is a significant body of literature (Ref 22-26) that describes the crazing behavior of various plastics in contact with liquid nitrogen, argon, oxygen, and carbon dioxide. This phenomenon can be partially explained by invoking the plasticization mechanism, (as detailed above), which is that the gas is absorbed at the tip of





Fig. 8 Solubility parameter map of critical strain to craze in polycarbonate, taking into account molar volumes and polar contributions to the solubility parameter. The numbered symbols represent critical strain to craze. Source: Ref 20  $\sigma_{\rm c} = 3 \left[ \left( \frac{2\gamma\beta_{\rm s}}{r} \right) + (4.3 \ \sigma_{\rm y}\beta_{\rm p}) \right]$ 

where  $\sigma_c$  represents the critical stress to craze,  $\gamma$  represents surface energy, *r* represents the radius of submicroscopic voids,  $\sigma_y$ represents the yield point for shear deformation,  $\beta_s$  represents the factor by which surface energy is reduced by the environment, and  $\beta_p$  represents the factor by which yield point is reduced by the environment.

Although two of the parameters in the above equation are not available experimentally, the equation is useful in conceptualizing the two separate effects of plasticization and surface energy reduction. Subsequent literature clearly suggests, however, that the plasticization effect is dominant.

**Polyethylenes.** It has been suggested (Ref 27, 28) that ESC of polyethylenes involves the same environmental criteria as do glassy polymers. The solubility parameter of polyethylene is  $35 (J/cm^3)^{1/2}$  (8 (cal/  $cm^3)^{1/2}$ ), and that of its most widely used ESC agent, nonylphenoxypoly(ethyleneoxy)ethanol, a surfactant better known by its trade name Igepal CO-630, is 40.8 (J/cm<sup>3</sup>)<sup>1/2</sup> (9.75 (cal/cm<sup>3</sup>)<sup>1/2</sup>). Igepal does not swell the polymer to any appreciable extent because

# Table 1 Activity of metal halides and thiocyanates in the crazing of nylon

		Activity(a)				
Solvent	Metal ion	Thiocyanate	Chloride	Bromide	Iodide	
Water	Zinc	+++	+++	+++	+++	
Water	Cobalt	+++	++	++	0	
Water	Calcium.		244 C	- 0	0	
Water	Barium	++	-	-	. <del></del>	
Water	Lithium	+++	+	+++		
Water	Iron <sub>111</sub>	++	+	0	C	
Water	Ammonium		-	-		
Methanol	Zinc		+++	+++	+++	
Methanol	Cobalt <sub>II</sub>		++	0	0	
Methanol	Calcium		++	0	0	
Methanol	Barium		-	++	++	
Methanol	Lithium	+++	++	+ + +	++	
Methanol	Iron <sub>III</sub>		++	0	C	
Methanol	Ammonium		-	-		

of its large molar volume. However, under stress, enough free volume can open up in the amorphous regions of the polymer so that the relatively large Igepal molecule can be accommodated. This process is known as stress-induced plasticization. In addition to its occurrence in various surfactants, ESC has commonly been reported in various alcohols (Ref 29) and silicone fluids (Ref 30), presumably due to the same mechanism.

**Nylons.** The mechanism of disruption of hydrogen bonds, as involved in the ESC of nylon by certain metal salts, and the mechanism of solvation are both difficult to predict *a priori*. Table 1 gives a number of such environments and their ESC activity in nylons.

## **Material Optimization**

Glassy Thermoplastics. Polymer orientation is the major material modification that can significantly improve craze resistance (Ref 1). If the system can be designed so that the applied stress is parallel to the orientation direction of the polymer, ESC resistance can be increased by a factor of two to four, as has been reported for polymethyl methacrylate. On the other hand, if the direction of applied stress is perpendicular to the direction of orientation, the opposite effect can occur. This orientation effect can be readily understood because chain segments preoriented in the stress direction require higher stress to be further oriented during crazing. By contrast, increasing molecular weight has a negligible effect on craze resistance. Significant improvements are often evident upon blending a second ESC-resistant phase. These improvements can become quite dramatic at the point of "phase inversion", that is, when the second phase becomes continuous and the first, discontinuous. Incorporation of glass fibers can also improve ESC resistance. Under these conditions, the fibers support the applied load and stop the growing cracks (Ref 32).

**Polyethylenes.** It follows from the discussion earlier that polyethylene materials containing relatively few tie molecules are more susceptible to ESC. Conversely, materials with more tie molecules are more resistant to this type of failure. However, it should be added that if the proportion of tie molecules to crystalline molecules is too high, the material will display high ductility, but very low stiffness.

Visualizing the mechanism of brittle failure in terms of this model can help identify molecular parameters of importance in order to optimize polyethylene resistance to ESC. Some of these parameters are discussed below.

*Molecular Weight*. The higher the molecular weight, the greater the resistance to ESC (Ref 33, 34). Figures 3 to 5 illustrate that the longer the polymer chains as a result of increased molecular weight, the greater the tie molecule concentration. Because commercial polymers are polydisperse, the entire molecular weight distribution is a critical factor (Ref 35). Since melt index is inversely proportional to molecular weight, it is desirable to work with material that has a low melt index to attain optimum ESC resistance.

However, the decision to use a polyethylene with a low melt index (that is, high melt viscosity) constitutes one of the classic engineering trade-offs relative to the use of this material. Although toughness and failure resistance are improved with increased molecular weight, the difficulty of processing a material with high melt viscosity must be considered. In addition, many in-service uses of the material necessitate melt fusion, specifically for pipe and liner applications, which are made considerably more difficult with materials of high melt viscosity.

*Comonomer Content*. ESC resistance can be dramatically improved with the placement of a small amount of comonomer on



Fig. 9 Effect of comonomer in increasing tie molecule concentration in polyethylene

the polyethylene chains to inhibit crystallinity in medium and linear low density polyethylenes. Higher comonomer concentrations and longer comonomer chain branches (that is, 1-hexene or longer) probably do not enter the tightly packed lamellar lattice and therefore produce additional intercrystalline tie molecules (Ref 36), as shown in Fig. 9.

Density/Degree of Crystallinity. The more crystalline the material, the lower its ESC resistance (Ref 33). This is because of the fewer number of tie molecules that hold it together. As a result, quenched material has better ESC resistance than material that is cooled slowly after processing from the melt (Ref 37, 38).

However, the use of lower-density material also constitutes a trade-off in engineering properties: Failure resistance and toughness improve with lower crystallinity, but stiffness and yield point are reduced. In many applications, these properties must be considered when designing a structure that must resist deformation from a variety of in-service loads.

Because resistance of polyethylene to ESC is so sensitive to these parameters, optimizing the material to resist this failure mode has been a high priority among material producers. Improvements, specifically in the optimum use of comonomer, have been very dramatic in recent years. Crack resistance has improved by an order of magnitude or more in many cases. This is particularly true in the relatively recent development of linear low density polyethylene, which incorporates the longer comonomers into its backbone chain in relatively high quantities.

Nylons. Just as in glassy plastics, orientation significantly improves the ESC resistance of nylons in the direction of stress (Ref 39). However, it has been found that slight orientation with subsequent relaxation reduces failure times, presumably because of the expansion and coalescence of preexisting microcracks. Although average molecular weight does not appear to make a significant difference, removing the lowest molecular weight "tail" of the molecular weight distribution by water extraction significantly improves ESC resistance. In contrast to polyethylene, it was found that slow cooling also improves ESC resistance.

# Testing

There are basically two types of tests used to determine relative susceptibility to ESC: those based on a constant load, and those based on a constant strain. There is an important conceptual limitation using either approach that must be addressed before discussing the various testing options available. In addition, it is important to normalize data initially for differences in the yield point when comparing different materials in a given test.

**Constant-Load Versus Constant-Strain** Testing (Ref 40). A present limitation of ESC testing is the inability to isolate the yield stress property as a parameter independent of the failure resistance of the plastic. Thus, constant-strain tests have been criticized because of stiffness variations between specimens. These variations give rise to an ambiguity when interpreting the results of these tests: Do differences between times to failure mirror a real difference in ESC resistance, or do these differences merely reflect the higher stress levels in the stiffer specimens? A similar objection can be directed to constant tensile load testing. Although a load is constant in the test, the response to it varies among materials. Therefore, specimen stiffness again becomes a complicating material parameter that obscures ESC resistance as an indepen-

#### Table 2 Constant-strain versus constant-load testing of high- and low-density polyethylene

Ber	nt	Constant load test, failure time, h	
strij failu time	p, re	At 3.51 MPa (0.50 ksi)	At 9.0 MPa (1.3 ksi)
High-density polyethylene <1 Low-density polyethylene 20		4.7 1.9	0.6 Yield
Source: Ref 40			

dent property. Hence, the question arises as to whether a material fails quickly in this test as a result of its low ESC resistance or because its low stiffness allows more deformation under the constant load.

A prime example of the confusion created by this situation was demonstrated by testing high- and low-density polyethylene in both constant-strain and constant-load tests and comparing the data. The constant-strain test, in this case, was the bent-strip test (Ref 41), which involves notching polyethylene samples longitudinally, bending them in a channel, and placing them in a solution of Igepal CO-630 at 50 °C (120 °F). A schematic of the test is shown in Fig. 10. The constant-load test involved subjecting a double edge notched specimen of the same dimensions to various loads in a detergent solution until failure. The data are shown in Table 2.

As is readily evident, high-density polyethylene fails faster than low-density polyethylene in the constant strain bent-strip ESC test. On the other hand, the same samples exhibit the opposite effects in the constant tensile load ESC test.

The reason for the apparent contradiction in failure trends becomes clear when one considers the influence of mechanical properties on the response of a material to load (Fig. 11). Because of its relative stiffness, high-density polyethylene is stressed close to or beyond the yield point in a constantstrain test, and cracking takes place in the portion of the bend at which the material is just below the yield strain. Conversely, low-density polyethylene is more susceptible to failure than the high-density material in the constant tensile load test for the same reason that the high-density material failed faster than the low-density material in the constant-strain test; that is, the yield point was more closely reached by the less stiff, low-density material in the constant tensile load test. In contrast, the yield point was not even approached in the stiffer, highdensity material under the same loading conditions.

Therefore, unless the yield points between two specimens are very close, neither a constant stress nor a constant strain provides good criteria for discerning ESC resistance. The parameter deserving closer examination as the ordinate of an ESC plot in a constant-load situation is the percentage of yield stress or reduced stress. For a more realistic comparison of materials, this percentage should be kept constant, although the actual stress may vary widely between specimens.



Fig. 10 The bent-strip test for polyethylene. Appropriate dimensions are given in Ref 41.

Fig. 11 Environmental stress crack testing in polyethylene in relation to the yield point. Source: Ref 40

#### 802 / Failure Analysis



Fig. 12 Constant tensile load test setup for polyethylene pipe. At upper left is close-up view of specimen in the fixture. The specimen is placed under load in a given environment in the metal can, which is fastened to the base of the assembly. Source: Ref 40

**Constant Tensile Load Testing.** To illustrate the utility of the reduced stress parameter, the constant tensile load test was implemented directly on polyethylene pipe used for natural gas distribution. In this test, a ring 12.7 mm (0.50 in.) wide is cut from the pipe, which is then axially notched on both the inside and the outside, each notch depth being 25% of the minimum wall thickness. The ring is then placed in a split ring fixture and subjected to a constant load in the presence of a 1% solution of Igepal CO-630 (Fig. 12).

Figure 13(a) displays initial stress versus failure time data for seven polyethylene. piping materials. The typical curve displays a shallowly sloped region followed by a steeply sloped region, although for two materials no such slope change is evident. Generally, ductile-type failure, showing large deformation and necking, occurs in the shallowly sloped region of the curve. In the region of lower stress and steeper slope, ESC occurs, characterized by little deformation at the point of failure. The point at which the slope changes has been termed a ductile-brittle transition, although prior use of this concept has been limited to impact fracture. The location of this transition gives a relative indication of ESC resistance: The later the transition, the better the resistance.

Comparing polyethylene materials with differing yield points results in a wide band of scattered data in the ductile portion of the



Fig. 13 Failure time for seven polyethylene piping materials in Igepal. (a) Plotted against nominal (initial) stress. (b) Plotted against reduced stress. Source: Ref 7

curve when the ordinate is labeled nominal stress. However, when the data are plotted in terms of reduced stress, as in Fig. 13(b), they tend to fall very close to the same straight line in the shallowly sloped region of the curve.

**Constant-Strain Testing.** In practice, it is considerably more difficult to normalize constant-strain data than load data because it is generally impractical to vary the strain between specimens to obtain the same percentage of yield strain. In the case of polyethylene, a given strain is induced in a given test regardless of the type of polyethylene being tested. The most common test is the bent-strip test, mentioned above.

For piping materials, a closely related test is the so-called compressed-ring test, in which a 12.7 mm (0.50 in.) wide ring of pipe is notched in the same way as in the bentstrip test and compressed between two plates (Ref 42). The specimen configuration is the same as in the bent-strip test, but allows the properties of the extruded product to be measured directly, rather than remolding the pipe into flat plaques.

Although effective material comparison is precluded in these constant strain tests because of the difficulty of normalizing the data for yield point differences, the test is, in fact, very effective for quality control purposes. Virtually any change in the product that is due to either basic resin or process variations results in different failure times. These changes include differences in molecular weight, degree of crystallinity, and comonomer content, as already mentioned, but can also include additives and surface features (Ref 32).

**ESC Testing of Glassy Plastics and Nylon.** It has been suggested in the literature that crazes will initiate in a plastic when a critical limit is reached in stress, strain, dilation, distortion strain energy, or stress



Fig. 14 Constant-load test for glassy plastics. Source: Ref 48

bias. Wang *et al.* (Ref 43) evaluated all these criteria and concluded that critical strain is the most consistent. However, from a practical standpoint, a designer may wish to test either under constant strain or constant load, based on in-service conditions.

A variety of constant-strain and constantload tests appear in the literature. Generally, the constant-load tests use the same principle as the test described above. However, instead of razor notches, holes or a condition of no stress concentration at all is imposed on the specimen. Constant-strain tests can involve an imposed curvature in which a specimen is bent to conform to a given radius, or they can involve free bending similar to the bent-strip test. Alternatively, they can impart strain through threepoint bending. Two reviews of testing methods appear in Ref 44 and 45. Two investigators used constant-strain tests, coupled with strain gages and force transducers, to determine stress relaxation in the specimens as the tests proceeded (Ref 46 and 47). For nontransparent specimens, stress relaxation must be the measure of craze initiation because the crazes cannot be detected visually. Other tests on more complicated specimen configurations involve imposing biaxial stress or inserting steel or metal balls into the specimen. Alternatively, there are a number of end-use tests available that require immersion of a plastic product in the stress cracking agent to determine whether residual molding stresses are sufficient to craze it (Ref 45).

A simple, representative constant-load test for glassy plastics is shown in Fig. 14. In this test, a cantilever beam made from the specimen, with one end fixed, is placed under load, and drops of the crazing environment are placed on the top side of the specimen. Using the equation shown in Fig. 14, a crazing stress can be calculated based on the distance (from the fixed end) that the crazes are visible. The crazing behavior of



Fig. 15 Constant-strain (three-point bending) test for glassy plastics. Source: Ref 47

polymethyl methacrylate was investigated in this way (Ref 48).

A constant-strain test is shown in Fig. 15, in which a specimen is placed under threepoint bending. The maximum strain on the outer surface of the specimen occurs opposite the center loading pin and is given by the equation:

$$=\frac{2 WL}{2EDT^2}$$

where W is applied load, L is span, E is Young's modulus, D is sample width, and Tis sample thickness. The crazing behavior of polycarbonate in the presence of various gasoline components was determined using this test (Ref 47).

The literature on nylon stress crazing discusses various testing procedures. Dunn and Sansom (Ref 14, 15) used either a stressed film oriented biaxially or a film stressed by suction over a circular orifice. Other investigators used a simple constant tensile load (Ref 2) or a tensile machine (Ref 39) to study the phenomenon.

#### REFERENCES

- R.P. Kambour, A Review of Crazing and Fracture in Thermoplastics, J. Polym. Sci., Part D, Reviews, Vol 7, 1973, p 1
- R.P. Burford and D.R.G. Williams, The Morphology and Mechanism of Crack Propagation in the Presence of Inorganic Salts, J. Mater. Sci., Vol 14, 1979, p 2872
- A. Lustiger and R.D. Corneliussen, Environmental Stress Crack Growth in High Density Polyethylene, J. Polym. Sci. Polym. Lett., Vol 17, 1979, p 269
- Sci. Polym. Lett., Vol 17, 1979, p 269
  4. A. Lustiger and R.D. Corneliussen, The Role of Crazes in the Crack Growth of Polyethylene, J. Mater. Sci., Vol 22, 1987, p 2470
- S. Bandopadhyay and H.R. Brown, Direct Evidence for the Existence of a Craze at the Crack Tip in Environmental Stress Cracking of Polyethylene, *Polym. Eng. Sci.*, Vol 20, 1980, p 720
- A.N. Gent, Hypothetical Mechanism of Crazing in Glassy Plastics, J. Mater. Sci., Vol 5, 1970, p 925
- A. Lustiger and R.L. Markham, The Importance of Tie Molecules in Preventing Polyethylene Fracture Under

Long Term Loading Conditions, Polymer, Vol 24, 1983, p 1647

- K. Friedrich, Crazes and Shear Bands in Semi-Crystalline Thermoplastics, in Advances in Polymer Science 1952-1953, Crazing in Polymers, Springer-Verlag, 1983
- P.D. Frayer, P.P.L. Tong, and W.W. Dreher, The Role of Intercrystalline Links in the Environmental Stress Cracking of High Density Polyethylene, *Polym. Eng. Sci.*, Vol 17, 1977, p 27
- S. Bandopadhyay and H.R. Brown, Evidence of Interlamellar Failure in Environmental Stress Cracking of Polyethylene, J. Mater. Sci., Vol 12, 1977, p 2131
- S. Bandopadhyay and H.R. Brown, Environmental Stress Cracking and Morphology of Polyethylene, *Polymer*, Vol 19, 1978, p 589
- T.W. Haas and P.H. MacRae, Microscopic Observation of Fracture in Spherulitic Films of Linear PE Under Biaxial Stress, SPE J., Vol 24, 1968, p 27
- M.K.V. Chan and J.G. Williams, Slow Stable Crack Growth in High Density Polyethylene, *Polymer*, Vol 24, 1983, p 234
- P. Dunn and G.F. Sansom, The Stress Cracking of Polyamides by Metal Salts, Part 1: Metal Halides, J. Appl. Polym. Sci., Vol 13, 1969, p 1641
- P. Dunn and G.F. Sansom, The Stress Cracking of Polyamides by Metal Salts, Part 2: Mechanism of Cracking, J. Appl. Polym. Sci., Vol 13, 1969, p 1657
- 16. F. Rodriguez, Principles of Polymer Systems, McGraw-Hill, 1970
- R.P. Kambour, Crazing, in Encyclopedia of Polymer Science and Technology, Vol 4, John Wiley & Sons, 1986
- R.P. Kambour, E.E. Romagosa, and C.L. Gruner, Swelling, Crazing and Cracking of an Aromatic Copolyether-Sulfone in Organic Media, *Macromolecules*, Vol 5, 1972, p 335
- R.P. Kambour, C.L. Gruner, and E.E. Romagosa, Solvent Crazing of "Dry" Polystyrene and "Dry" Crazing of Plasticized Polystyrene, J. Polym. Sci. Polym. Phys., Vol 11, 1973, p 1879
- C.H.M. Jacques and M.G. Wyzgoski, Prediction of Environmental Stress Cracking of Polycarbonate From Solubility Considerations, J. Appl. Polym. Sci., Vol 23, 1979, p 1153
- J. Brandrup and E.H. Immergut, Ed., *Polymer Handbook*, John Wiley & Sons, 1975
- A. Peterlin and H.G. Olf, Environmental Effects on Low Temperature Crazing of Crystalline Polymers, J. Polym. Sci. Polym. Symp., Vol 50, 1975, p 243
- 23. N. Brown, A Theory for Environmental Craze Yielding of Polymers at Low Temperatures, J. Polym. Sci. Polym.

#### 804 / Failure Analysis

Phys., Vol 14, 1973, p 2099

- 24. N. Brown and S. Fischer, Nucleation and Growth of Crazes in Amorphous Polychlorotrifluoroethylene in Liquid-Nitrogen, J. Polym. Sci. Polym. Phys., Vol 13, 1975, p 1315
- N. Brown and Y. Imai, Craze Yielding of Polycarbonate in N<sub>2</sub>, Ar, and O<sub>2</sub> at Low Pressures and Temperatures, J. Appl. Phys., Vol 46, 1975, p 4130
- E. Kamei and N. Brown, Crazing in Polyethylene, J. Polym. Sci. Polym. Phys., Vol 22, 1984, p 543
- 27. H.R. Brown, A Theory of the Environmental Stress Cracking of Polyethylene, *Polymer*, Vol 19, 1978, p 1186
- K. Tonyali, C.E. Rogers, and H.R. Brown, Stress Cracking of Polyethylene in Organic Liquids, *Polymer*, Vol 28, 1987, p 1472
- C.J. Singleton, E. Roche, and P.H. Geil, Environmental Stress Cracking of Polyethylene, J. Appl. Polym. Sci., Vol 21, 1977, p 2319
- M.E.R. Shanahan and J. Schultz, A Kinetic Effect in the Environmental Stress Cracking of Polyethylene Due to Liquid Viscosity, J. Polym. Sci. Polym. Phys., Vol 14, 1976, p 1567
- P. Dunn and G.F. Sansom, The Stress Cracking of Polyamides by Metal Salts, Part III: Metal Thiocyanates, J. Appl. Polym. Sci., Vol 13, 1969, p 1673
- 32. L.M. Robeson, Overcoming Stress Rupture of Amorphous Thermoplastics in Organic Environments, in *Proceed*ings of Symposium on Problem Solving

*in Plastics*, National Association of Corrosion Engineers, 1971, p 87

- J.B. Howard, Stress-Cracking, in Crystalline Olefin Polymers, R.A.V. Raff and K.W. Doak, Ed., John Wiley & Sons, 1964
- W.A. Dukes, The Endurance of Polyethylene Under Constant Tension While Immersed in Igepal, *Br. Plast.*, 1961, p 123
- J.N. Herman and J. Biesenberger, Molecular Weight Distribution and Environmental Stress Cracking of Linear Polyethylene, *Polym. Eng. Sci.*, Vol 6, 1966, p 341
- M.J. Hannon, Microscopic Aspects of Brittle Failure of Polyethylene Below the Yield Stress, J. Appl. Polym. Sci., Vol 18, 1974, p 3761
- J.B. Howard and W.M. Martin, Effects of Thermal History on Some Properties of Polyethylene, SPE J., Vol 16, 1960, p 407
- M.E.R. Shanahan, C. Chen-Fargheon and J. Schultz, The Influence of Spherulitic Size on the Environmental Stress Cracking of Low Density Polyethylene, *Makrol. Chem.*, Vol 181, 1980, p 1121-1126
- A.C. Reimschuessel and Y.J. Kim, Stress Cracking of Nylons Induced by Zinc Chloride Solutions, J. Mater. Sci., Vol 13, 1978, p 243
- 40. A. Lustiger, Environmental Stress Cracking, the Phenomenon and Its Utility, in *Failure of Plastics*, W. Brostow and R.D. Corneliussen, Ed., Hanser-

Verlag, 1986

- 41. "Standard Test Method for Environmental Stress-Cracking of Ethylene Plastics," ASTM D 1693, Annual Book of ASTM Standards, American Society for Testing and Materials
- 42. A. Lustiger, R.L. Markham, and M.M. Epstein, Environmental Stress Crack Growth in Medium-Density Polyethylene Pipe, J. Appl. Polym. Sci., Vol 26, 1981, p 1049
- 43. T.T. Wang, M. Matsuo, and T.K. Kwei, Criteria of Craze Initiation in Glassy Polymers, *J. Appl. Phys.*, Vol 42, 1971, p 4188
- 44. H.J. Orthmann, Environmental Stress Cracking of Thermoplastics, *Ger. Plast.*, Vol 73, 1987, p 17
- 45. W.V. Titow, A Review of Methods for the Testing and Study of Environmental Stress Failure in Thermoplastics, *Plast. Polym.*, Vol 43, 1975, p 98
- 46. L.F. Henry, Prediction and Evaluation of the Susceptibilities of Glassy Thermoplastics to Environmental Stress Cracking, *Polym. Eng. Sci.*, Vol 14, 1974, p 167
- M.G. Wyzgoski and C.H.M. Jacques, Stress Cracking of Plastics by Gasoline and Gasoline Components, *Polym. Eng. Sci.*, Vol 17, 1977, p 854
- D.M. Bigg, R.I. Leininger, and C.S. Lee, Stress-Cracking Behavior of Poly-(Methyl Methacrylate) and a Poly-(Methyl Methacrylate)-Ethyl Acrylate Copolymer, *Polymer*, Vol 22, 1981, p 539