Organic Chemical Related Failure

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THE SUSCEPTIBILITY OF PLASTICS to environmental failure, when exposed to organic chemicals, limits their use in many applications. Organic liquids, such as cleaning fluids, detergents, gasoline, lubricants, and sealants, may seriously reduce the mechanical properties of plastics. It is therefore important for design engineers to consider the effects of environment on plastics.

The most serious problems arise when a material is exposed to aggressive fluids under stress. The nature of the failure is usually brittle, compared to that occurring in air. The applied stresses on the components may be as low as less than one-tenth of the yield (or failure) stress of the material in air. An understanding of the failure phenomenon associated with aggressive agents is important because of the many cases in which sufficiently high stresses are introduced into plastics in the form of residual stresses during processing, as in shrinkage, or in the form of external stresses incurred during the service life.

A combination of chemical and physical factors, along with stress, usually leads to a serious deterioration in properties. A stress or chemical environment alone does not appreciably weaken a material. The failure mechanism in a particular plastics-chemical environment can be quite complex and in many cases is not yet determined. Examples of individual cases are examined in a number of recent reviews on the subject (Ref 1-6).

Environmental factors can be classified into two categories: chemical and physical effects. Chemical attack occurs when chemical reactions result from the interaction between the environment and polymer molecules. This type of interaction may involve chain scission, which is an irreversible effect. Crazing and microcracking, which are also irreversible processes, may be more noticeable. Physical effects, which are reversible, include fluid absorption or swelling, that is, plasticization. With reversible effects, the material regains its original properties once the environment is desorbed. Both chemical and physical effects are discussed below.

Chemical Interactions

Aggressive environments may interact with plastics, causing changes in the chemical character and structure of individual molecules. These changes may involve a decrease in the molecular weight by chain scission or the incorporation of a new chemical group onto the polymer chain. Chain scission may cause a reduction in mechanical properties such as tensile strength, elastic modulus, and fracture toughness. In some cases, chain scission may be followed by depolymerization (unzipping) of the chains, which releases gaseous fragments that cause bubble formation, crazes, and crack formation. For example, polyoxymethylene can be depolymerized to formaldehyde in highly acidic or alkaline environments (Ref 6). The incorporation of new chemical groups onto the polymer chain through chemical reaction may also induce hardening, decrease toughness, and lower the resistance to aggressive environments (Ref 5).

Condensation polymers, such as acetals, polyamides, polyesters, and thioesters, are susceptible to hydrolysis (Ref 1-6). Polycarbonate (PC) and polyphenylene sulfide are attacked by formic acid and amines. Formic acid can decrease the tensile strength of polyphenylene sulfide by 25% (Ref 7).

The tensile properties of polyester-base polyurethane (PUR) samples have been studied as a function of the time of exposure to water, methanol, and a water-methanol mixture (Ref 8). It has been shown that water induces hydrolysis of the ester group, while methanol causes a transesterification reaction. In both situations, these reactions result in losses in tensile properties via molecular weight reduction through random chain scission. It has been observed that the tensile strength decreases as a function of increasing exposure time (Fig. 1). The methanol is believed to swell the PUR, thus reducing the mechanical properties by a plasticization mechanism and causing transesterification. In this system, the overall effect is a physiochemical process because both a chemical reaction and swelling are observed.

Polycarbonate fails in a sodium hydroxide-ethanol mixture as a result of main chain scission through hydrolysis under low stresses (Ref 3). It has been proposed that the fibrils in a very short craze, which forms at the crack tip, are exposed to the chemically aggressive environment. The hydrolytic cleavage of the exposed macromolecules causes failure of the fibrils, followed by crack propagation.

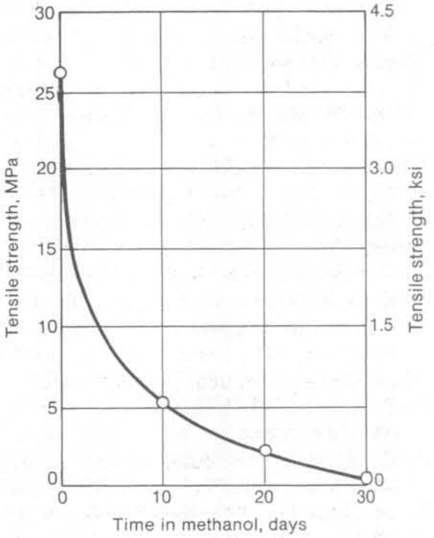

Fig. 1 Tensile strength of PUR aged in methanol at 60 °C (140 °F) as a function of exposure time. Source: Ref 8

The failure mechanism in chemically aggressive agents is far more complex than a simple chain scission mechanism. It is often difficult to pinpoint the controlling factors in a failure process. Generally, sequential processes are thought to occur during crack growth. In the ozone cracking of rubbers, for example, it has been shown that the diffusion of ozone to the crack tip is the rate-controlling step, although ozone induces chain scission (Ref 4). Very few studies have been conducted in the area of chemically induced polymer cracking that involve crack propagation tests. It is thought that the overall failure mechanism occurs through chain scission by the chemical reaction.

Physical Interactions

Generally, plastics are permeable to organic chemicals to varying degrees. This is a disadvantage because the presence of environmental liquids in a plastic material has a profound effect on its mechanical properties. The action of sorption may induce plasticization, swelling, dissolution, recrystallization, and leaching of additives in solids, all of which reduce mechanical properties.

Characterization of the diffusion or sorption of penetrants into plastics may promote an understanding of environmental effects on failure properties. After a plastic component is exposed to an organic chemical, aggressive molecules may diffuse into the component, leading to plasticization. Swelling of the material results in high stresses, which can cause crazing or cracking. Fracture has been observed in many glassy plastics, such as polymethyl methacrylate (PMMA), polystyrene (PS), and PC, because of anisotropic swelling (Ref 9-14).

Swelling Kinetics. The diffusion of organic penetrants into plastics may occur either by a Fickian diffusion (Case I) or a non-Fickian process (Case II), in which the rate of the diffusing front in the plastic follows the square root of time, for Case I, or the first power of time, for Case II (Ref 12-14). A sharp, moving front that propagates at a constant velocity through the material develops in the Case II process, which is the one that usually occurs in glassy polymers. Although there is little evidence, it is also believed to occur in crystalline polymers, such as polyethylene(PE)-hydrocarbon systems (Ref 9). As a result of this sharp boundary between the swollen and unswollen material, high swelling stresses are introduced (Ref 10-16). These stresses are large enough to cause crazing or cracking.

The sorption of n-heptane in PS induces extensive bulk crazing in the swollen regions (Ref 17, 18). The formation of crazed networks is usually associated with Case II swelling behavior. A model involving the Case II swelling of PS-alkane systems to explain the propagation of a crazed front (that is, the velocity of the sharp boundary) is suggested in Ref 17 and 18 such that:

$$\dot{\lambda} = K(\alpha\pi - \sigma_c) \tag{Eq 1}$$

where $\dot{\lambda}$ is the propagation rate of the swollen boundary (crazed front), K is a temperature-dependent constant, α is a constant, σ_c is the critical stress for craze propagation in dry PS, and π is the osmotic pressure induced by swelling. The theory uses an experimental relationship for the craze propagation of PS in air and replaces the external applied stress with $\alpha\pi$. However, the theory is applicable only to PS.

A theory to explain Case II diffusion kinetics has been proposed for glassy polymers. It couples the diffusive processes ahead of the diffusive front with the mechanical resistance of the glassy polymer to swelling (Ref 16, 19-24). The growth rate of the front, $\dot{d}$, is:

$$\dot{d} = \sqrt{\frac{D(\phi_m)}{\phi_m}\left[\frac{\partial\phi_m}{\partial t}\right]_{\phi_m}} \tag{Eq 2}$$

where ϕ_m is the solvent volume fraction at the position of maximum osmotic pressure, D is the diffusion coefficient, and $\partial\phi_m/\partial t$ is the mechanical resistance of the polymer. Attempts have been made to apply this model to the environmental failure of plastics (Ref 25, 26). Assuming that the external stress, σ, is added to the osmotic pressure, P, $\partial\phi_m/\partial t$ can be written as:

$$\frac{\partial\phi}{\partial t} = \mathrm{f}\,(P + \sigma) \tag{Eq 3}$$

Considering the simple viscous flow, Eq 3 can be given by:

$$\frac{\partial\phi}{\partial t} = \frac{P + \sigma}{\eta} \tag{Eq 4}$$

where η is the viscosity of the swollen material under stress, which can be described by (Ref 21, 23, 24):

$$\eta = \eta_0 \exp(-m\,\phi)\exp[-n\,(P + \sigma)] \tag{Eq 5}$$

where η_0 is the viscosity of the unswollen polymer and m and n are constants. The diffusion constant may also be dependent on ϕ and $P + \sigma$ exponentially. Therefore, Eq 2 can be rewritten as:

$$\dot{d} = \left[\frac{D_0}{\eta_0}\,\frac{(P + \sigma)\exp[l\,(P + \sigma)]}{\phi\exp(k\,\phi)}\right]^{1/2} \tag{Eq 6}$$

where D_0 is the diffusion constant in a glassy polymer, and k and l are constants. Equation 6 can be used only at low solvent activities in plastics (Ref 23, 24).

It is apparent from Eq 6 that the external stress increases the rate of advance of the propagating front. Indeed, it has been shown experimentally that mechanical deformation induces considerable increases in the propagation rate in the PMMA-methanol system (Ref 20-22). Therefore, as the total stress ($P + \sigma$) approaches the yield stress of the material, the failure rate should also increase. The propagation rate of the swollen front in the PMMA-methanol system (~1×10^{-9} m/s, or 3.3×10^{-9} ft/s) without external stress at room temperature (Ref 19) and that of craze growth under low stresses (Ref 27) have been observed to be in the same range. Therefore, the craze growth rates and the swollen front propagation velocities are comparable.

Dissolution and Swelling. An understanding of the solution (or swelling) and dissolution of polymers in solvents is needed to postulate some explanations for environmental failure. Qualitatively, it is convenient to use the Flory-Huggins relationship. The basic idea is that like dissolves like; that is, if a solvent has characteristics similar to those of the plastic, it may dissolve the plastic (Ref 6). For a plastic-solvent system, the activity, a_1, is given by:

$$\ln a_1 = \ln\phi_1 + \phi_2 + \chi\,(\phi_2)^2 \tag{Eq 7}$$

where ϕ_1 and ϕ_2 are the volume fraction of the solvent and of the plastic in a swollen plastic, respectively, and χ is the interaction parameter between the plastic and solvent molecules, which can be estimated by (Ref 28):

$$\chi = a + \frac{V_1}{RT}(\delta_p - \delta_s)^2 \tag{Eq 8}$$

where a is a constant, V_1 is the molar volume of the solvent, R is the gas constant, T is the absolute temperature, and δ_p and δ_s are the solubility parameters (that is, square roots of the cohesive energy densities) of the plastic and solvent, respectively.

Equation 7 shows that at equilibrium swelling ($a_1 = 1$), $\ln\phi_1$ is proportional to $(\delta_p - \delta_s)^2$. As an approximation, this suggests that when the difference between the solubility parameters approaches 0, the solvent will be the most effective for dissolving the plastic. In the case of linear polymers, a value of $\chi < 0.5$ leads to full solubility, while $\chi > 0.5$ indicates partial solubility or swelling rather than dissolution. Partial solubility may arise either from limited compatibility or from the strain energy of a swollen network that resists further expansion (Ref 4, 29). The solvent uptake by the plastic induces swelling. The swollen material is plasticized; that is, its mechanical properties are below those of an unswollen solid, but the elongation at break increases.

Fracture processes may not occur at the equilibrium swelling. Figure 2 shows that the absorbed amount of alcohol present in PMMA can substantially reduce tensile yield stress (Ref 30).

Swelling causes plasticization, thus reducing the glass transition temperature, T_g, of the plastic. The T_gs of a swollen aromatic copolyether-sulfone in various organic chemicals were determined as a function of the sorbed volume (Ref 31). It was found that the T_g decreases with increasing sorbed volume.

The role of solvent absorption in the crazing and cracking of plastics has been demonstrated for various systems (Ref 1, 2, 4, 30-35). The critical strain to induce crazing in polysulfone (PSU) as a function of the T_g of the solvent-equilibrated films is shown in Fig. 3. The T_g of the equilibrated plastic depends on the solubility parameter and the equilibrium swelling of the plastic, and the reduction in T_g decreases the critical strain for crazing due to the plasticization efficiency of the liquid.

Critical stresses (or strains) for the crazing of PS, which is internally plasticized with dichlorobenzene to varying degrees, were measured as a function of the T_g of the plasticized polymer (Ref 2). It was observed that a similar critical strain dependence on T_g is obtained when the samples are swollen to equilibrium in the environmental liquids. This observation supports the plasticization mechanism for environmental failure.

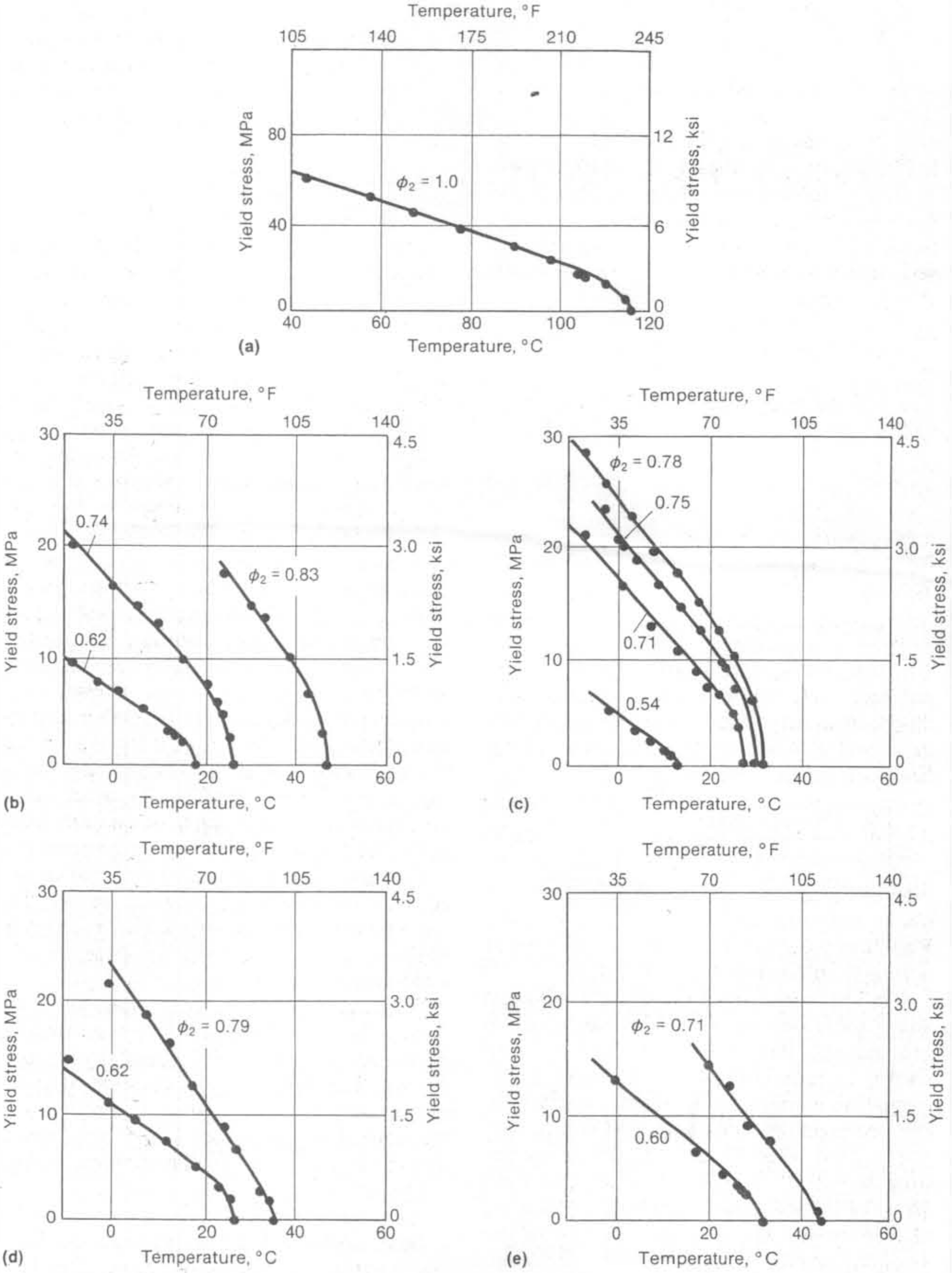

Fig. 2 Yield stress of swollen PMMA samples as a function of the polymer volume fraction, ϕ_2, and temperature. (a) Air. (b) Methanol. (c) Ethanol. (d) *n*-propanol. (e) *n*-butanol. Source: Ref 30

The critical strain or stress to obtain the crazing (or cracking) of plastics was measured in organic media, and it was observed that the behavior is determined approximately by the difference between the solubility parameters of the plastic and the organic agent (Ref 1-2). Figure 4 shows the critical strain to induce crazing or cracking of poly(2,6-dimethyl-1,4-phenylene oxide) versus the solubility parameters of the aggressive environments (Ref 32). The liquids include alkanes, aliphatic alcohols, amides, ketones, esters, and halogenated alkanes. The plastic has a solubility parameter of 18.2 $\sqrt{\text{J/cm}^3}$ (8.9$\sqrt{\text{cal/cm}^3}$). Figure 4 shows that plasticization plays a major role in causing the failure of plastics exposed to aggressive agents; that is, the environment becomes the most effective when the difference between the solubility parameters approaches 0.

In strong polar or hydrogen bonding liquids, the relationship between the failure properties and solubility parameters is not well correlated (Ref 2, 36). The effect of hydrogen bonding has been taken into account for PMMA, polyvinyl chloride, and PSU, and it has been shown that the solubility effect is similar to that of nonpolar liquids (Ref 36).

The molar volumes, V_m, of the environmental liquids are also found to be important in determining the environmental cracking behavior (Ref 37). The fracture of PC in linear aliphatic hydrocarbons is well described when the critical strain is plotted as a function of $V_m(\delta_p - \delta_s)^2$.

In strong swelling agents, T_g of a plastic is greatly reduced. The fibrils in a craze obtained in such an environment are highly plasticized and therefore cannot withstand external stresses. In this case, cracks are formed rapidly, followed by instantaneous fracture of the plastic (Ref 2, 35). However, in relatively weak swelling agents, the extent of plasticization is limited, and crazing is more pronounced than the formation of cracks. For example, the fatigue failure of PC was studied in various liquid environments. It was found that the craze growth rate at the crack tip decreased and that crack growth and dissolution became more important as the difference between the solubility parameters of the plastic and the solvent approached 0 (Ref 35).

Structural components are generally subjected to external loading during their service lives. The applied stress may affect the sorption kinetics of the environments and the equilibrium swelling (Ref 9, 16, 38, 39). The rate of diffusion for the stressed samples is enhanced by the applied stress due to the defects induced by deformation; therefore, the diffusion rate increases exponentially with stress (Ref 40). The effect of the applied stress on the equilibrium solubility is also considered (Ref 38, 39). The tensile stress increases the equilibrium solubility, which decreases the resistance of the material to crazing and cracking. If a stressed sample with microcracks (or defects) is considered, the stresses are highly concentrated at the crack tips, where the aggressive environment is sorbed more. Inhomogeneous swelling leads to a higher plasticization efficiency at the highly swollen regions, resulting in a reduced flow stress of the material.

The kinetics of craze/crack growth of stressed polymers in environments are considered in detail in the articles "Accelerated Life Prediction" and "Environmental Stress Crazing," respectively, in this Volume. It has been suggested that the fracture mechanics approach can describe the environmental crack growth behavior and that a unique relationship exists between the stress intensity factor, K_I, and the crack speed, $\dot{c}$ (Ref 3, 41, 42). Such K_I and $\dot{c}$ plots consist of three regimes:

- Region I is controlled by the relaxation processes at the crack tip at low K_I values
- Region II is determined by the hydrodynamic transport properties of the liquid at moderate K_Is, where the crack speed is inversely proportional to the viscosity of the environment and is usually constant

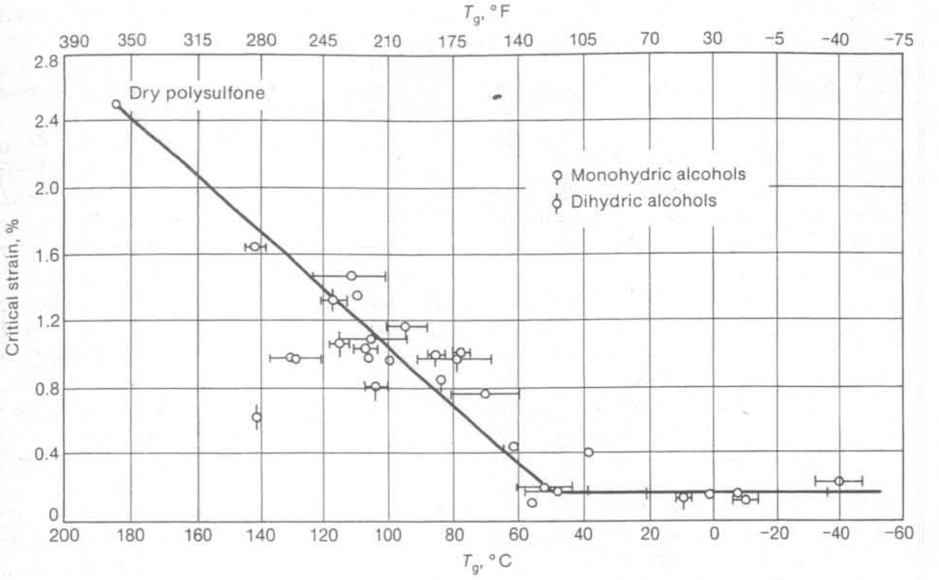

Fig. 3 Critical strain for the crazing or cracking of swollen PSU as a function of the T_g of solvent-equilibrated films. Source: Ref 31

- In region III, crack propagation occurs as in air

The model has been used to interpret the kinetics of the environmental crazing/cracking behavior of polymers (Ref 3).

With organic agents, which sorb into polymers very little, failures of plastics are still observed under low stresses (Ref 1-4). In the absence of an applied stress, no apparent chemical or physical change is observed in plastics properties. The fracture surfaces show evidence that the failure is relatively brittle compared to that obtained in air. The environmental cracking of polyolefins in detergents and alcohols is an example of such a failure process (Ref 41-47). It is generally agreed that the cause of the problem is some form of plasticization due to stress-induced swelling at the defect points (Ref 39). Using infrared spectroscopic techniques, it has been shown that the absorption of low molecular weight ethylene oxide adducts of the detergent and nonyl phenol occurs in PE (Ref 48). Furthermore, it has been observed that a small amount of dissolution of PE occurs in detergents. The absorption of alcohols is also observed (Ref 42-43).

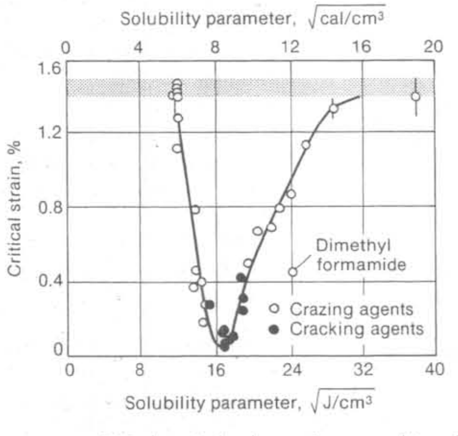

Fig. 4 Critical strain for the crazing or cracking of polyphenylene oxide as a function of solubility parameter. Crosshatched area shows range of ϵ_c values in air. Source: Ref 32

It has been argued that the environmental cracking of PE can be described by the three-region crack growth model (Ref 41, 42). The constant crack speed region (region II) especially has been attributed to the hydrodynamic flow-controlled behavior. At the moderate stress levels, the existence of a dry craze zone at the crack tip was reported (Ref 42). However, recent findings suggest that the constant crack speed region is not flow controlled (Ref 46, 47). The crack growth rates have been determined in the detergent solutions containing various detergent concentrations. It has been found that the constant crack speed increases with increasing detergent concentration. It is well known that the viscosity of a detergent solution is an increasing function of the detergent concentration. Therefore, the constant crack growth rate increases with increasing solution viscosity, which is in contrast to the flow-controlled model. However, in the case of a plasticization mechanism, the condition of the crack tip is irrelevant if it is filled fully or partially (dry craze zone). That is, as soon as some of the load-bearing fibrils are wetted at the crack tip, followed by swelling or dissolution, crack growth should occur (Ref 46), although the exact reasoning for dry craze zone formation is not completely understood.

The solution composition of the environmental media is found to be important in stress cracking (Ref 46, 47). It has been reported that the same amount of a detergent in alcohol is less aggressive than that in water, although the detergent and alcohol are more aggressive separately. The greater degree of aggressiveness in the water solution is attributed to micelle formation by the detergent molecules in water as opposed to the alcohol solution. In the water solution, a micelle contains highly aggressive detergent molecules that are held together, while in the alcohol solution, the aggressive molecules are individually dispersed. Therefore, as soon as a micelle reaches the crack tip, it can induce better plasticization locally because the detergent activity is high. Furthermore, it has been shown that the environmental solution becomes more aggressive if the detergent concentration is beyond its critical micelle concentration. This is probably because the detergent molecules are not aggregated below the critical micelle concentration.

The addition of swelling agents to the water solution (such as xylene, which locates itself in the micelles only, being insoluble in water) induces a higher cracking efficiency (Ref 46, 47). The micelles act as carriers for aggressive molecules. This information is important because very small amounts of aggressive agents, or impurities, may be present in cleaning solutions. Nonyl phenol is an example of such an agent found in nonionic detergents.

Surface Energy Effects. Organic liquids usually have low surface tensions and can be readily spread on plastics surfaces. This process has been considered for some time to reduce the surface energy of plastics to accelerate crazing and cracking. It is generally agreed that surface energy reduction appears to be of secondary importance in environmental failure (Ref 1, 2, 30, 49).

The surface energy effect for the PS-methanol system has been measured (Ref 49). It has been shown that crazing is primarily induced by reduction in the flow stress of the swollen material due to plasticization. This is also supported by the results for other glassy polymers (Ref 1, 2, 30).

Destruction of Hydrogen Bonding. Some organic acids can disrupt hydrogen bonding between the macromolecular chains in bulk polymers (Ref 1, 2). Solvent molecules can form a new hydrogen bond between the solvent and polymer molecules. This causes a dissolution process in the material. Polyamides such as nylons can be included in this class of materials because formic acid or phenols can promote stress cracking (Ref 2).

Solvent Recrystallization. The crazing of some glassy polymers is attributed to recrystallization of the polymer during swelling (Ref 2, 50). The diffusion of acetone into PC causes opacity to develop in the polymer as a result of an increase in crystallinity with the concurrent formation of macroscopic voids (Ref 51). It is proposed that the swelling agent reduces the T_g of the polymer sufficiently to allow the mobile polymer chains to crystallize (Ref 51). A stress cracking environment should be an effective swelling agent to induce crystallization (Ref 50). As a result of chain ordering, the formation of crystallites introduces high shearing stresses that are sufficient to propagate crazes or cracks.

Incorporating a miscible polyester into a PC improves stress cracking resistance in strong swelling agents (Ref 52). Polyester crystallizes much more rapidly than PC; therefore, further swelling is restricted because of the recrystallization that stabilizes the craze fibrils. The solvent recrystallization effects remain open to debate until extensive studies have been conducted.

Solvent Leaching of Additives. Additives such as plasticizers, fillers, stabilizers, and colorants are introduced into plastics to improve their physical properties. Leaching of these additives may create serious problems in the working life of plastics components (Ref 53). The chemical resistance of plasticized plastics to organic liquids is usually less than that of the unplasticized plastics, such as polyvinyl chloride (Ref 6). The interaction between the additives and the organic chemicals determines the resistance of the system in terms of solubility parameters.

Adding a plasticizer increases the mobility of the polymer chains, which enhances the effective diffusion coefficient of liquids (Ref 9, 13). Organic additives can be extracted from plastics even if they are not greatly soluble in the solvent. The diffusion and migration of additives from the material induce losses in physical properties because of the development of a somewhat porous structure in the solid (Ref 54). Such defects reduce mechanical properties for practical use. Plasticizer migration, or deplasticization, leads to embrittlement of the compound. On the other hand, the regions of additives may swell anisotropically, thus causing differential expansion or cluster formation, which results in crazing and cracking of the structure (Ref 9). In the case of a stabilizer, plastics durability, or resistance to oxidative degradation, is reduced because the stabilizer is leached from the plastic. Therefore, the interaction of organic liquids with additives as well as the plastic itself must be considered for design purposes.

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