

Environmental Stress Cracking

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MANY FRACTURE MECHANISMS exist that can lead to failure of a plastic component; however, environmental stress cracking (ESC) is recognized as one of the leading causes of plastic failure. It is estimated that approximately 25% of plastic failures are attributed to ESC (Ref 1). The ESC mechanism of failure is prevalent throughout most industries and market sectors. Some examples of plastic parts commonly seen in day-to-day failure analysis investigations that fail from ESC include:

- Housings and enclosures for medical devices
- Assemblies joined with metal screws
- Poly(acrylonitrile-butadiene-styrene), polyvinyl chloride, and chlorinated polyvinyl chloride pipes
- Automotive lenses
- Handheld devices
- Architectural and multilayer glazing

Lately, ESC failures have become increasingly prevalent in the medical device industry due to the changes in cleaning methods and aggressiveness of new disinfection solutions. While certain ESC failures could be attributed to changes in an industry that were unforeseen by designers and manufacturers, ESC has been a long-standing issue that has resulted in numerous failures in plastic components over the years. Part of the reason for this is a lack of awareness and understanding of the mechanism and of the complexities involved in being able to properly characterize it.

Plastics production uses a recipe of numerous compounds that make up the final product. The base material is the polymer, essentially many long molecules tightly entangled together to form a viscoelastic structure. Polymer molecules of amorphous plastics are generally less packed and more randomly organized, while semicrystalline materials include regions of tightly and orderly packed polymer molecules together with less-ordered regions (Fig. 1).

Within the plastic formulation, additional compounds are added for numerous reasons. Examples of such compounds are antioxidants, ultraviolet (UV) stabilizers, processing aids, nucleating agents, pigments and colorants, fillers, and antistatic agents, to name a few. Each compound added to the polymer serves

a purpose and occupies free space (free volume) between the less orderly spaced polymer molecules (Fig. 1). Much effort is spent by engineers and scientists to find additives that show the correct affinity to the polymer so that when the substance is compounded (added, distributed, and uniformly mixed) with the polymer, it remains in the plastic, serving its intended function during the life of the part.

Some additives are intended to move or migrate from within the free volume of the polymer, while others are intended to remain within the structure. The ability of an additive to remain within the polymer is related to its molecular and chemical affinity/attraction between the additive, the polymer, and any other substances that may be occupying space in the free volume. Scientists have developed different constants and equations to help describe these interactions. The solubility parameters are commonly used when evaluating interactions of solvents with polymers (Ref 2). The general idea is that materials with similar solubility parameters will show interaction with each other, resulting in solvation, miscibility, or swelling.

The concept of ESC involves similar types of chemical interactions, but the effects leading to

failure can result from chemical agents that show only mild-to-moderate affinity to the polymer. For instance, these mild-to-moderate ESC agents may reveal no significant weight gain or no detectable change in mechanical properties when the substance is tested against the polymer in a stress-free immersion condition. For this reason, the designer may consider these substances to be chemically compatible in service. In other instances, the plastic may be interacting with a foreign chemical substance that likely contacted the part in a manner that was unexpected or not considered during design and development stages. In all of these situations, proper validation testing was not conducted for exposure of the plastic to the ESC agent.

The fact that most of the ESC compounds that cause failures in service are generally not the same compounds that have similar solubility parameters to the polymer (those expected to cause solvation or plasticization of the polymer) makes ESC testing a difficult endeavor. The ESC agents are generally mild and will only cause cracking of the plastic at a certain threshold of stress and time. This means that when the chemical contacts the plastic, certain parallel conditions must take place for the

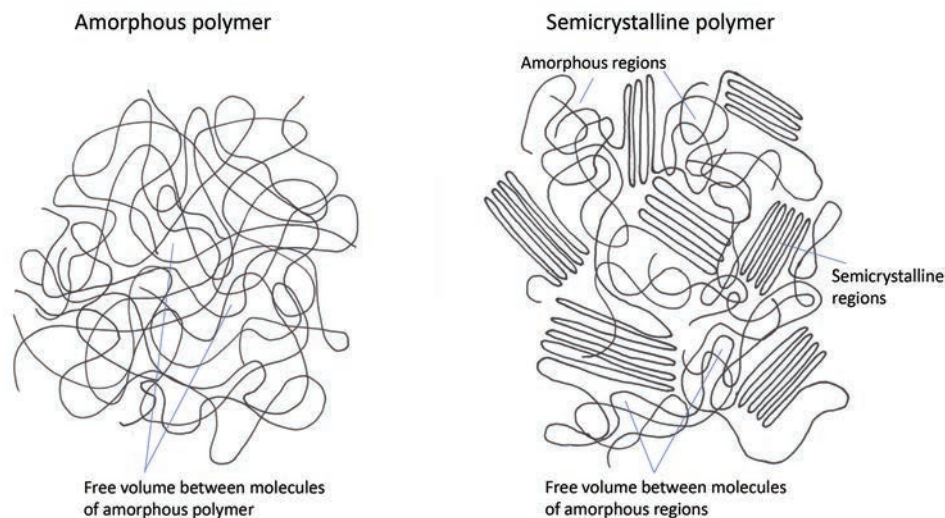


Fig. 1 Generic molecular arrangement for an amorphous and a semicrystalline polymer

substance to have the ability to enter into the free volume of the polymer. This makes determining which compounds could be ESC agents for a plastic material more difficult. Additional complexity is added by the fact that chemical interactions that lead to ESC not only must take place through immersion or surface contact of a liquid or gaseous chemical substance, but migration of a chemical substance from another solid material in contact with the plastic part is a common cause of ESC failures. Furthermore, chemicals acting individually versus the same chemicals acting together can have different effects on the polymer. The following sections focus on unpacking the basic concepts of ESC to provide the engineer with a better understanding of how to evaluate and prevent it.

What Is Environmental Stress Cracking?

Environmental stress cracking is a mechanism of fracture that results from the simultaneous and synergistic exposure of a plastic to chemical and stress. To properly understand the mechanism, it is important to have a basic knowledge of the molecular structure of plastics and how they can crack. As shown in the simplified schematics in Fig. 1, the polymer within the plastic recipe is made up of multiple long-chain molecules. Their long lengths allow the molecules to interact. Depending on the shape and orientation of the molecules and the attraction forces between them, they may form crystalline and/or amorphous regions. Crystalline regions result from greater intermolecular forces that lead to tightly knit and organized structures called lamellae (Fig. 2) (Ref 3). These lamellar structures are comprised of polymer molecules that have created organized folding patterns upon cooling. As the polymeric molecules move, fold, and interact, some regions entangle but are not able to

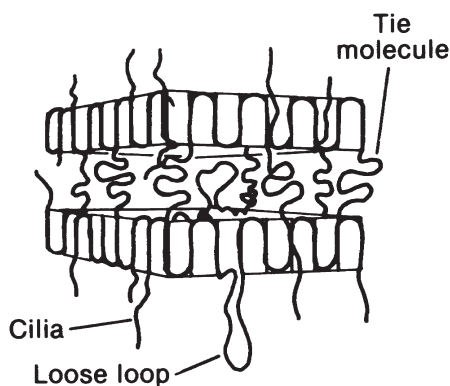


Fig. 2 Conceptual conformation of polymer molecules into lamellae connected by less-ordered tie molecules

crystallize. Ultimately, the material organizes into a unique conformation of amorphous and semicrystalline regions that is dictated by the material chemistry and processing conditions. The polymer backbone chemistry will have the greatest effect in the ability of a material to form crystals or remain amorphous.

The atoms that form the backbone of the polymer are all attached together by covalent bonds, resulting in very strong backbones that are difficult to break. Chain scission, known as the action of breaking these covalent bonds, requires that the molecules be exposed to high energy levels. These may result from high shear heating, very aggressive chemicals, UV energy, or other sources of high energy. The mechanism of ESC varies from other chemical fracture mechanisms, such as chemical degradation, in this specific aspect: the covalent polymer backbone bonds do not need to be affected for ESC to take place. The craze formation that initiates an ESC mechanism of fracture results from the slippage and disentanglement of polymeric molecules rather than by chain scission. In essence, the ESC mechanism parallels creep. Creep in plastics occurs due to the natural slippage and disentanglement of the molecular structure when a part is under load. The same process holds for ESC. Although for the case of ESC, the environment includes a chemical exposure that accelerates the disentanglement mechanism.

Individual long-chain molecules in a thermoplastic are held together by means of molecular entanglement and by lower-energy intermolecular forces of attraction, such as van der Waals forces, London dispersion forces, hydrogen bonding, and dipole interactions. Figure 3 provides an example of such forces for a polyamide 6,6, showing how polymer molecules that are next to each other will be attracted to each other as a result of hydrogen bonding. During an ESC failure, the chemical interacts with the less-organized amorphous regions of the polymer, causing a reduction of these intermolecular forces and leading to molecular slippage and craze formation.

Environmental stress cracking is a mechanism whereby failure can occur while the

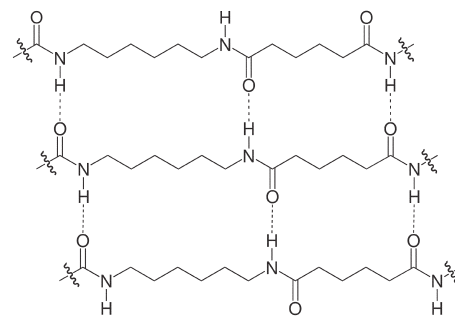


Fig. 3 View of hydrogen bonding molecular interactions in a polyamide 6,6, resulting in attraction between neighboring molecules

material is exposed to lower levels of energy and less-aggressive chemical interactions. No bulk solvation or plasticization is necessary for ESC to occur. For a chemical to have an effect on the polymer, the chemical must have a certain affinity to the polymer so that it can penetrate between the molecules, occupy free volume, and interfere with the polymer-to-polymer attractions, thereby reducing these attractions. In general, these polymer-to-polymer intermolecular forces are strong enough and the free volume is small enough that a chemical cannot easily migrate in, unless there is a significant attraction to the polymer, such as what would be expected from a solvent or plasticizer. However, because ESC chemical agents are less aggressive (have less attraction to the polymer), they rely on a compounding factor to ease their entry into the polymer. This factor is stress.

When a plastic material is stressed, the orientation of the molecules changes. Intermolecular forces of attraction counteract against the stress. Stressed locations that are under tension become regions where the molecules are effectively being pulled apart. The resulting stress effect allows the chemical to interact and alter the polymer structure more easily. For semicrystalline thermoplastics, a possible scenario for introducing this mobility was described by evaluating intrinsic crazing, which is crazing induced solely by stress and not accelerated by chemical effects (Ref 4). It is suggested that when a stress is applied, free volume can increase in local regions where the polymer is under stress. In fact, molecular orientation, such as that created by polymer flow, plays a significant role in this phenomenon. If stress is applied parallel to the orientation direction of the polymer molecules, ESC resistance can be increased by factors of up to four times, as reported for polymethyl methacrylate (Ref 5). Conversely, for stresses applied perpendicular to the direction of orientation, the opposite effect can occur. An easy way to understand this is to imagine that polymer molecules that have been oriented during processing are like a bundle of strings oriented in a similar axis. Pulling on the string bundle perpendicular to their length will simply open the space between them, effectively increasing their free volume.

Figure 4 provides an example of how an ESC chemical substance would be expected to work on a surface, penetrating the surface and causing crazing and cracking over time. The figure is described as a process of six steps, with essentially the last step being a repetition of the first but happening deeper into the plastic. These steps continue to repeat themselves over time until a fracture occurs. The process is described in further detail as follows:

1. The first step involves the exposure of the plastic to a chemical agent. Specifically, an ESC agent finds its way to the surface

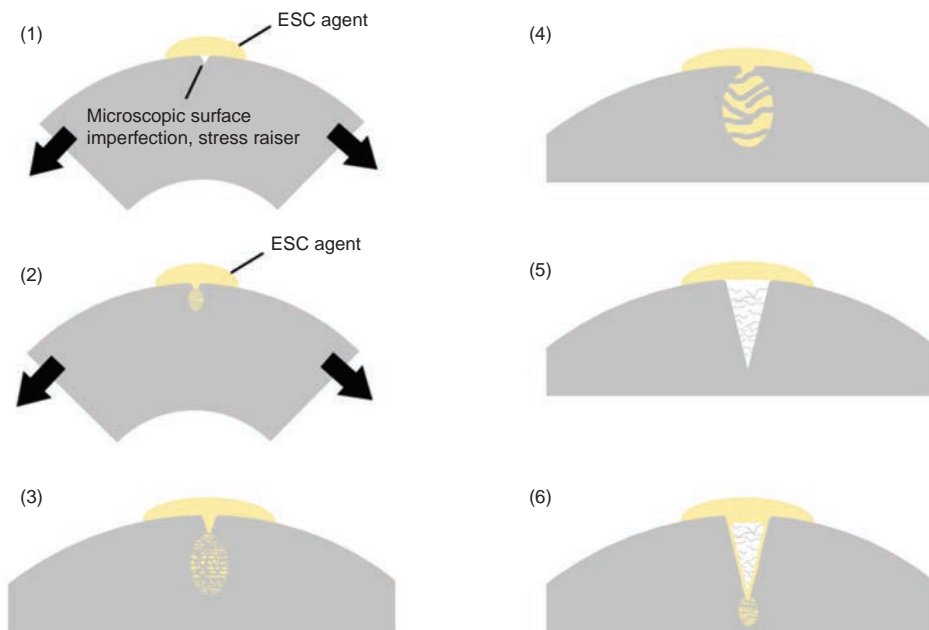


Fig. 4 Generalized schematic of the steps involved in the formation of an environmental stress-cracking (ESC) fracture

of a plastic that is under stress. The stress may involve multiple sources, including mechanical stress, assembly stresses, or even residual stresses from molding. The chemical sits over the surface, and surface tension controls its displacement over the polymer. In reality, no surface is perfectly smooth and defect-free. As a result, the chemical is likely able to easily find a defect zone that serves as a localized stress-concentration site over the surface of the polymer. This is where the chemical first does its work. These defect zones could be created from a scratch or simply could be a surface irregularity that, at the microscopic level, can serve as a notch. Contributions from the molecular conformation of the polymer at the surface can also play a significant role in the ability of the chemical to penetrate the surface. Multiple stress-concentration sites or locally weaker regions may be available, which explains why this fracture mechanism is one that typically results in multiple initiation sites and, eventually, coalescing fracture planes. Typically, these defects can range in stress-concentration factors of anywhere from 1 to 50 times (Ref 1).

2. The next step involves movement of the chemical agent into the polymer structure. The chemical affinity to the polymer is such that it has the ability to permeate into the plastic surface. Locations of high stress allow for the chemical to enter the free volume of the polymer. With the chemical absorbed, it can easily interact with the intermolecular forces that hold the polymer structure together.

3. Therefore, the next step involves chemical effects whereby chemical-to-polymer interactions overcome and reduce the amount of polymer-to-polymer intermolecular forces that are locking the molecules in place. This effect is very similar to how a plasticizer works on a polymer and can be described in a similar way. The overall effect that a plasticizer has on a polymer is that it can interact with the intermolecular forces, thereby causing a reduction in the glass transition temperature (T_g) of the material. The reduction in T_g means that, under the same temperature condition, the material will effectively have greater molecular mobility. It is for this reason that if intrinsic crazes are compared to crazes created by chemical effects, the environmentally induced crazes tend to be much longer and more extensive (Ref 5). Although the environmental effect is in fact very similar to plasticization in terms of the chemical interactions taking place, the main difference is that ESC agents act more locally rather than creating a bulk effect, such as what a plasticizer would be intended to do. Over a certain period of time, the chemical plasticizes or locally solvates the material (at the microscopic level), causing a reduction of strength of the material at this location. The weaker material is unable to withstand the continuous part stress, leading to molecular movement that results in the next step in the process.

4. In this step, stress over a locally plasticized region allows for much easier molecular sliding of the chains of the polymer. This leads to disentanglement and microscopic gaps in the structure. For semicrystalline

materials, the same effect as that of amorphous materials occurs, with the only difference being that tie molecules between the interlamellar regions begin to disentangle (Ref 6–11). The further separation leads to crazes, which are essentially microscopic fissures that form between groups of disentangling long molecules that are sliding past each other. It should be noted that chain scission is not necessary to cause ESC crazes to form. The primary mechanism that drives the formation of crazes and eventual crack growth is molecular disentanglement.

5. The next step involves the transition of crazes into cracks. When enough localized plasticization and disentanglement has occurred, the material becomes locally weak to the point that the stress can quickly overcome the strength of the plastic at that region. This causes quick rupture of crazes and progression of the cracking. The crack tip penetrates further into the polymer, reaching the neighboring nonchemically affected region. The greater strength of the nonaffected material at the crack tip causes the crack to arrest.

From here on, any next steps are simply a repetition of the previous steps, creating a cycle. Now that a crack has formed, the crack tip is a recognized stress-concentration site that can be easily and further affected by the chemical. Crack formation is a stress-relief mechanism. However, the crack tip is a very large stress-concentration site. Therefore, as long as the stress in the material remains high enough to allow the chemical to be absorbed at the crack tip and able to overcome the strength of the locally plasticized material at the crack tip, the crack continues to grow in a stepwise manner.

Plastics Susceptibility to Environmental Stress Cracking

Plastics, as a family, are a diverse group of materials that find utilization across a wide range of industries, including automotive, medical, appliances, aerospace, consumer goods, and much more. While they give product designers and manufacturers great versatility, they also come with a unique set of challenges. Plastics are robust materials, but if many have an Achilles' heel, it is generally resistance to chemical contact. The relatively high number of failures attributed to ESC can be attributed to two primary dynamics: the increasingly demanding applications that plastics are being placed into, exposing them to higher levels of stress, elevated temperatures, and a broad range of contact; and a general lack of understanding of the interaction between plastics and chemicals across the entire plastics supply chain.

Inevitably, questions are asked regarding a plastic being put into service:

- What plastic can be used in this application to avoid ESC failure?
- Will my plastic part fail through ESC when exposed to chemicals in manufacturing or service?
- What chemicals can be used safely with my plastic part?

These are not straightforward questions to answer. There are several factors that play a role in the susceptibility of plastics to ESC. There are three contributing elements required for ESC, namely, a susceptible plastic material, a chemical agent that affects the plastic, and stress acting on the plastic article. The combination of these three, together with environmental factors, determines whether ESC will occur and, if so, over what time period.

Environmental Stress-Cracking Factors

There are numerous factors that affect and contribute to the susceptibility of a plastic to ESC. Each factor influences the final performance of a part and its response to chemical interactions in different ways. The following sections explore the different factors and provide the fundamentals for understanding their contributions to this complex fracture mechanism.

Material Factors

One of the most important factors that helps determine compatibility between a plastic material and a chemical agent is the composition of the plastic itself. Plastics vary substantially in their inherent resistance or susceptibility to ESC.

Molecular Construction—Crystallinity

The most significant material-related factor, and possibly the single greatest generality that can be made regarding plastic ESC resistance, is that amorphous polymers are far more susceptible to ESC than semicrystalline polymers (Fig. 1). The tightly packed, orderly crystalline domains act as barriers to infiltration of the chemical agent into the molecular structure of the polymer. In contrast, the unordered organization of amorphous polymers and the corresponding free volume allow penetration of the chemical. A list of amorphous and semicrystalline polymers is presented in Table 1. Given its widespread use and its molecular construction, including its amorphous nature, polycarbonate is disproportionately high in regard to ESC failure compared with its usage. While polycarbonate has many positive attributes, it is highly susceptible to ESC failure.

A study that illustrates this point was conducted on polyetheretherketone (PEEK), which is normally a semicrystalline polymer. However, through rapid cooling, an exclusively amorphous structure can be produced.

Table 1 List of amorphous and semicrystalline polymers

| Amorphous polymers | Semicrystalline polymers |
|--|--|
| Cyclic olefin polymer (COP) | Polyethylene (PE) |
| Cyclic olefin copolymer (COC) | Polypropylene (PP) |
| Polystyrene (atactic) (PS) | Polymethylpentene (PMP) |
| Poly(styrene-acrylonitrile) (SAN) | Polyacrylonitrile (PAN) |
| Poly(acrylonitrile-butadiene-styrene) (ABS) | Polystyrene (syndiotactic) (SPS) |
| Polyphenylene oxide (PPO) | Polyacetal (POM) |
| Poly(cellulose-acetate-butyrate) (CAB) | Polyphenylene sulfide (PPS) |
| Poly(acrylonitrile-styrene-acrylate) (ASA) | Polyethylene terephthalate (PET) |
| Polyethylene terephthalate glycol (PETG) | Polybutylene terephthalate (PBT) |
| Copolyesters | Polycyclohexylenedimethylene terephthalate (PCT) |
| Polyethylene naphthalate (PEN) | Nylon 4/6 (PA46) |
| Polymethyl methacrylate (PMMA) | Nylon 6 (PA6) |
| Polycarbonate (PC) | Nylon 6/6 (PA66) |
| Poly(ester)carbonate (PCC) | Nylon 6/9 (PA69) |
| Poly(carbonate-siloxane) | Nylon 6/10 (PA610) |
| Poly(methyl methacrylate-acrylonitrile-butadiene-styrene) (MABS) | Nylon 6/12 (PA612) |
| Nylon 6-3-T (PA63T) | Nylon 11 (PA11) |
| Nylon 6I/6T (PA6I6T) | Nylon 12 (PA12) |
| Polysulfone (PSU) | Poly(lactic acid) (PLA) |
| Polyphenylsulfone (PPSU) | Polyphthalamide (PPA) |
| Polyethersulfone (PESU) | Polyarylamide (PARA) |
| Polyether-imide (PEI) | Polyetherketone (PEK) |
| Polyvinyl chloride (PVC) | Polyetheretherketone (PEEK) |
| Chlorinated polyvinyl chloride (CPVC) | Polyetherketoneketone (PEKK) |
| Thermoplastic polyurethane (TPU) | Polyetherketoneetherketoneketone (PEKEKK) |
| | Polyvinylidene fluoride (PVDF) |
| | Polytetrafluoroethylene (PTFE) |
| | Poly(ethylene-chlorotrifluoroethylene) (ECTFE) |
| | Fluorinated poly(ethylene-propylene) (FEP) |
| | Polychlorotrifluoroethylene (PCTFE) |
| | Perfluoroalkoxy (PFA) |
| | Poly(ethylene-tetrafluoroethylene) (ETFE) |
| | Thermoplastic polyimide (TPI) |

Samples of the two morphologies were exposed to chemical agents. Across the board, the amorphous PEEK specimens showed a higher rate of fluid absorption as well as an increased level of craze formation (Ref 12).

This clearly illustrates the increased susceptibility of semicrystalline polymers to ESC if undercrystallized during the molding process. Undercrystallization can result from molding in a cold tool, which results in frozen-in amorphous content in a preferentially crystalline polymer. In particular, this can pose an issue to surface skin, which can be vulnerable to rapid cooling.

While it is generally true that crystallinity within a polymer affords a greater level of ESC resistance, there are exceptions. Within some semicrystalline polymer families, there is an optimal level of crystalline structure, above which and below which ESC resistance diminishes. This has been suggested for fluoropolymers through studies performed using copolymers to inhibit the level of crystallinity (Ref 13). Studies performed on polyethylene have showed mixed conclusions. Some indicate that the addition of copolymers to reduce the crystallinity has enhanced the ESC resistance (Ref 14), but others show better ESC resistance with higher levels of crystallinity, as achieved through slow cooling during injection molding (Ref 15). It appears likely that the phenomenon is coupled in these studies. The presence of copolymers, both in the fluoropolymer and polyethylene, can enhance the ESC

resistance. The overall research shows that within an analogous family of polymers, decreased crystallinity enhances ESC resistance. This is likely because the higher proportion of amorphous content contributes to a relative increase in the concentration of tie molecules binding the crystalline content. Also, the higher crystallinity leads to an elevated stiffness that renders the material susceptible to brittle fracture.

Molecular Weight

The molecular weight of the polymer is another important material-related variable that affects ESC resistance. Higher-molecular-weight polymers offer improved ESC resistance. According to Ref 16, "Increasing molecular weight and therefore decreasing melt flow index increases ESC resistance." This superior ESC resistance is in large part due to an increased level of chain entanglement. The greater the level of chain entanglement, the better the ESC resistance will be for an analogous group of materials.

The combined importance of molecular weight and chain entanglement further highlights the criticality of molding to ESC resistance. In addition to achieving adequate crystallinity within semicrystalline polymers, as mentioned previously, molding has a direct effect on the level of chain entanglement and the molecular weight of the molded article. If the material undergoes molecular degradation during processing, the polymer chains can be

substantially shortened, which reduces inherent entanglement. Further, if the molding process produces poorly fused knit lines, these can act as localized weakened areas, which are highly susceptible to ESC. As such, it is essential that the molding process maintains the integrity of the molding resin by producing adequate crystallinity, polymer chain entanglement, and the retention of molecular weight.

Molecular Weight Distribution

Molecular weight distribution is another material factor that plays a role in ESC failure. For polymers with similar average molecular weights, increased levels of polydispersity decrease the ESC resistance (Ref 17). Further, for materials with comparable average molecular weights, the high molecular weight fraction has been shown to have the greatest effect on ESC resistance (Ref 16). The greater the fraction of low-molecular-weight chains within a material, the greater the likelihood of ESC failure (Ref 14). Thus, generally, a molecular weight distribution that maximizes the higher-molecular-weight fractions offers the greatest level of resistance to ESC failure.

Additives

While there are no additives for plastic specifically designed to increase ESC resistance, some formulation constituents can achieve that as a side benefit. One such example is fiber reinforcement, including fiberglass. "Fiberglass (and other fibrous reinforcements) offer a facile method to significantly enhance the resistance to environmental stress failure. In essence, fibers can bridge the cracks or crazes which may develop at the surface and inhibit easy propagation through the material" (Ref 18). Nonreinforcing fillers, however, provide limited to no improvement. The addition of nanoparticles to produce nanocomposites is being explored as a means to improve ESC resistance, with initial studies reporting promising results (Ref 19).

Another type of additive that has been demonstrated to increase the ESC resistance of plastic is rubber impact modifiers, in particular for styrenic polymers (Ref 20, 21). It has been identified that the rubber particle size is important, with larger particles having improved ESC resistance compared with smaller particles (Ref 21). An improvement in ESC resistance has also been obtained within polycarbonate using poly(ethylene-propylene) rubber and acrylic rubber modifications (Ref 22), hydrogenated styrene-butadiene-styrene block copolymers (Ref 23, 24), and thermoplastic urethanes (Ref 25). It appears likely that the rubber particles blunt the propagating crack, thus interfering with fracture extension.

Chemical Factors

Environmental stress cracking is analogous to creep rupture, with the cracking accelerated by a chemical agent. "As most fluids have a

greater affinity for plastics than does air, then most fluids, including water, will accelerate the embrittlement process" (Ref 16). The key is that different chemicals will affect plastics to a greater or lesser degree and as such can be generally categorized as mild, moderate, or aggressive ESC agents. It is important to note that the chemical/plastic interaction is a unique characteristic. Because of that, a chemical may be a relatively mild ESC agent for one plastic but act aggressively on another. This is illustrated by the effect of silicone oil, which acts as an aggressive ESC agent in conjunction with low-density polyethylene but generally has a more moderate effect on polycarbonate. The severity to which a chemical affects a particular plastic can be distinguished by the time to cracking under a particular load. The shorter the time to cracking, the more aggressive a chemical agent is in conjunction with that plastic material.

The chemicals or chemical-based products that can act as ESC agents can be found in a wide range of residential, commercial, and industrial substances, including:

- Solvents
- Fuels
- Degreasers
- Lubricants, natural and synthetic
- Aerosols
- Paints and coatings
- Paint removers
- Paint thinners
- Insect and rodent repellents
- Adhesives
- Rubber plasticizers
- Food oils
- Lotions
- Soap and detergents
- Disinfectants and sanitizers
- Ice melt

A distinction can be made within chemicals/products, based on their application, as to whether they are primary or secondary ESC agents. Primary chemical agents are those that are intended for use in conjunction with the plastic they are contacting. Examples of this include a commercial detergent solution in conjunction with the high-density polyethylene (HDPE) container it is sold in, or gasoline in tandem with polyvinylidene fluoride fuel lines. Environmental stress crack failures associated with primary chemicals are generally infrequent. Sufficient testing is commonly done to ensure compatibility and longevity of the product.

On the other hand, ESC failures in conjunction with secondary chemicals are far more widespread. Secondary chemicals have inadvertent contact with the plastic material in question, and as such, their interaction is unintentional. Because of this, it is likely that compatibility testing has not been performed. Examples of this include residual cutting oil present on a metal fastener used in conjunction

with a polycarbonate housing, and methanol present in commercial windshield washer fluid being used to clean automotive headlights coated with polymethyl methacrylate.

Chemical Structure

Just as the plastic composition, and particularly the molecular construction, is the most significant plastic-related ESC factor, so too the molecular structure of the chemical agent is of primary importance. The ability of the chemical agent to permeate into the molecular structure of the polymer is in large part determined by the interaction between the functional groups within the polymer and those that make up the chemical agent. The presence of the chemical agent serves to disrupt the intermolecular forces that keep the polymer chains entangled.

One method that was explored as a means of predictively assessing the interaction between a chemical/polymer combination is solubility parameters. Early research into solubility parameters indicated that the total solubility parameter of the chemical was an important factor. This is a measure of the total cohesive attraction between the molecules in a chemical agent. If this attraction is identical to that between polymer molecules, then that particular chemical/polymer combination would be assumed to be miscible, resulting in swelling and solvation. Under that condition, ESC is predicted to be likely. If the solubility parameters are very different, then it would be predicted that the combination would not be susceptible to ESC.

Continued testing, however, has revealed that a single chemical and polymer parameter is not reliable in the prediction of ESC. For most chemicals, the actual molecular attraction is attributed to multiple different types of interactive forces, and the same applies to polymers. Given the difficulty and inaccuracy of measuring solubility parameters for chemicals, and even more so for polymers, and the fact that the level of stress plays a significant role in ESC failures, this method of predicting ESC can be unreliable (Ref 16).

While solubility parameters may be unreliable, the intermolecular forces of a chemical have a direct effect on their purity as an ESC agent. Normally, chemicals that exhibit moderate levels of hydrogen bonding tend to be the most aggressive, while chemicals with high and low levels of hydrogen bonding are generally weak ESC agents (Ref 16). The level of hydrogen bonding directly affects the ability of the chemical agent to permeate into the molecular structure of the polymer and interfere with the intermolecular forces holding the chains together. Chemicals with moderate levels of hydrogen bonding allow the optimal combination of permeation into the polymer structure and interference with polymer intermolecular bonding. However, it should be recognized that this is a generality. For some

plastics, chemicals with high or low levels of hydrogen bonding can act as aggressive ESC agents:

- *Low hydrogen bonding*: aliphatic hydrocarbons
- *Moderate hydrogen bonding*: aromatic hydrocarbons, halogenated hydrocarbons, ethers, ketones, aldehydes, esters, and amines
- *High hydrogen bonding*: carboxylic acids, alcohols, water, amides, inorganic acids, and inorganic bases

Given the relatively aggressive nature and their widespread use, organic esters are the most common chemical family associated with ESC failures. The ester functional group structure is such that, in addition to hydrogen bonding, the molecules also have dipole-dipole interactions and van der Waals dispersion forces. This aggressively facilitates polymer chain disentanglement. Esters are present in many products found in residential, commercial, and industrial settings. Some typical sources include synthetic lubricants, plasticizers, solvents, adhesives, cosmetics, personal care lotions, soaps and detergents, fragrances, medications, vegetable oils, and animal fats.

An area in which the relationship of chemical composition to ESC resistance is not always clear-cut is when two organic chemicals are used in conjunction. In many cases, two or more solvents are used in a system to achieve the desired performance. In many cases, these solvents do not act as aggressive ESC agents individually. However, when coupled, the mixture of these solvents creates an azeotrope. An azeotropic mixture is a combination of two or more liquids whose proportions cannot be altered or changed by simple distillation. In effect, the two liquids combine in such a way as to form a single chemical system. In doing so, an azeotropic mixture achieves intermolecular forces uniquely different than either of the individual chemical agents. Thus, the combination of these solvents may act as an aggressive ESC agent, where neither of the individual chemicals would. An example of this is the solvent mixture of cyclohexanone and isopropanol. Separately, neither of these is an aggressive ESC agent for polycarbonate. However, when blended in the correct proportion, the resulting azeotrope is highly aggressive.

Chemical Molecule Size

Another chemical-related factor that plays a role in ESC is the size of the molecule itself. Within an analogous series of chemicals, the lower-molecular-weight chemicals tend to be more aggressive ESC agents. This is associated with molecular mobility, viscosity, and the ability of the chemical to permeate within the molecular structure of the polymer. For example, ethyl acetate is more aggressive than ethyl stearate.

Chemical Concentration

While it may seem logical that chemical concentration would be relatively straightforward in

regard to ESC, this is not the case. It may be expected that the higher the concentration of chemical, the more aggressive it would be as an ESC agent. In most cases, this generality is true. However, there are some notable exceptions, the most important one being IGEPAL (Rhodia), a family of nonionic surfactants used in numerous applications. Importantly, grades of the chemical are also used in ESC testing, because such surfactants are ESC agents for polyethylene. It has been found that 10 to 15% solutions of the surfactant in water are substantially more aggressive than the pure chemical (Ref 26, 27). This is likely attributed to the optimal combination of intermolecular forces within this concentration range. Furthermore, the viscosity of chemical compounds and thus the ability of wetting the surface of the plastic can be affected by changes in chemical concentration.

It should be noted that, while not as common, ESC failure can occur within plastics due to contact with chemicals in the gaseous form. While contact with liquids is more common, aggressive chemicals in the vapor form can produce ESC failure.

Stress

After plastic composition and chemical structure, the third leg of the ESC triangle is tensile stress. The presence of stress is an essential component of ESC. Polymers exposed to chemicals that have a severe swelling or wetting effect will not undergo ESC unless there is stress present.

Environmental stress cracking is analogous with creep, simply accelerated by the interference of the chemical agent on the intermolecular forces holding the polymer chains together. Another way to think of this is that the chemical agent reduces the critical stress or strain for crazing or cracking to occur (Ref 16). Because of this relationship, the effects of stress are relatively straightforward. The higher the level of tensile stress acting on a plastic component in conjunction with a particular chemical agent, the faster ESC failure will occur. Tensile stress is required to separate the molecules for disentanglement. It is important to remember, however, that other load configurations, including bending, shear, and even compression, often result in localized tensile loads within a structure.

When evaluating parts under continuous strain applications, the same behavior is to be expected where higher tensile strains accelerate ESC. However, if the material is strained up to yield, the resulting permanent deformation rapidly reduces the stress and may reorient the molecules in a more linear manner against the orientation of load. These effects may inadvertently increase the ESC resistance.

It is important to remember that the stress acting on a part is the combination of externally applied stress as well as any internal stress. There can be many sources of stress that result in ESC failure, often in combination. These include:

- Molded-in residual stress within the molded parts
- Interference stress between the molded-in inserts and the overmolded plastic
- Stress resulting from joining, bonding, or welding two individual components
- Assembly stress resulting from fitting together mating components
- Externally applied stress from service

From experience analyzing numerous failure investigations, it has been observed that molded-in residual stress is often sufficient to cause ESC within plastic components that are otherwise not under load.

The design of a plastic component also influences ESC failure regarding stress concentration. Designs that include sharp corners or other points of stress concentration accelerate ESC failure due to the elevated, and often unanticipated, levels of stress. This is routinely seen in the case of molded-in metal inserts. These inserts frequently have a relatively sharp exterior profile, which produces corresponding sharp internal corners within the molded plastic component. The sharp corners, together with the stress induced by shrinkage of the plastic onto the molded-in insert, routinely produce ESC failure, particularly if the inserts are covered with residual metalworking fluids.

Environmental Factors

The environment in which a plastic component is used can play a distinct role regarding ESC. While not part of the plastic-chemical-stress triad, the environment can influence the time period over which a failure may occur.

Temperature

Under most circumstances, elevated temperature acts to accelerate ESC failure (Ref 28) in the same way it accelerates creep rupture. As the temperature increases, the polymer chains are farther apart and there is more kinetic energy in the system. This facilitates the ability of the polymer chains to slide past one another and undergo disentanglement. Additionally, at elevated temperatures there is more free volume, which facilitates the ability of the chemical agents to permeate into the molecular structure of the polymer. Notably, the relationship between temperature and ESC does not follow the Arrhenius rule, because no chemical reaction takes place.

One possible exception to the association of reduced time to ESC failure with increasing temperature is in the case of volatile chemical agents. The high volatility of the chemical agent at elevated temperature could reduce or even eliminate the direct contact exposure due to evaporation. If the chemical is sufficiently volatile at the temperature of exposure, the increased temperature may actually serve to slow or even eliminate ESC.

Time

The factor of time in ESC failure is relatively basic. The longer the contact between a

plastic and a chemical agent while under stress, the more likely that cracking will occur. Although basic, this relationship does merit discussion. In cases of continuous strain application, the effects of stress relaxation diminish the applied stress over time. In this way, the relationship between time and ESC failure is not linear. This is important because most structural designs and service environments place components under continuous strain and not continuous stress. Because of this, the use of a log scale or other nonlinear treatment to represent time may be appropriate.

As indicated, ESC failure is a relatively common plastic failure mechanism that occurs under a variety of circumstances. Typical examples of various factors that play a role in ESC failure include:

- Polycarbonate enclosures cracked after assembly using metal fasteners, due to the presence of residual hydrocarbon oil. The relatively high level of interference stress together with stress concentration from the formed thread groups was sufficient to produce cracking.
- Poly(acrylonitrile-butadiene-styrene) automotive mirror housings failed prematurely through contact with a rubber O-ring formulated with a phthalate-based plasticizer. The assembly stress was sufficient to cause cracking in conjunction with the relatively aggressive ESC agent.
- A medical handle produced from a polycarbonate/polybutylene terephthalate resin cracked shortly after assembly. The UV-curable adhesive used to bond individual sections was not properly cured, resulting in exposure of the plastic to relatively aggressive monomeric chemical constituents. The stress responsible for the failure was identified as molded-in residual stress within the molded handle sections.
- Chlorinated polyvinyl chloride pipes used in a hotel underwent ESC failure due to contact with soundproofing caulk that contained a softening agent. Bending stresses combined with internal pressure precipitated the cracking.
- Housings on a portable handheld medical monitor produced from polycarbonate failed as a result of contact with sunscreen lotion. A combination of molded-in residual stress and assembly stress produced the ESC failure.
- An audio headset used in a residential setting cracked under normal use. Food oils, such as those found on potato chips, were identified as the ESC agent. The design bending loads on the headset were sufficient to facilitate the cracking.

It can be seen that a large number of factors play a role in whether a particular chemical acts as an ESC agent in contact with a specific plastic material. These factors, as summarized in Table 2, can be used as generalizations to assess whether it is likely that a potential issue

Table 2 Typical relationship between property and environmental stress-cracking (ESC) resistance

| Property | Improved ESC resistance |
|--|---------------------------|
| Amorphous or semicrystalline | Semicrystalline |
| Crystallinity | Varies |
| Molecular weight | Higher |
| Molecular weight distribution | Narrow |
| Polymer molecular fusion/entanglement | More |
| Unfilled or glass-fiber reinforced | Glass-fiber reinforced |
| Standard or impact modified | Impact modified |
| Chemical agent level of hydrogen bonding | High or low, not moderate |
| Chemical molecular size | Larger |
| Chemical concentration | Varies |
| Stress | Lower |
| Part radius | Generous |
| Molded-in stress | Lower |
| Temperature | Lower |
| Chemical exposure time | Lower |

exists in a chemical/plastic combination. The generalizations, however, can only serve to suggest potential problematic situations and are not definitive in ensuring failure prevention.

An alternative is finding published data that indicate whether a plastic/chemical combination is prone to ESC. Unfortunately, chemical compatibility literature often does not provide the right combination of plastic and chemical that is in question and tends not to differentiate between different chemical-effect mechanisms. A typical critical shortcoming of such available data is that often the testing is done without applied stress, assessing molecular degradation and not ESC.

Back then to the original questions:

- What plastic can be used in this application to avoid ESC failure?
- Will the plastic part fail through ESC when exposed to chemicals in manufacturing or service?
- What chemicals can be safely used with the plastic part?

Only testing provides an absolute determination and is an essential means to prevent ESC failure.

Testing for Environmental Stress Cracking

One of the most effective ways to determine if a plastic has been subjected to ESC is through fractographic analysis of the cracks. The fracture generally provides unique features that help identify and confirm an ESC fracture mode. In parallel to the fractographic analysis, chemical analysis techniques can be applied to determine if a known ESC chemical agent is present in the fracture. These chemical analysis techniques generally involve Fourier transform infrared (FTIR) spectroscopy, or if lower concentrations of chemicals are expected, including volatile substances that

may be difficult to detect by FTIR, chromatography techniques such as gas chromatography/mass spectroscopy may be useful. Examples of the testing methods and procedures typically used to confirm ESC fracture modes are described in the next section, "Failure Analysis of ESC Fractures," in this article. This section focuses on the testing and evaluation of materials for resistance to ESC, a critical step during the initial stages of product development for any plastic component.

Multiple approaches can be taken to evaluate the possibility of ESC for any given plastic. Generally, designers tend to rely on chemical-resistance databases as a starting point in determining the chemical effects that a substance may have on a plastic. While this is a great starting point, proper interpretation of the data is critical to assess ESC effects. Chemical-resistance charts may include testing at different chemical concentrations as well as testing at different temperatures. In addition, the failure criteria may vary for each chart. Some may establish a failure criterion based on changes in tensile properties, while others may consider a change in mass, dimensions, or volume. Furthermore, the specific test procedure becomes critical to properly assess ESC effects. This is because ESC is a failure mode that results from the synergistic effects of chemical exposure and stress. A common way to evaluate chemical resistance of a material is to expose a stress-free sample to a chemical for a predetermined period of time.

After completion of the chemical exposure, the sample is then mechanically tested or inspected to establish if the chemical had detrimental effects on the plastic. While this procedure may be valid when evaluating chemicals that cause degradation or for those that lead to bulk solvation or plasticization, this is not adequate for mild-to-moderate ESC agents. Testing for ESC requires that the sample be exposed to the chemical agent while under stress. This is because the stress is necessary to induce cracking. In many instances, ESC agents may result in negligible effects to a plastic material when the plastic is exposed to the chemical under a no-stress condition. However, over a given stress threshold, the chemical is able to effectively accelerate cracking of the plastic.

When developing a test to evaluate ESC, the material factors discussed in the previous section should be well understood and carefully considered. These four factors (material, chemical, stress, and environment) can be reorganized and grouped into individual aspects specific to the material being tested, the exposure conditions (accounting for both the chemical substance and the environment), and all stress influencers, including those from physical loads and part geometry (Ref 2):

- Material effects
 - a. Chemical structure and composition
 - b. Morphology
 - c. Residual-stress state

- Ambient exposure
 - a. Physical and chemical properties of the substance of exposure
 - b. Temperature
 - c. Humidity
- Loading
 - a. Type of loading and orientation
 - b. Rate or time
- Geometry
 - a. Part dimensions and features
 - b. Surface finish
 - c. Preexisting defects or imperfections

While many of these factors can be controlled through proper testing methodologies, it is evident that others may be beyond the control of the test procedures. It is for this reason that standardized methods have been developed and are critical for limiting the variables that can be directly influenced during testing. There are many tests that have been developed for quality control and evaluation of molded parts. These are tailored to the specific design and application. For development purposes, ESC testing using simple geometries is very common and an excellent method for comparing material performance during materials selection stages. Generally, such tests are conducted on flat strips, bars, or plates exposed to bending loads under constant strain, and in tension for constant stress tests. Another alternative commonly used when multiaxial stresses are of interest is a pin load method, where a tapered pin of controlled dimensions is inserted through a hole. A defined pin geometry can allow for constant strain tests, and constant stress tests can be conducted by the application of weights. The most common pin impression method consists of accurately drilling a hole with a defined diameter into a plate specimen and inserting an oversized pin that will generate a predetermined amount of strain. While under load, the specimen is exposed to the substance of investigation for evaluation of potential cracking.

It is important to remember that while strain-controlled tests have the benefit of being easier to conduct, the plastic material suffers stress relaxation as a result of the viscoelastic properties of the polymer. This means that the highest value of stress is reached only immediately after the loading step and continues to quickly and nonlinearly decrease over time (Ref 29–31). This mechanical response is one that generally applies to any type of viscoelastic material. Figure 5 shows an example of how stress relaxation and creep are related and affected by a viscoelastic material behavior (Ref 32, 33). When stress is held constant, the strain continues to increase over time (creep). Conversely, when strain is held constant, the stress quickly decreases during the first stages of testing and then slowly levels off as the material continues to relax due to molecular movements and reorientation (stress

relaxation). In stress-relaxation experiments, where the material is exposed to a continuously decreasing stress level, the ability of the material to form crazes and continue to crack is a function of the quantity of initial strain applied and any environmental effects that can influence the formation of crazes and eventual cracking.

Under no environmental effects, the initially applied strain must be high enough to allow for enough molecular mobility over time for the formation of cracks while not exceeding the yield point of the material. This suggests that for stress-relaxation experiments, there is a threshold where cracking will not occur because the stress can be relieved through material displacement at the molecular level that does not lead to crazing. However, above this threshold, crazing and cracking will take place. The factors listed earlier that influence ESC affect this threshold. The presence of an ESC agent contributes to the molecular mobility, thus reducing the actual stress level necessary to induce cracking.

Several common standards developed to evaluate ESC of plastics include:

- ISO 22088, “Determination of Resistance to Environmental Stress Cracking”
 - a. ISO 22088-1, “General Guide”
 - b. ISO 22088-2, “Constant Tensile Load Method”
 - c. ISO 22088-3, “Bent Strip Method”
 - d. ISO 22088-4, “Ball or Pin Impression Method”

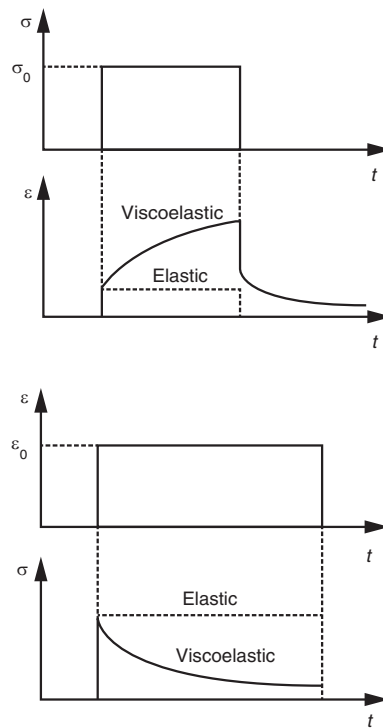


Fig. 5 Simplified schematic of creep and stress-relaxation behavior in polymeric materials. Adapted from Ref 32, 33

- e. ISO 22088-5, “Constant Tensile Deformation Method”
- f. ISO 22088-6, “Slow Strain Rate Method”
- ASTM D543, “Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents, Practice B (Mechanical Stress and Reagent Exposure)”
- ASTM D1693, “Standard Test Method for Environmental Stress-Cracking of Ethylene Plastics”
- ASTM F2136, “Standard Test Method for Notched, Constant Ligament-Stress (NCLS) Test to Determine Slow-Crack-Growth Resistance of HDPE Resins or HDPE Corrugated Pipe”
- ASTM F1473, “Standard Test Method for Notch Tensile Test to Measure the Resistance to Slow Crack Growth of Polyethylene Pipes and Resins, PENT (Pennsylvania Notch Test)”
- ASTM D5397, “Standard Test Method for Evaluation of Stress Crack Resistance of Polyolefin Geomembranes Using Notched Constant Tensile Load Test”

Testing under constant stress and constant strain are both successful methods to evaluate ESC in a plastic material. However, testing under constant strain has generally been the most common method due to the simplicity of the testing procedure and equipment. Figure 6 shows a schematic of the creep equipment necessary for measuring ESC formation in a tensile creep test according to ISO 22088-2 (Ref 34).

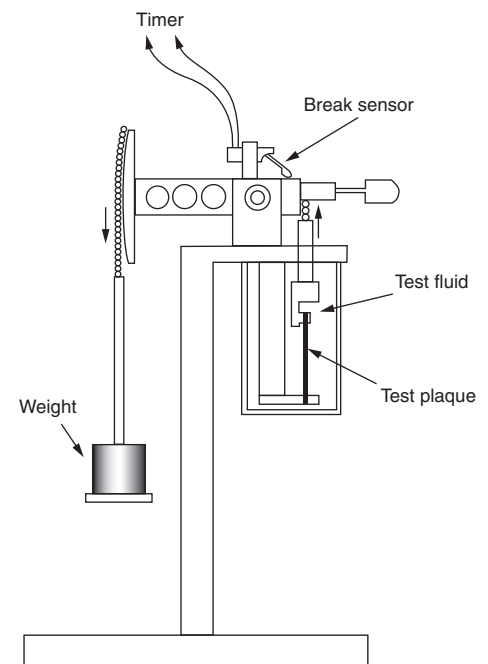


Fig. 6 Tensile creep equipment schematic for measuring environmental stress crack formation according to ISO 22088-2. Adapted from Ref 34

The specimen type for this test is a bar loaded with a constant tensile load below the yield point of the material. The test is essentially a creep test where the sample is immersed in a chemical medium. This testing is beneficial because one can determine tensile creep strength and time to fracture in the chemical medium, which can be compared to the resistance to creep in air. Figure 7 shows how ESC parallels creep (Ref 16). Creep is a molecular disentanglement mechanism that leads to rupture under the application of a continuous stress. This depiction clearly shows that ESC and creep are very similar mechanisms, except that ESC suffers accelerated molecular disentanglement as a result of the chemical interactions.

For test methods such as ISO 22088-2 that involve an exposure chamber, another benefit is the ability to have temperature control. Because increases in temperature generally

result in significant acceleration to the ESC effects, testing under conditions that more closely replicate those of the application becomes important. Modifications to the testing can also be conducted where the tensile bar is exposed to the substance of concern via different means than full immersion. This becomes important in applications where a material may be subjected to sporadic contact with a chemical substance rather than continuous immersion. It should be noted that these modifications to methods of exposure are relevant to all standards and test methods discussed. Multiple chemical application methods have been developed that allow the testing to be conducted in general accordance with the standards but may result in more relevant data for a specific application. In general, the chemical application method to use should be whichever best mimics the in-service conditions. Examples of various application methods include:

- Cyclic immersion
- Partial immersion
- Timed spray
- Wet patch
- Wet wipe
- Direct contact of solid body
- Pressure contact of solid body
- Exposure to gaseous medium

While most methods can provide valuable data for a specific application, the closer the test method replicates the service condition, the more realistic the data can be. For example, experience has shown that ESC effects can be very different using a spray or wipe method when compared to a full immersion or wet-patch method.

For strain-controlled methods such as ISO 22088-3 and ASTM D543, Practice B, the general concept is to clamp strips or tensile specimens to a controlled radius of curvature that allows calculation of the constant strain being applied to the material in bending (Fig. 8). By having fixtures with different radii of curvature, multiple flexural strains can be applied to the material being tested. Modified versions of these tests are available, such as the Dow test, where the fixture is designed with a controlled and variable radius of curvature that allows the application of varying strain along the same specimen. With varying strain, the stress crack formation is characterized by measuring the critical strain, which corresponds to the smallest local curvature where optically visible stress cracks form after a defined period of time (Ref 2).

Standards ASTM D1693, F2136, F1473, and D5397 are material-specific developed specifically for polyethylene materials. All of these standards focus on the evaluation of slow crack-growth stress cracking. The cracking is induced at a localized region that is subject to stress concentration by notching the sample. The various standards are intended to satisfy specific requirements that may be more

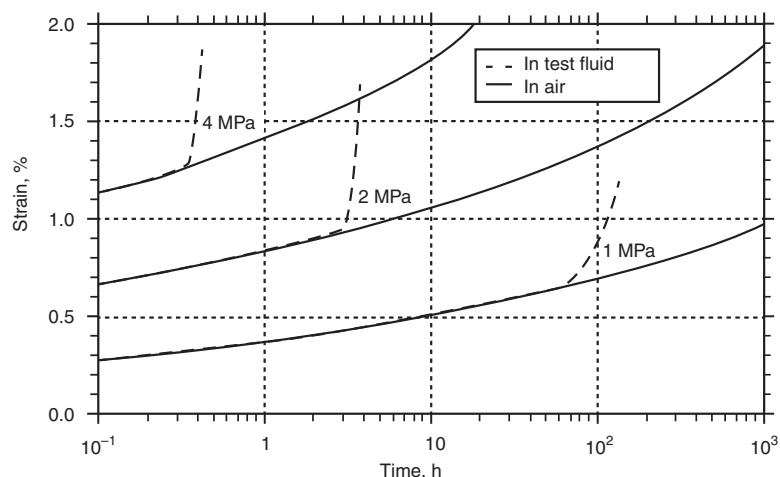


Fig. 7 Static creep-rupture curves of a polymer in air compared to the same polymer in contact with an environmental stress cracking agent. Adapted from Ref 16, 34

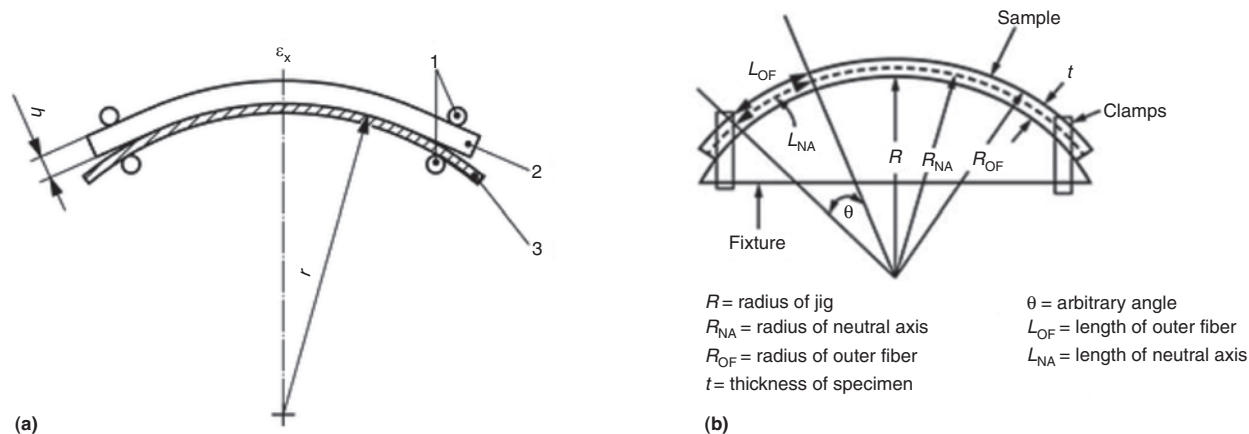


Fig. 8 Environmental stress cracking fixtures for strain-controlled bent test according to (a) ISO 22088-3 and (b) ASTM D543, Practice B

applicable to specific polyethylene grades or an application. For ASTM D1693, rectangular strips that have been notched parallel to their length are bent perpendicular to the notch for a full 180° into a U-shaped form. Multiple samples are supported by a metal brace in this U-shaped form, as depicted in Fig. 9.

The fixturing results in a constant strain. All samples are then immersed in the chemical solution for a predetermined period of time. The time is measured at which 50% of the specimens exhibit cracking extending from the notch. This test method is known as the Bell Telephone test and is primarily used for quality-control testing using a known ESC chemical agent for polyethylene, typically IGEPAL.

The other standards listed for polyethylene rely on a constant stress rather than a constant strain. Each method includes unique and predetermined ways of notching the specimens to concentrate stress and accelerate crack formation. ASTM F2136 is intended for evaluating the susceptibility of HDPE resins of 0.15 to <0.4 melt index ranges and >0.947 up to 0.955 g/cm³ density ranges to slow crack growth. While it is expected that the method may be applicable to materials beyond these specifications, no data are presented to support this. ASTM F1473, recognized in the United States as the polyethylene notch tensile (PENT) test, is designed to measure the slow crack-growth resistance from compression-molded plaques or specimens directly machined from pipe that are tested at controlled elevated temperature and pressure (stress). This test method is primarily used to test polyethylene pipe-grade materials exhibiting high ESC resistance values, because the method generally provides more timely results. Typical test conditions are 80 °C (175 °F) air and 2.4 MPa (0.35 ksi) stress. ASTM was developed for analysis of sheet materials used for geomembranes, although other polyethylene materials have been tested to gage slow crack-growth performance. The method is generally used to develop time-to-failure curves (stress-time plots) by testing samples over a series of constant load levels. Sheet material is exposed to tensile loads while also exposed to an accelerated environmental condition. Typical test conditions are 50 °C (120 °F) in a 10% IGE-PAL solution, with a sample notched depth of 20% of the sample thickness.

Failure Analysis of Environments Stress-Cracking Fractures

When cracking occurs within a plastic part, there are a number of ways to approach the failure. Often, a failure prompts a brainstorming exercise to identify the cause of the failure. This can happen as random opinions or as part of an organized root-cause analysis. Regardless, such theories are based on conjecture, often without sound scientific data. Alternately, the failure can be investigated using a

systematic methodology, which allows the science to direct the investigation. This scientific approach is the most efficient and effective way to determine the nature and cause of the failure (Ref 35). As famed computer scientist and U.S. Navy Rear Admiral Grace Hopper said, "One accurate measurement is worth a thousand expert opinions." The goal of the failure analysis is to understand the mechanism and cause of the failure, essentially how and why the product failed.

The use of the scientific approach is especially important for ESC, given the relatively high occurrence of this type of failure. There is no set recipe for a failure analysis performed on a plastic component. The testing performed depends on the unique situation. However, a comprehensive failure analysis generally includes the collection of background information to understand the circumstances surrounding the failure, a fractographic evaluation to assess the cracking, and analytical testing to evaluate the material, design, manufacturing, and environmental factors.

Fractographic Examination

Fractography is the systematic study of fractures and fracture surfaces (Ref 36). It is a useful tool in failure analysis. A fractographic examination involves the interpretation of the morphology and topography of a fracture surface to gain an understanding of the nature of the cracking. In a way, it is a roadmap to understanding the failure. Much of the information regarding the failure mechanism can be obtained by interpreting the features found on the fracture surface. The fracture-surface characteristics are created based on a number of parameters:

- Type of material and formulation constituents
- Type of applied forces (tensile, compression, shear)
- Magnitude of forces
- Frequency of forces (continuous, intermittent, rapidly applied)
- Environmental effects (temperature, presence of chemicals, radiation)

The key to interpreting fracture surfaces is the ability to recognize and interpret the features left from crack generation.

The fractographic examination begins with a thorough macroscopic inspection of all the failed parts. The amount of information that can be obtained by macroscopic examination should not be underestimated. This inspection should address:

- The macrofeatures of the failure (ductile versus brittle)
- The consistency of failure location and overall fracture features
- The proximity of contributing design features, especially stress concentrators, to the failure location
- Potential manufacturing contributions (knit lines, molding defects, injection molding gate location)

Several features are consistent with ESC failure from a macroscopic standpoint. Similar to creep fractures, multiple parallel cracks can be an indication of ESC (Fig. 10). Environmental stress cracking failures commonly produce the initiation of numerous individual fractures, typically more than a corresponding creep failure, that propagate along the same or parallel planes. Additionally, macroscopic examination is key to providing information regarding potential stress-concentration factors inherent to the design. Cracks associated with ESC failure commonly initiate at localized areas of stress concentration, such as a design corner or notch in the part, a defect, a surface scratch, or a crack (Fig. 11).

The macroscopic inspection is typically followed by examination at increasingly high magnifications using a microscope. The

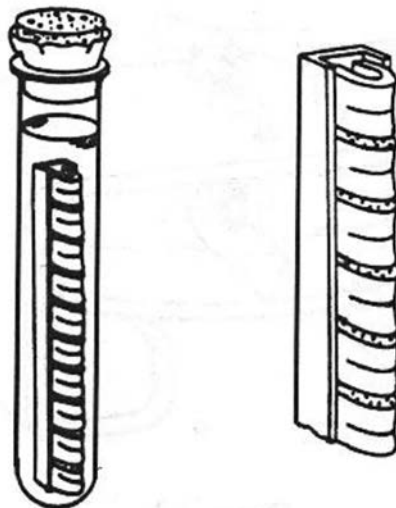


Fig. 9 View of typical bent-strip fixture for polyethylenes

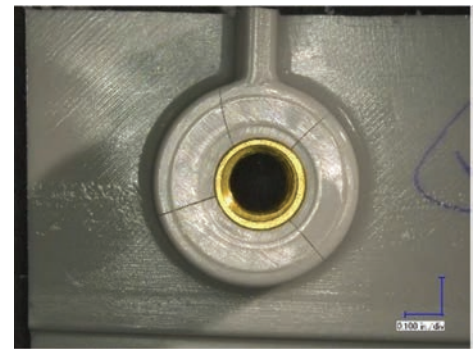


Fig. 10 Micrograph showing the presence of multiple parallel cracks associated with environmental stress cracking in a boss

microscopic examination, typically performed at magnifications ranging from 5 to 200 \times , provides more information regarding the failure, such as the crack origin location and direction of crack propagation. As indicated, ESC often results in the initiation of multiple individual cracks, and as such, multiple origins may be present (Fig. 12, 13). The ESC fracture surfaces routinely show ridgelike features, corresponding to crack unions, representing the coalescence of multiple individual fractures as they propagate through the part wall

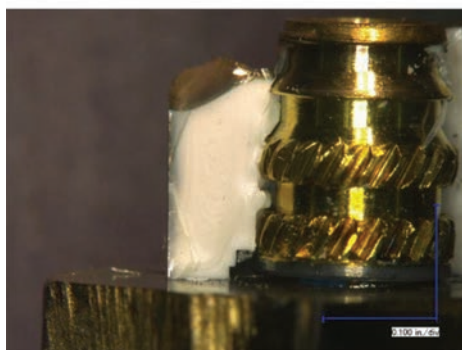
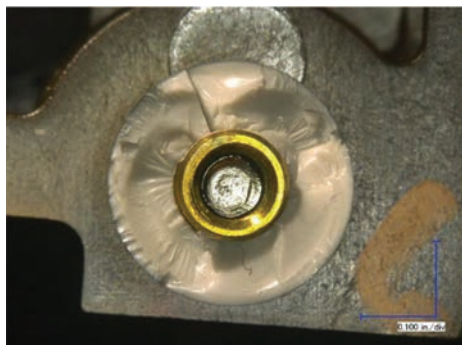


Fig. 11 Micrographs showing environmental stress crack initiation adjacent to a molded-in boss with sharp corners. These corners act as points of significant stress concentration.



Fig. 12 Micrograph showing environmental stress cracking fractures originating at a design corner within a molded component. Multiple cracks initiated, extended, and subsequently coalesced to form the fracture. Ridgelike features representing crack unions are present between the individual cracks.

(Fig. 12, 13). The crack origins are usually in localized areas of elevated stress within the part that are in direct contact with the ESC agent. In some cases, features known as thumbnail markings, a concave mark, surround and delineate the crack origin locations (Fig. 14).

Importantly, microscopic examination allows further assessment of the fracture surface for ductility. Environmental stress crack failures occur through brittle fracture, even in plastics that would be expected to produce a ductile failure mechanism. Accordingly, ESC origin areas typically exhibit a relatively smooth morphology associated with slow crack growth (Ref 37) (Fig. 15). For amorphous polymers, this smooth morphology can be glassy in appearance, while for semicrystalline materials such as acetal and polyethylene, a morphology presenting more microductility can be observed. The combination of stress below the yield point of the material and the interference with intermolecular bonding caused by the chemical agent results in a brittle fracture slow crack-growth mechanism. However, under conditions of relatively high stress and/or contact with aggressive chemical agents, the fracture surface can present more coarse surface features.



Fig. 13 Micrograph showing the initiation, propagation, and coalescence of multiple environmental stress cracks. The individual cracks are separated by ridgelike crack unions.



Fig. 14 Micrograph of an environmental stress crack fracture surface exhibiting the clear location of crack initiation. The crack origin has a very smooth texture and is bounded by a thumbnail marking.

The examination of the fracture surface at relatively high magnifications provides additional information regarding the failure mechanism. Scanning electron microscopy (SEM) allows inspection at magnifications up to and exceeding 10,000 \times . However, magnifications within the range of 1000 to 3000 \times are often sufficient to identify ESC as the failure mechanism on the fracture surface. Several locations on the fracture surface are of particular interest. An examination of the crack origin allows assessment of the part for additional features indicating whether the fracture surface presents significant microductility. Microductility within the SEM is indicated by the presence of a significant concentration of stretched fibrils or flaps. As indicated, ESC failure is typically a brittle mechanism and exhibits a relatively smooth morphology, without evidence of such microductility. Often the SEM examination reveals the presence of multiple, otherwise unseen individual crack-initiation sites clustered in close proximity (Fig. 16).

Outside of the origin, within the midfracture, the presence of opened craze remnants, often in a series of radiating bands, can be indicative of ESC (Fig. 17). However, not all ESC failures exhibit these bands, and some creep-rupture failures present similar features. These features represent split fibrils remaining

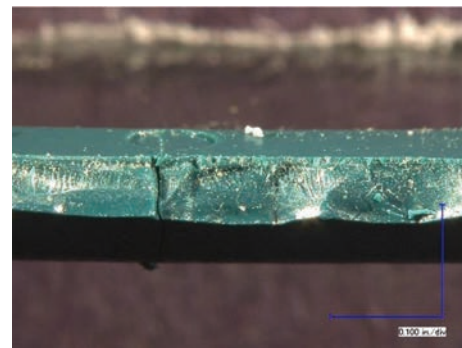


Fig. 15 Micrograph of an environmental stress crack fracture surface exhibiting a relatively smooth texture. The fracture transitions into more coarse features representing the final fracture zone.

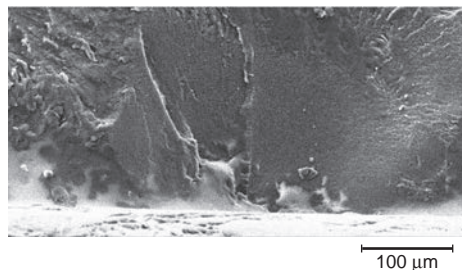


Fig. 16 Scanning electron micrograph showing the initiation of multiple individual cracks. The discrete cracks are separated by ridgelike features representing crack unions. Residual chemical is present within the crack origin zone.

after the rupture of crazes preceding cracking. If banding is present, the crack origin is positioned on the concave side of the bands. Environmental stress cracking can take place through continuous crack growth or via a stepwise progressive mechanism of cracking and arrest, depending on the molecular structure of the plastic, the composition of the chemical agent, the level of stress, and other environmental conditions.

In many cases, the final fracture zone exhibits features associated with mechanical overload (Fig. 18). This occurs once the remaining ligament of the fracture surface can no longer withstand the applied load.

Analytical Testing for Chemical Agents

When the results of the fractographic evaluation indicate that a plastic component failed via ESC, the next logical question to answer is: What chemical caused the failure? There are a variety of analytical methods that can

provide information about potential chemical contact of the failed plastic component. Two of the most important and commonly used are Fourier transform infrared (FTIR) spectroscopy and gas chromatography/mass spectroscopy (GC-MS). For both techniques, there are two general analytical strategies to identify the chemical agent: direct analysis of the plastic component, and solvent separation to isolate the chemical agent. The direct analysis methodology offers the advantage of minimal sample preparation and limited opportunity for contamination or alteration. However, some type of solvent separation is often required to isolate the chemical agent, due to relatively low concentration. Solvent separation can take two basic forms: rinsing and extraction.

Fourier transform infrared spectroscopy is a nondestructive microanalytical spectroscopic technique used in the qualitative identification of organic materials. An infrared spectrum represents a fingerprint of the sample based on the bonds comprising the molecules being analyzed. During the visual and microscopic examinations, residual materials are sometimes identified on or adjacent to the fracture surface. If these materials can be isolated from the base plastic component, then a direct analysis is a suitable technique to generate a representative spectrum. This residue isolation can typically be achieved via direct contact using an attenuated total reflectance crystal. If no residue is found, then a different approach is employed. A spectrum is obtained on a core sample of the plastic as a control. A second spectrum is then collected on the fracture or adjacent surface of the part. A comparison is made, and a spectral subtraction is performed, thereby removing the absorption bands associated with the plastic from the results obtained on the suspect area (Fig. 19). If no discernible spectral features are generated, then no material is identified. If chemical separation techniques are employed, either

through rinsing or extraction, the resulting material is analyzed after evaporation of the extraction solvent. Regardless of the sample-preparation technique, either direct analysis, spectral subtraction, or chemical separation, the resulting spectrum is evaluated manually and with the aid of library-searching techniques. In most cases, FTIR can characterize the type of chemical agent but may not provide an absolute identification. For example, FTIR may characterize the chemical as an adipate ester but may not identify the material as dinonyl adipate.

The second method, GC-MS, is a hybrid technique that combines the separation and quantification of gas chromatography with the identification of mass spectroscopy. GC-MS offers the advantage over FTIR of being able to separate complex mixtures and has a much lower threshold of detection. However, it is a much more sophisticated technique and is more expensive and more difficult to interpret. Like FTIR, there are two basic analysis strategies. The plastic sample can be heated, and the evolved gases can be concentrated and then passed through the instrumentation for analysis. The most common techniques employed for such analyses are thermal desorption and headspace GC-MS. Alternately, the plastic sample may be extracted or rinsed and the resulting solvent/chemical mixture analyzed. Regardless of the sample-preparation technique, the results of the GC-MS analysis provide a semiquantitative breakdown of the various chemical agents present in the mixture and their identifications based on library matching. Compared with FTIR, GC-MS often can be more specific regarding chemical analogies. Going back to the previous example, with GC-MS it would be possible to detect the presence of and identify both dinonyl adipate and dioctyl adipate and give a relative idea of their proportions.

Other techniques, including energy-dispersive x-ray spectroscopy, ion chromatography,

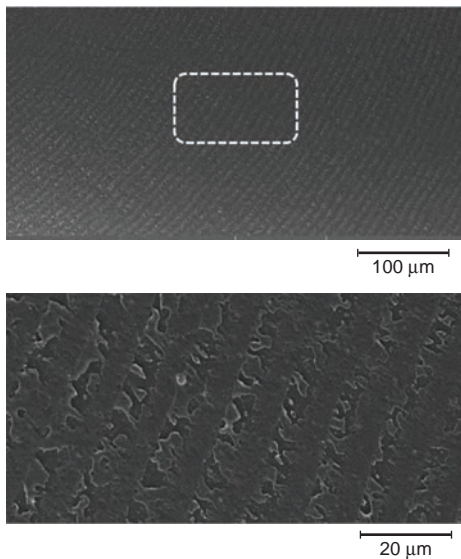


Fig. 17 Scanning electron micrographs showing a series of radiating band features corresponding to opened craze remnants

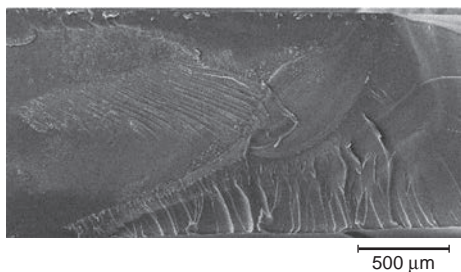


Fig. 18 Scanning electron micrograph showing a final fracture zone on an environmental stress crack fracture surface. The features are characteristic of final mechanical overload.

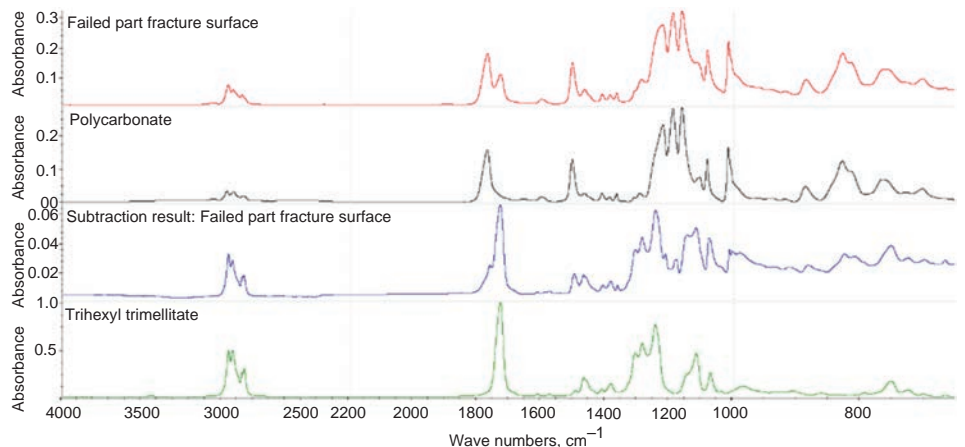


Fig. 19 Fourier transform infrared spectral comparison illustrating the identification of a trimellitate ester on the fracture surface of a polycarbonate part

inductively coupled plasma/optical emission spectroscopy, x-ray photoelectron spectroscopy, and time-of-flight/secondary ion mass spectroscopy, may also be employed to analyze a plastic sample for chemical agents. Their use, however, is far less frequent.

The analytical techniques discussed only provide for guidance in terms of any chemical agents that may be detected over the failure region. It should be stated unequivocally that the determination as to whether a plastic component has failed through ESC is to be made using information obtained during the fractographic inspection. The presence or absence of chemical agents has no bearing on this determination. It is quite possible that no chemical residue is identified because it has been washed from the surface or has migrated or evaporated, yet the failure is ESC. Equally applicable, it is possible that a chemical is present yet played no role in the failure. It is the fractographic features that identify the failure mechanism.

Other analytical, thermal, or mechanical tests can be performed to further assess the failure mode or to confirm identification of factors contributing to the failure. Additional testing that may be conducted to evaluate contributors to an ESC mechanism of failure may include:

- Direct or indirect molecular weight determination methods
- Analytical tests for resin identification or evaluation of plastic contaminants
- Thermal analysis techniques to evaluate the material and processing
- Residual-stress testing techniques to evaluate possible internal stress contributors to the failure

The failure analysis process of a plastic should evaluate all three of the interactive variables that define the likelihood of ESC in service: the stressed state; environmental exposure conditions, including the presence of chemical agents; and the material characteristics (Ref 38). The culmination of the investigation, including review of the background data, the fractographic examination, and the analytical testing, provides the analyst with the required information to assess whether the part has failed through ESC and the important factors of the failure.

Failure Case Example

Housings from pumps used for a food processing application failed during service. The housings had been injection molded from an unfilled polyphenyl sulfone (PPSU) resin. An internal component is attached to the housing through the insertion of thread-forming screws into formed bosses on the housing. A powdered metal steel plate covers the bosses, separating the housing from the internal components. It was indicated that the steel plates are resin impregnated with a thermoset resin.

This resin is a low-viscosity liquid sealant designed for sealing porosity in metal castings and powdered metal parts. It is formulated to cure at room temperature. The supplier of the steel plates indicated that there may have been a problem with curing of the plates used in conjunction with the failed parts. In addition to the failed housings, as-molded housings, impregnated steel plates from the lot used to produce the failed housing, and newly cured steel plates from a new lot were also available for analysis.

Tests and Results

A visual inspection of the housings confirmed the presence of cracking within the bosses adjacent to the steel plate (Fig. 20). Microscopic examination showed that multiple individual longitudinal cracks were present within the failed part bosses (Fig. 21). The cracks exhibited features characteristic of brittle fracture, with no evidence of macroductility. After removal of the internal components and the metal plate, the examination revealed a significant number of radial cracks. Inspection of the opened cracks revealed isolated

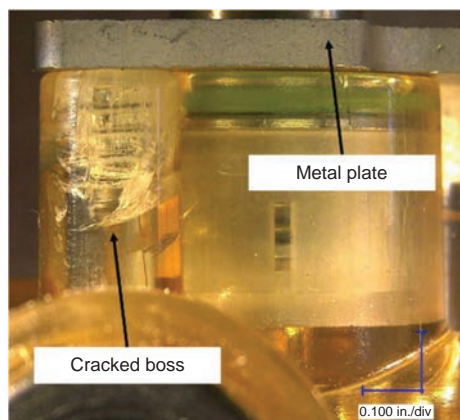


Fig. 20 Micrograph showing the pump housing construction. Cracking was evident within the bosses adjacent to the steel plate.

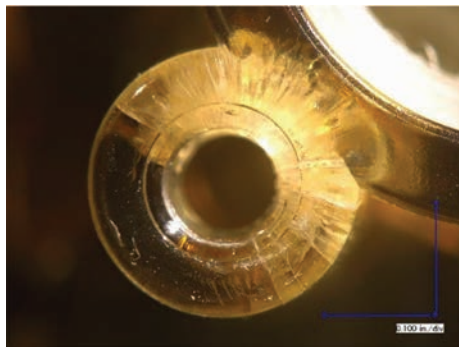


Fig. 21 Multiple longitudinal cracks were present with the housing bosses.

areas that were relatively smooth and other areas exhibiting sharp features. The observed features were indicative of brittle fracture. Signs of trace amounts of a residual viscous liquid were evident on the fracture surfaces.

Scanning electron microscopy of the fracture surfaces revealed multiple areas of crack initiation along the upper face of the boss, which had been in contact with the metal plate as-assembled (Fig. 22). The points of initiation exhibited a relatively smooth morphology, characteristic of a slow crack-growth mechanism. This smooth surface texture was bordered by radiating band features that represented alternating bands of opened craze remnants (Fig. 23).

The location of crack initiation on the parts was significant because it was not positioned along the inner diameter of the boss at locations obviously damaged through insertion of the thread-forming screws. This damage would be expected to result in a relatively high level of stress concentration at an area under the greatest level of interference stress. The initiation of cracks outside of this zone is indicative of other factors driving the failures.

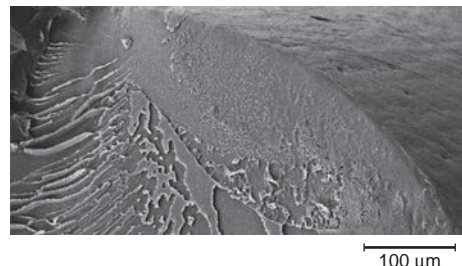
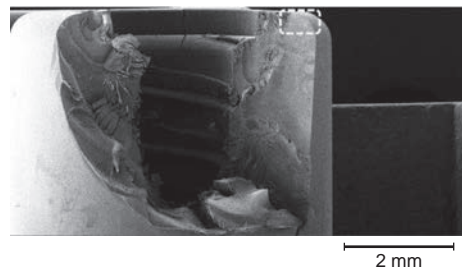


Fig. 22 Scanning electron micrographs showing crack origins along the upper face of the boss

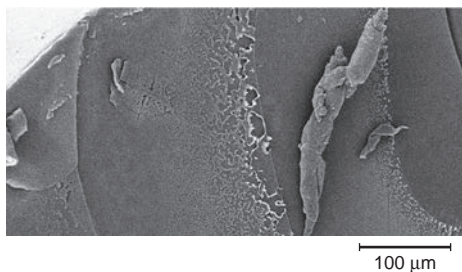


Fig. 23 Scanning electron micrograph showing radiating bands of open craze remnants extending away from the crack origin

Examination of an area of the fracture surface created during completion of the crack, corresponding to a laboratory fracture, showed a significant level of microductility in the form of stretching and deformation. This microductility provided evidence that the material was not inherently brittle (Fig. 24).

Fourier transform infrared spectroscopy was initially performed on a core sample of one of the failed housings remote to the cracking. The obtained spectrum was characteristic of a PPSU resin (Fig. 25). No evidence was found in the results to indicate the presence of bulk contamination.

Analysis of the as-received metal plates associated with the failures generated results indicative of a glycol dimethacrylate chemical agent. This result matched the primary ingredient indicated on the material safety datasheet for the impregnation resin, polyglycol dimethacrylate. It would be expected that under conditions of proper curing, this chemical would have reacted to form the thermoset resin. After removal of the plate from the FTIR sampling crystal, a residue remained; analysis of this material showed it to be glycol dimethacrylate chemical transferred from the plate. Once cured, the resin impregnated into the metal plate should no longer be a liquid and should not be able to flow from the steel plate.

The cracked surface of the boss that mated with the metal plate as-installed was analyzed for several of the failed parts, and the results showed the presence of the glycol dimethacrylate chemical (Fig. 26). Further, analysis of the corresponding opened fracture surfaces also showed the glycol dimethacrylate chemical. Thus, impregnation resin had transferred from the metal plate to the housing.

Analysis of the surface of a metal plate designated as "properly cured" produced results showing spectral bands associated with a thermoset acrylic resin. A direct comparison indicated that the results obtained on the properly cured plate were distinctly different than those representing the previously supplied as-received plates (Fig. 27). Specifically, the glycol functionality appeared to be gone, likely as a result of the curing process. Subsequent analysis of the sampling crystal produced results without significant spectral absorbances. As

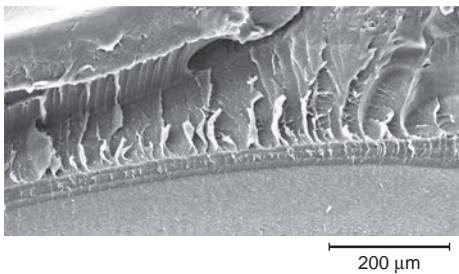


Fig. 24 Scanning electron micrograph showing a significant level of microductility within the final fracture zone

such, no evidence was found to indicate transfer of material from the properly cured plate to the crystal.

It was the conclusion of the evaluation that the pump housings failed via ESC. The cracking initiated on the upper face of the screw boss, which had been in contact with the

mating steel plate as-assembled. The fracture-surface features indicated that the requisite stress was the result of interference between the boss and the inserted thread-forming screw. The chemical agent responsible for the ESC failures was identified as a glycol dimethacrylate material, a formulation constituent of the

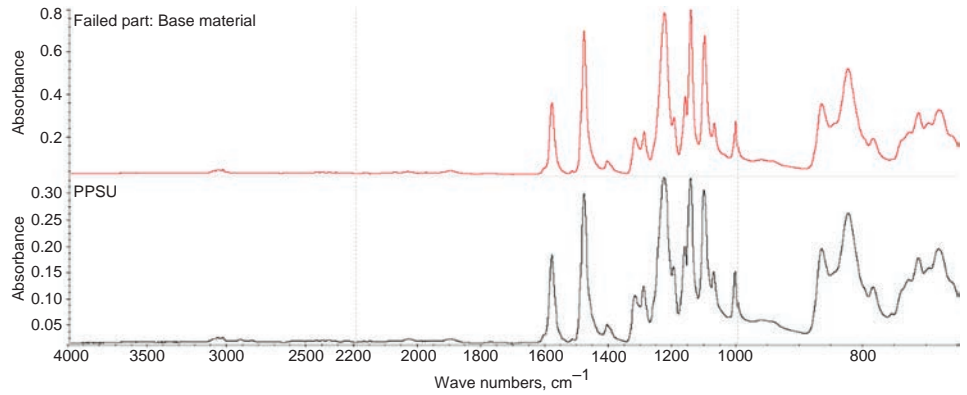


Fig. 25 The Fourier transform infrared spectrum obtained on a core sample of the housing produced results characteristic of polyphenyl sulfone (PPSU). No evidence of contamination or material anomalies was found.

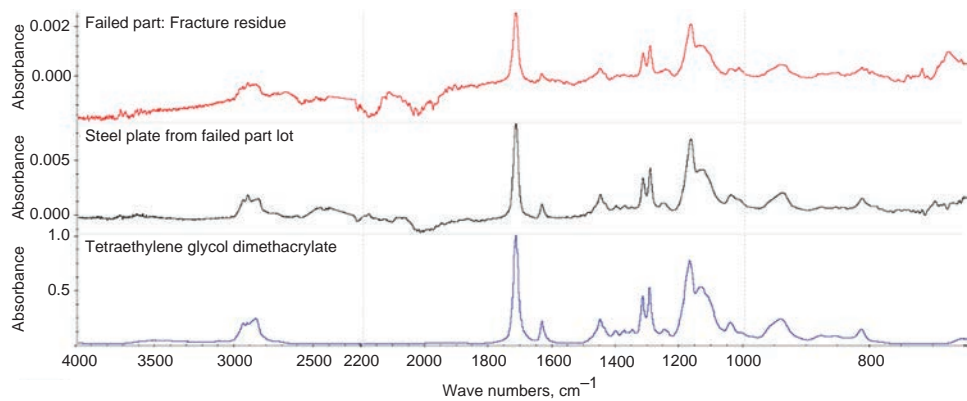


Fig. 26 The Fourier transform infrared spectra representing the fracture-surface residue and the steel plate from a failed part produced an excellent match. The results were characteristic of glycol methacrylate chemical agent.

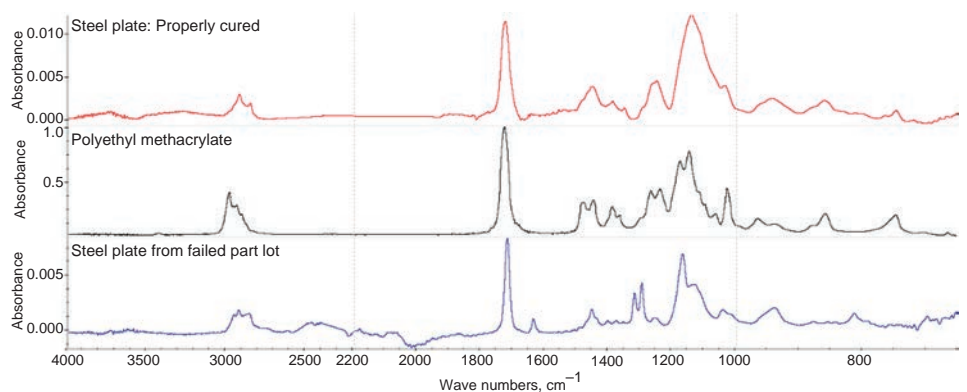


Fig. 27 The Fourier transform infrared spectrum obtained on a properly cured steel plate exhibited bands characteristic of a thermoset acrylic resin. The results were noticeably different than the results from the plate associated with a failed part.

uncured impregnation resin. In the monomeric, uncured state, a glycol dimethacrylate acts as an aggressive ESC agent in conjunction with many plastics, including PPSU. Further analysis showed that the residual glycol dimethacrylate was the result of incomplete curing of the impregnation resin used in conjunction with the steel powdered metal plates. This undercuring of the impregnation resin was identified as the cause of the pump housing failures.

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