Environmental Stress Cracking – THE PLASTIC KILLER

Environmental stress cracking is involved with some 25% of plastic part failures.

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Environmental stress cracking (ESC) is a phenomenon in which a plastic resin is degraded by a chemical agent while under stress, and it is the leading cause of plastic component failure. It is a solvent-induced failure mode, in which the synergistic effects of the chemical agent and mechanical stresses result in cracking. A recent study showed that 25% of plastic part failures are related to ESC.

To adequately understand the ESC failure mechanism, some background on analogous cracking in air is required. In the absence of chemical interaction, cracking is associated with prolonged static stress through a creep mechanism. Creep, sometimes called static fatigue, is a brittle fracture mode in which continuous stress results in molecular disentanglement within the polymer chains.

The creep failure mechanism involves a series of distinct steps. The first step is craze initiation, the second is craze growth that leads to crack initiation, then crack extension, and finally catastrophic fracture. Creep failure is common within plastic materials at room temperature, but rare in metals. It is a result of the viscoelastic properties of polymeric materials.

This article details the steps involved with ESC, describes the characteristics of such failures, and discusses the three factors involved with failure. Two case histories illustrating ESC failures are also presented.

Steps in environmental stress cracking

ESC is a phenomenon in which a particular plastic resin is cracked through contact with a specific chemical agent while under stress. The synergistic effects of the chemical agent and mechanical stresses result in cracking.

The chemical agent does not cause direct chemical attack or molecular degradation. Instead, the chemical penetrates into the molecular structure and interferes with the intermolecular forces binding the polymer chains, leading to accelerated molecular disentanglement.

The mechanism steps involved in ESC failure are similar to those responsible for creep failure, and include fluid absorption, plasticization, craze initiation, crack growth, and finally fracture. Because the ESC process depends on the diffusion of the chemical into the polymer structure, the rate of fluid absorption is a critical parameter in the rate of both craze initiation and crack extension. The more rapidly that the chemical agent is absorbed, the faster the polymer will be subjected to crazing and subsequent failure.

Recent comparisons have illustrated creep as a special condition of ESC. Under this model, creep is simply ESC with air as the chemical agent, the principal difference being that the presence of an active chemical agent accelerates the disentanglement process. This acceleration results in a significant reduction in the time to crack initiation, and substantially increases the speed of the extending crack, thus shortening the time to failure. Alternatively, ESC cracking develops at reduced stress or strain levels relative to creep failure in air.

It has been theorized that

> "Highly localized fluid absorption is probably the mechanism for acceleration. The fluid is preferentially absorbed at sites under high dilatational stress such as a stress concentrating defect, a craze, or the tip of a crack. The absorbed fluid locally plasticizes the material, reducing its yield strength. Critical strains and stresses for craze initiation with the most active fluids can be as low as 0.1% and a few megapascals. Stresses and strains due to processing and / or assembly can often exceed the critical condition." (Rapra Technology)

Characteristics of ESC

Environmental stress crack failures share several typical characteristics:

- *Brittle fracture:* ESC failures are caused by brittle fracture, even in materials that would normally be expected to produce a ductile yielding mechanism. The crack initiation sites for ESC failures are always on the surface. They normally correspond to localized areas of high stress, such as microscopic defects or points of stress concentration. The initiation location is generally related to direct contact with an active chemical agent, either liquid or gas.
- *Multiple cracks:* Multiple individual cracks are initiated, and these subsequently coalesce into a unified fracture. Numerous crack origins and the corresponding unions are illustrative of an ESC failure mechanism.
- *Smooth morphology:* The crack origin areas usually exhibit a relatively smooth morphology, indicative of slow crack growth. However, aggres-

Latch handle failure

A high number of latch handles on an enclosure suddenly began to fail after a relatively short time. Standard service included periodic actuation of the handles at normal exterior temperatures. The handles were molded from a commercial grade of a polycarbonate / polyacrylonitrile: butadiene:styrene (PC / ABS) resin blend. The handle assembly is held together in a base unit with a metallic roll pin and a spring. A review of molding and assembly processes revealed no variations to account for the sudden change in performance.

Fig. 3 - Photomicrographs show the crack location within the hinge and the fracture surface.

A visual inspection of the failed parts showed significant cracking, consistent across all of the failed parts. The cracks were present within the molded boss that secured the roll pin, and had a shape that was irregular but continuous. Upon disassembly of the units, additional non-catastrophic cracks were apparent within similar locations around the boss hole. **The fracture surface displayed features characteristic of brittle fracture, with many crack origins adjacent to the inner diameter surface.** A typical crack is shown in Fig. 3. An oily residue was readily apparent on and adjacent to the fracture surface.

Typical fracture surfaces were further examined via scanning electron microscopy (SEM). The SEM inspection of the fracture surface confirmed the presence of multiple apparent crack origins along the inner diameter of the molded boss in an area that had been in direct contact with the roll pin. Locations within the crack origins showed evidence of craze remnants, as shown in Fig. 4. This suggested the formation of micro-crazes as part of the crack initiation. Locations adjacent to the apparent crack origins revealed features indicative of brittle fracture, and secondary cracking was also apparent. Examination of the final fracture zone showed continued evidence of brittle fracture, as indicated by the presence of hackle marks.

Analytical testing of the failed handle material via Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) produced results characteristic of an unfilled PC / ABS resin, consistent with the indicated material. No evidence was found to indicate contamination of the material. The determination of the melt flow rates of several of the failed handles produced values that indicated adequate retention of molecular weight, without evidence of degradation.

Fig. 4 - Scanning electron images show a typical hinge fracture surface. The failure mode was identified as ESC.

The oil residue found on the inner diameter surfaces of the failed handles was analyzed by FTIR and the results were characteristic of a hydrocarbon-based oil containing an ester-based additive. The oil present within the formed roll pins was also analyzed, and a direct spectral comparison yielded an excellent match with the results obtained on the part residue. Spectral library searching produced good matches with commercial fluids for metal processing.

The investigators concluded that the enclosure handles failed via ESC. The chemical agent responsible for the failure was identified as the fluid used in the forming and processing of the metal roll pin, a hydrocarbon-based oil containing an organic ester additive. This material had not been properly cleaned from the roll pin, and chemicals of this type are known to produce ESC in ABS resins and corresponding blends. The stress appeared to come from the interference fit between the roll pin and the handle boss.

The failure mode was identified as ESC by the characteristic features observed during the visual, microscopic, and SEM examinations. These included the irregular but continuous crack formation, the presence of multiple apparent crack initiation sites, the generally brittle fracture features, and micro-craze remnants within the crack origin location.

sive chemical agents can produce rapid initiation and extension, characterized by more coarse surface features.

• *Craze remnants:* The presence of opened craze remnants, either within the crack origin regions or in adjacent areas, is further indication of ESC. In many cases, the final fracture will develop via ductile overload after the crack length has reached a critical size.

• *Stretched fibrils:* The final fracture zone can include stretched fibrils and other features indicative of ductile cracking. It is important to note that ESC is not a chemical attack mechanism; therefore, features that are normally associated with chemically induced molecular degradation will not normally be present.

• *Alternating bands:* Recent experimentation has shown that ESC commonly develops by a progressive crack-extension mechanism. Examination of fracture surfaces created under laboratory conditions reveals a series of alternating bands corresponding to crack extension cycles, as illustrated in Fig. 1. The observed bands are thought to represent repeated cycles of crazing, followed by crack extension via brittle fracture, consistent with the steps involved in creep and ESC failure mechanisms. This is illustrated in the diagram shown in Fig. 2.

Elements of ESC

Environmental stress cracking follows several tendencies regarding all three of the essential ele-

Sprinkler housing failure

Several molded plastic housings utilized in a commercial sprinkler application failed shortly after installation. The housings were molding from a polyacrylonitrile:butadiene: styrene (ABS) resin and were used in conjunction with a standard pipe-fitting. Fluoropolymer tape was the only allowed sealing method. The failures were typified by cracking within the plastic housing, which produced a substantial leak in the system. All of the parts failed within a single installation, and no formal complaints had been received from other sites.

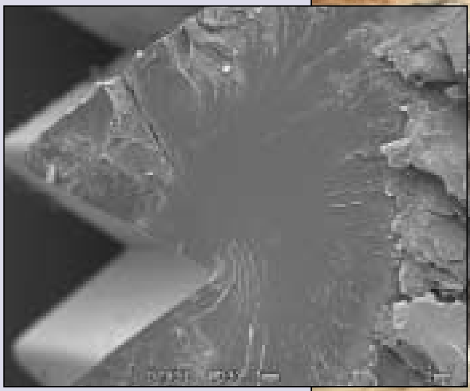

Fig. 5 - Images illustrate the cracking in the sprinkler housings.

Visual examination of the failed housings confirmed a high concentration of cracks on each of the parts. The observed fractures extended longitudinally down the housing, predominantly through the threaded region along the inner diameter, as shown in Fig. 5.

The cracks were generally oriented in a parallel pattern, and several cracks had progressed through the entire housing wall to the outer diameter. The macro features, especially the high concentration of parallel cracks, were characteristic of ESC failure. The housings were covered with dirt and debris from the agricultural application, as well as a soft, gummy material with the consistency of putty.

Microscopic examination of the fracture surfaces revealed multiple individual crack origins, with the apparent initiation sites located within the thread roots. The fracture surfaces presented a relatively coarse texture, with the overall appearance consistent with brittle fracture, in contrast to the normally ductile behavior exhibited by ABS resins.

Selected fracture surfaces were examined via SEM, and the observed features further indicatred ESC as the failure mode. The SEM inspection showed multiple crack origins. The crack origin areas displayed a relatively smooth morphology, indicative of slow crack growth. The origins were located at the thread roots, which exhibited a small radius, normally associated with severe stress concentration. Outside of the origin area, the fracture surface showed coarse features produced through rapid crack extension. A substantial level of secondary cracking was present over the entire fracture surface. Limited ductility, in the form of stretched fibrils, was observed exclusively within the final fracture zone.

Analytical testing of the rotor material, including FTIR, TGA, DSC, and melt flow rate determination, produced results consistent with the stated material description. No evidence of molecular degradation associated either with service conditions or the molding operation was found. Testing of the adherent, putty-like debris sampled from the housing threads generated an FTIR spectrum characteristic of an organic ester-based oil, blended with a silicate mineral filler. These results were characteristic of a commercial pipe dope sealant.

It was the conclusion of the investigation that the sprinkler housings failed via brittle fracture associated with ESC. The tensile stresses driving the cracking originated from the interference between the housing threads and the mating metal plumbing fixture. These stresses were likely severely concentrated by the relatively small radius at the thread root. The requisite chemical agent responsible for the failure was identified as an ester-based oil with a commercial pipe dope sealant. Ester-based oils are known to produce ESC failure within ABS resins, and pipe dope sealants have been widely recognized as deleterious to ABS pipe and fittings.

ments of the failure mode. These factors include the resin type, the chemical agent, and the type of stress.

Resin type

• *Amorphous structure:* Amorphous plastics are considerably more susceptible to ESC than semicrystalline resins. This is primarily attributed to the substantially greater free volume associated with amorphous resins, as compared with the orderly, compact structure of semicrystalline resins.

• *Low molecular weight:* ESC resistance decreases with reduced molecular weight of the plastic. This is true in terms of the material selected, and also in cases where molecular degradation has resulted in molecular weight reduction. The superior ESC resistance imparted by elevated-molecular-weight resin results from the increased level of molecular entanglement.

• *Lower crystallinity:* Within semicrystalline resin families, the level of crystallinity significantly impacts the ESC resistance. In general, higher levels of crystallinity, normally accompanied by an increased specific gravity, produce improved resistance to ESC failure.

Chemical agent

• *Hydrogen bonding:* Fluids with moderate levels of hydrogen bonding are generally more aggressive ESC agents than chemicals with extreme levels of hydrogen bonding. As such, organic esters, ketones, aldehydes, aromatic hydrocarbons, and chlorinated hydrocarbons are more severe than organic alcohols and aliphatic hydrocarbons.

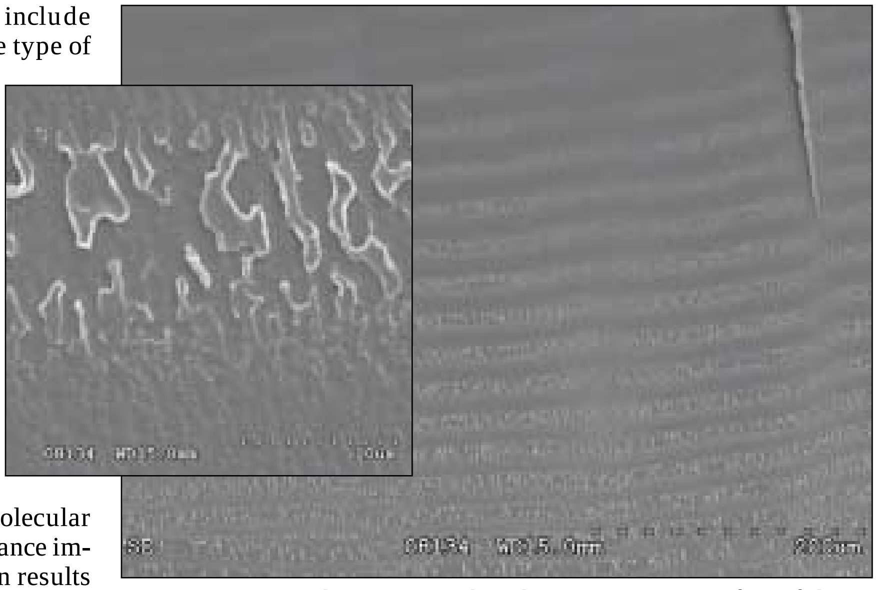

Fig. 1 - Scanning electron images show the progressive nature of ESC failure within a polycarbonate laboratory fracture.

• *Molecular size:* Chemicals with lower molecular weights are more aggressive ESC agents than higher molecular-weight counterparts. Thus, silicone oil is more severe than silicone grease, and acetone is more severe than methyl isobutyl ketone. This results directly from the size of the molecule, with smaller molecules having a greater ability to permeate into the molecular structure of the polymer.

Stress effects

• *Tensile stress:* ESC failure will occur within a material only under conditions of tensile stress. Tensile stresses are required to create the molecular disentanglement that leads to ESC. Compressive stresses, while sufficient to cause mechanical failure under some conditions, do not orient the molecules in ways conducive to ESC.

• *Residual stress:* Internal molded-in residual stresses combine with external stress to produce ESC. In many cases, the magnitude of the molded-in stress is sufficient to result in ESC. ■

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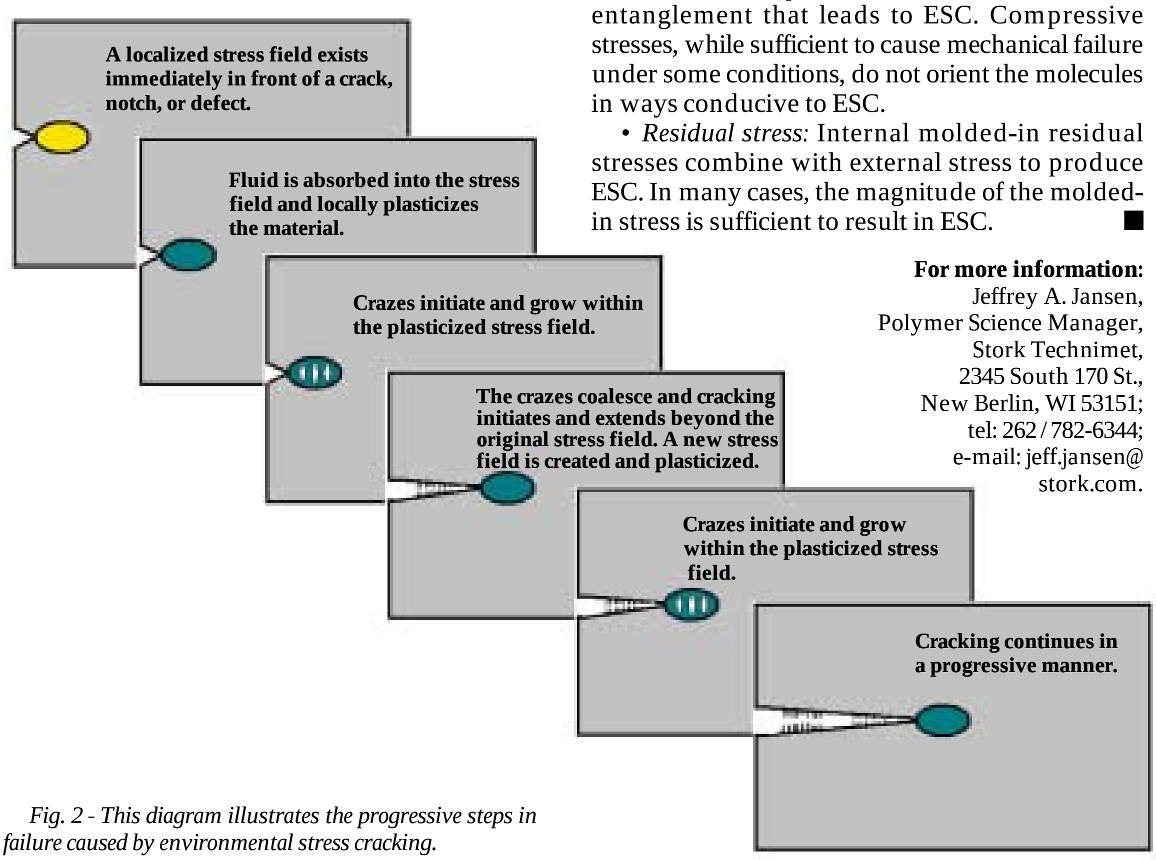

Fig. 2 - This diagram illustrates the progressive steps in failure caused by environmental stress cracking.