PLASTIC PART FAILURE CAUSED BY ENVIRONMENTAL STRESS CRACKING
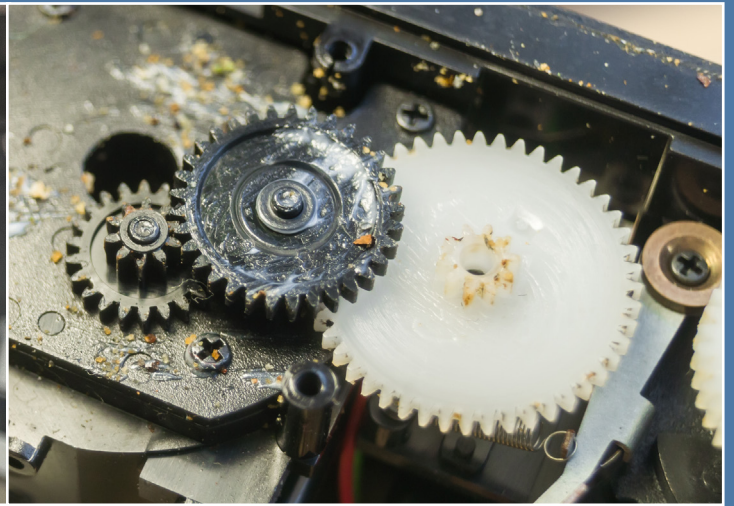
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PLASTICS

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Environmental stress cracking is the premature brittle failure of plastic materials caused by the combination of stress and chemical contact.

Amorphous thermoplastics like acrylic, polycarbonate, Noryl® modified PPO, and Ultem® (polyetherimide) are susceptible to brittle failure when exposed to adverse environmental conditions. Despite being strong, stiff, and tough engineering thermoplastics, their amorphous (disordered) molecular structure allows for the propagation of microcracks - usually emanating from mechanical fasteners, sharp internal corners, or other areas of high-stress. This characteristic failure mode can be facilitated by outdoor weathering, vibration, or most commonly by the combination of mechanical stress and incidental chemical contact.

This paper is intended to address the key considerations of plastic material selection, part design, and assembly in order to avoid environmental stress cracking and costly part failures.

Threads and mechanical fasteners create high levels of stress and crack-initiation points in plastic parts.

Self-lubricating gears and other mechanical components are often manufactured from semi-crystalline thermoplastics which are resistant to stress-cracking in industrial environments.
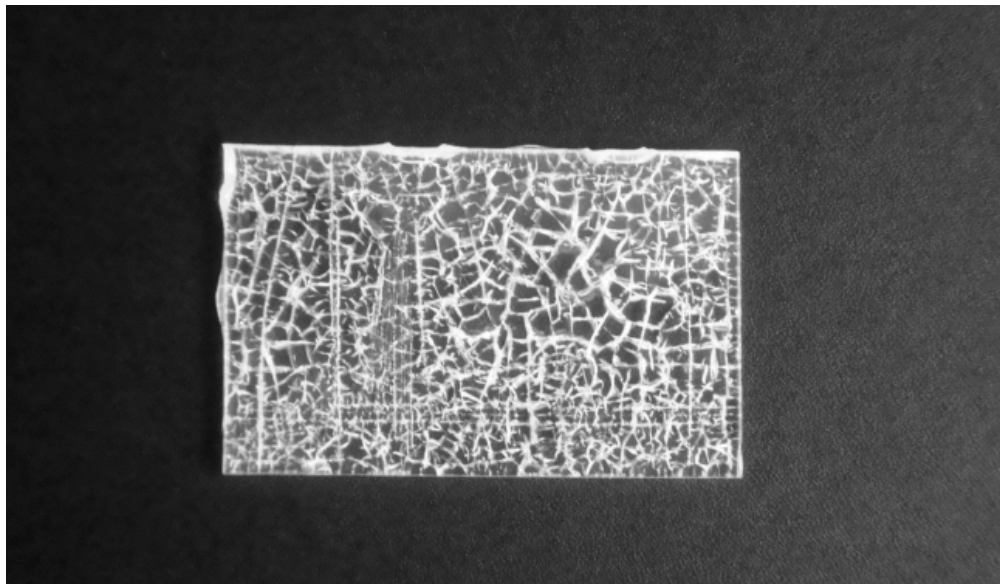
CREEP RUPTURE

When a plastic material is subjected to a constant stress below its yield point, there is a gradual change in dimension referred to as *creep strain* [1, 2]. After a certain amount of time, the *accumulated creep strain* may exceed design limits. Eventually, the intermolecular forces that hold the polymer chains together are overcome, the chains disentangle, and the part fractures in a brittle fashion [1-3]. This failure mode is called *creep rupture*. It can be caused purely by mechanical stress or by a combination of mechanical and environmental factors, such as chemical contact [4]. In the latter case, the failure mode is referred to as *environmental stress cracking (ESC)*.

ESC IS A FORM OF ACCELERATED CREEP RUPTURE

Environmental stress cracking is the premature brittle failure of plastic materials caused by the combination of stress and chemical contact [1, 4-6]. It is a form of accelerated creep rupture and one of the most common failure modes of plastic parts [1, 3, 5]. Characteristic signs of ESC include thin spider-web-like fibrils called *crazes* and multiple crack origins on the plastic surface [1, 7].

An effective way to demonstrate ESC is to perform a tensile creep rupture test, both with and without chemical contact. Figure 2 shows typical results [2]. For specimens in contact with the ESC fluid, the sharp increase in strain indicates the onset of ESC and the appearance of visible crazes in transparent polymers [2]. ESC involves brittle fracture rather than ductile yielding.

Figure 1. Photograph of an acrylic sample contacted with acetone, leading to failure. In addition to the large visible cracks, the surface contains many microscopic cracks.

Source: Neogi [8]

Figure 2. Typical tensile creep curves for a polymer in air (solid lines) and in contact with an ESC fluid (dashed lines) subject to various tensile stress levels. Contact with the ESC fluid expediates rupture.
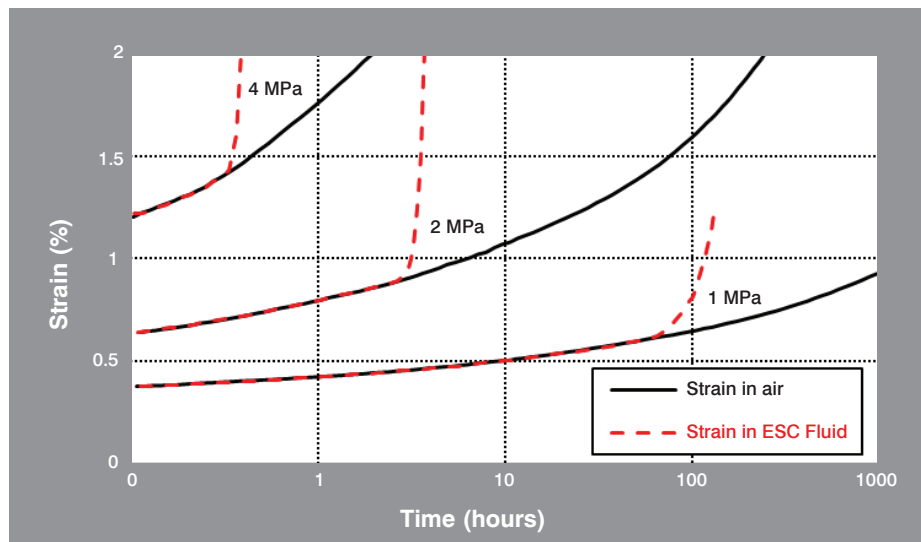
Source: Adapted from McKeen [2]

HOW IT WORKS (MECHANISM)

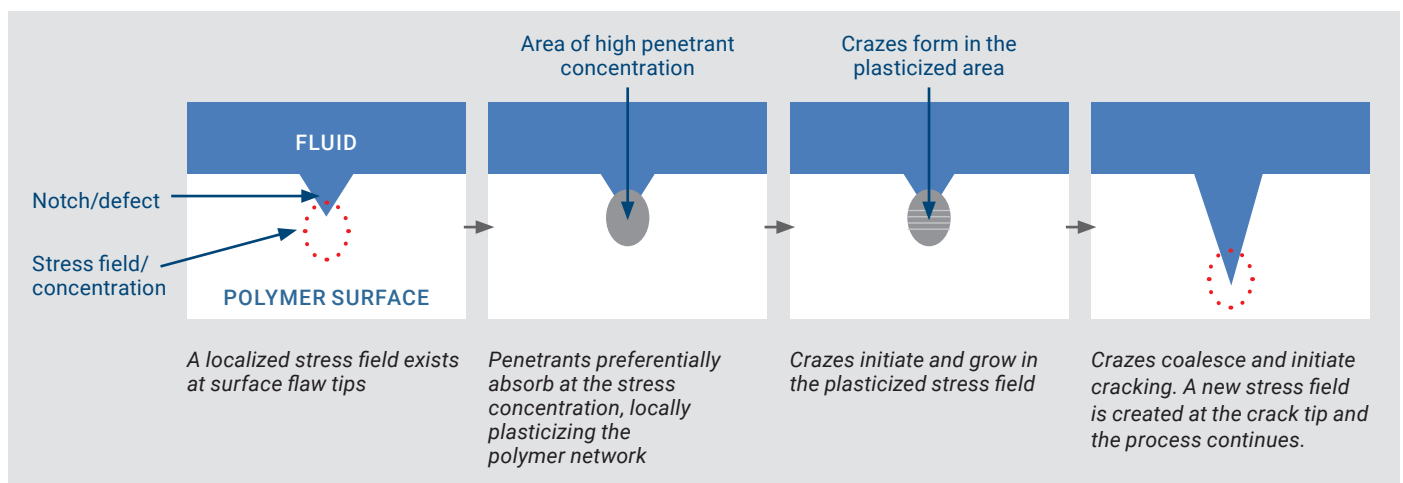Chemicals preferentially absorb into polymer surfaces at points of high stress such as notches, crack tips, inhomogeneities, or other surface flaws [1, 6, 7, 9-11]. The relatively small penetrant molecules plasticize the polymer network, leading to a localized reduction in mechanical properties and increased polymer chain mobility [1, 6, 7, 11]. The polymer chains tend to realign in the direction of maximum strain at the defect/crack front. Planar micro-voids emerge between the highly oriented chains which forms the "craze zone" [1, 11-13]. In a time-dependent process, the voids coalesce to form crazes which then rupture to form cracks [1, 12, 14]. The stress field created around the newly formed crack facilitates crazing at the crack front, and crack propagation continues until catastrophic failure occurs [1, 12, 14].

ESC is facilitated by the synergistic interactions of stress and chemical contact. Note that ESC does not proceed by chemical attack of the polymer. When chain scission reactions do occur, they are not considered to be a dominate factor in the failure mode [13]. The mechanism is purely physical in nature [2].

Figure 3. Environmental Stress Cracking Mechanism via Fluid Absorption at a Surface Notch

A localized stress field exists at surface flaw tips

Penetrants preferentially absorb at the stress concentration, locally plasticizing the polymer network

Crazes initiate and grow in the plasticized stress field

Crazes coalesce and initiate cracking. A new stress field is created at the crack tip and the process continues.

Source: Adapted from D.C. Wright and Jansen [12, 14]

SWELLING

The absorption of a penetrant into a polymer will also cause surface swelling. This forced increase in volume can cause an internal tensile stress that further facilitates crazing (working alongside the plasticization effect), especially in glassy polymers [7]. The amount of swelling depends on the compatibility of the penetrant and the polymer. Contact with moisture or chemicals that are soluble in the polymer can cause appreciable mass gain and dimensional changes. A method used to estimate the compatibility of a polymer-penetrant pair is given in a later section.

TESTING FOR ESC RESISTANCE

There are several ways to test the *environmental stress cracking resistance* (ESCR) of plastic materials (i.e., resistance to slow crack growth). ESCR can be quantified by critical strain, critical stress, or stress-time to failure [7]. However, ESC testing is primarily used as a comparative tool rather than for performance prediction.

The most well-known ESCR test is ASTM D1693 Standard Test Method for Environmental Stress-Cracking of Ethylene Plastics. Developed in the 1970s, the test involves multiple strips of polyethylene being notched and bent to a predetermined strain and then exposed to a chemical (a surface-active agent in this case) for a specified amount of time. The number of specimens that show evidence of ESC are noted.

The development of the test dates to the discovery of ESC in the late 1940s when H. G. Johnstone of the Western Electric Co. noticed cracking in low-density polyethylene (LDPE) wire jacketing after soap was used to help draw the wires through conduits [15]. Bell Telephone Laboratories developed the bent strip test to investigate this failure. The test would evolve into the ASTM D1693 test method still used today [11].

ISO 22088 test methods for ESCR can be applied to any thermoplastic and any chemical agent. In general, samples of plastic materials are bent (flexural) or pulled (tensile) to a certain strain and then contacted by a chemical. It is inherently difficult to compare the ESCR of different polymer chemistries since they are viscoelastic materials and undergo a time-dependent stress-relaxation during the test. Moreover, the level of stress at a specified strain is a function of modulus.

THE ESC PROBLEM

Approximately 15% to 25% of all plastic part failures are estimated to be related to ESC [7, 12, 16]. For glassy polymers, it is 40% or higher [7].

Amorphous Thermoplastics

ESC is a critical problem for amorphous (glassy) polymers such as PC, PMMA, ABS, PPO, PS, PSU, PEI, and PES. This is due to their disordered molecular structures and higher free volume (amount of empty space in the molecular structure) [4]. Molded-in stresses (i.e., residual or "frozen-in" stress from processing) can be enough to cause ESC in glassy polymers after contact with an ESC agent without any externally applied stress [7]. ESC occurs most commonly in glassy polymers such as polycarbonate by contact with organic solvents like acetone [17].

Semi-Crystalline Thermoplastics

On the other hand, tightly packed crystalline domains provide significant ESC resistance by reducing the free volume available for solvent penetration and providing a barrier to crack propagation [14]. However, ESC is still a concern for certain semi-crystalline polymers in adverse environments [7]. For example, many common detergents (i.e., surfactants or surface-active agents) are known to cause ESC in high-density polyethylene (HDPE).

ESC AGENTS: ABSORPTION AND DIFFUSION

The propensity of ESC depends on the *absorption rate* and *diffusion rate* phenomena of the polymer-penetrant pair. The absorption rate, or rate of chemical uptake, is directly related to solubility (interactions between the solvent and the polymer). A simple way to determine if a chemical is soluble in a polymer is to check the proximity of the solubility parameters. In fact, this quantity on its own is correlated to the potential severity of stress-cracking for many polymer-penetrate combinations. The closer the solubility parameters are, the more soluble (compatible) the chemical will be in the polymer which increases the likelihood of ESC.

In general, polymer-penetrant pairs with solubility parameters within 10 $cal^{1/2}cm^{-3/2}$ or 20 $MPa^{1/2}$ of each other may cause cracking or crazing under mild conditions (see Figure 4) [7]. Increasing the difference in solubility parameters generally increases the stress required to cause crazing. At the other extreme, where the solubility parameters are nearly equal, dissolution may disrupt plasticization effects and glassy crack propagation, or even induce crystallization (often observed in polycarbonate) which would actually *increase* stress-crack resistance [7, 18]. Therefore, the most aggressive solvents have solubility parameters close to but not equal to the solubility parameter of the polymer [18]. Table 1 on pages 9-12 includes solubility parameters for a variety of chemicals and polymers.

Figure 4. Typical correlation between the critical strain to crazing/cracking and the solubility parameter difference between the polymer and the ESC agent [7]. The dotted line illustrates how *very good* solvents may not be the most severe ESC agents.
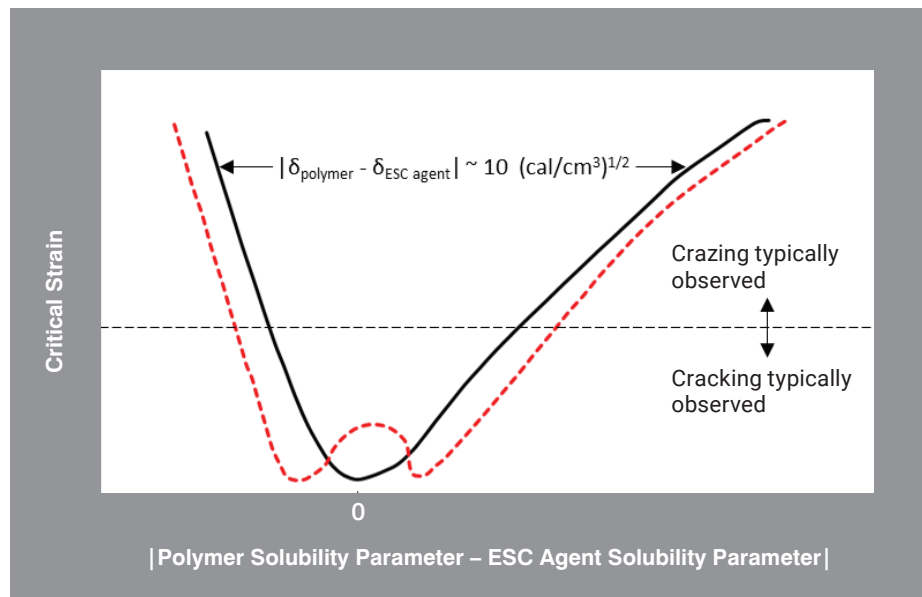
Source: Adapted from Robeson [7]

The correlation works well for polymer-alkane systems, but less so for pairs with significant degrees of hydrogen bonding or polar interactions. Nonetheless, the one-component solubility parameter approach is commonly used to predict the solubility of chemicals and plastics [19].

The total (one-component) solubility parameter for various polymers and chemical agents are widely available in the literature [7, 9, 16, 19-21]. An extensive list is included in Table 1 beginning on page 9 [19].

To account for molecular interactions such as dispersive forces, polar interactions and hydrogen bonding, partial solubility parameters may be applied. Hydrogen bonding effects are particularly significant. Fluids capable of *modest hydrogen bonding* tend to be the most aggressive ESC agents [14]. These compounds include halogenated hydrocarbons, ethers, ketones, aldehydes, esters, and nitrogen and sulfur-containing compounds [14, 19].

On the other hand, *strongly hydrogen-bonding* compounds like alcohols and aliphatic hydrocarbons tend to be less aggressive ESC agents [14].

The other principal factor that determines the propensity of ESC is the ability of a chemical to readily diffuse throughout a polymer network once it has been absorbed. Smaller and more linear molecules diffuse more rapidly and are more likely to cause severe stress cracking. In other words, low molecular weight, low molar volume, and low viscosity fluids tend to be more aggressive. For example, silicone oil is a stronger stress crack agent than silicone grease [14].

To obtain a reasonable guess for ESC propensity, consider (1) the proximity of the solubility parameters; (2) the expected degree of hydrogen bonding based on the chemical family; and (3) the molar volume of the fluid. Table 1 on page 9 includes each of these parameters for a variety of chemicals and polymers.

Note that the nature of contact between the chemical and the polymer can play a significant role as well. For instance, repeated wiping contact may be more detrimental to a plastic compared to complete solvent immersion, depending on the chemical, the polymer, and the part design.

In summary,

- Polymer-penetrant pairs with nearly equal solubility parameters are compatible with each other which increases the likelihood of ESC.

- Fluids capable of moderate hydrogen bonding are usually the most aggressive ESC agents.

- Low molecular weight, low molar volume, low viscosity fluids are usually more aggressive ESC agents.

- Predictive methodologies help filter candidate materials, however, empirical tests that closely resemble application conditions are required to make final determinations.

Table 1. Total Solubility Parameters for Polymers and Chemical Agents - Part 1

Compound	Degree of H-bonding*	δ (cal$^{1/2}$cm$^{-3/2}$)	Molar Volume (cm³/mol)
Polymers			
Polyethylene (PE)		8.0	
Polypropylene (PP)		8.0	
Polystyrene (PS)		9.2	
Polyvinyl chloride (PVC)		9.5	
Polymethyl methacrylate (PMMA) (Acrylic)		9.2	
Polyphenylene Oxide (PPO)**		8.5	
Polyetherimide (PEI)**		11.0	
Polycarbonate (PC)		10	
Acetal resins		11.1	
Nylon 6/6		13.5	
Alkanes			
n-Butane	L	6.8	101.4
n-Pentane	L	7	116.2
n-Hexane	L	7.3	131.6
n-Heptane	L	7.4	147.4
n-Octane	L	7.6	163.5
Dodecane	L	7.9	228.6
Cyclohexane	L	8.2	108.7
Methylcyclohexane	L	7.8	128.3
trans-Decahydronaphthalene (trans-Decalin™)	L	8.8	156.9
Aromatic hydrocarbons			
Benzene	L	9.2	89.4
Toluene	L	8.9	106.8
Naphthalene	L	9.9	111.5
Styrene	L	9.3	115.6
o-Xylene	L	8.8	121.2
Ethylbenzene	L	8.8	123.1
Mesltylene	L	8.8	139.8
Tetrahydronaphthalene	L	9.5	136
Halohydrocarbons			
Methyl chloride	M	9.7	55.4
Methyl dichloride	L	9.7	63.9
Chlorodifluoromethane (Freon 21)	L	8.3	72.9
Ethyl bromide	M	9.6	76.9
1,1-Dichloroethylene	L	9.1	79
Ethylene dichloride	L	9.8	79.4
Methylene diiodide	M	10.2	80.5
Chloroform	L	9.3	80.7
Ethylene dibromide	L	9.7	87
n-Propyl chloride	M	8.5	88.1
Trichloroethylene	L	9.2	90.2
Dichlorodifluoromethane (Freon 12)	L	5.5	92.3
Carbon tetrachloride	L	8.6	97.1
Tetrachloroethylene	L	9.3	101.1
Chlorobenzene	L	9.5	102.1
1,1,2,2-Tetrachloroethane	L	9.7	105.2
Bromobenzene	L	9.9	105.3
o-Dichlorobenzene	L	10	112.8
1,1,2-Trichlorotrifluoroethane (Freon 113)	L	7.3	119.2
1-Bromonaphthalene	L	10.6	140

Table 1. Total Solubility Parameters for Polymers and Chemical Agents - Part 2

Compound	Degree of H-bonding*	δ (cal$^{1/2}$cm$^{-3/2}$)	Molar Volume (cm³/mol)
Ethers			
Furan	M	9.4	72.5
Epichlorohydrin	H	11	79.9
Tetrahydrofuran	M	9.1	81.7
1,4,-Dioxane	M	10	85.7
Diethyl ether	M	7.4	104.8
Ketones			
Acetone	M	9.9	74
Methyl ethyl ketone	M	9.3	90.1
Cyclohexanone	M	9.9	104
Diethyl ketone	M	8.8	106.4
Mesityl oxide	M	9	115.6
Acetophenone	M	10.6	117.4
Methyl isobutyl ketone	M	8.4	125.8
Methyl isoamyl ketone	M	8.4	142.8
Isophorone	M	9.1	150.5
Di(isobutyl) ketone	M	7.8	177.1
Aldehydes			
Acetaldehyde	M	10.3	57.1
Furfural	M	11.2	83.2
Butyraldehyde	M	9	88.5
Benzaldehyde	M	9.4	101.5
Esters			
Ethylene carbonate	M	14.7	66
γ-Butyrolactone	M	12.6	76.8
Methyl acetate	M	9.6	79.7
Ethyl formate	M	9.4	80.2
Propylene-1,2 carbonate	M	13.3	85
Ethyl acetate	M	9.1	98.5
Diethyl carbonate	M	8.8	121
n-Butyl acetate	M	8.5	132.5
Isobutyl acetate	M	8.3	133.5
Isoamyl acetate	M	7.8	148.8
Dimethyl phthalate	M	10.7	163
Diethyl phthalate	M	10	198
Di-*n*-butyl phthalate	M	9.3	266
Tricresyl phosphate	M	8.4	316
Diocytl phthalate	M	7.9	377
Sulfur compounds			
Carbon disulfide	L	10	60
Dimethyl sulfoxide	M	12	71.3
Dimethyl sulfone	M	14.5	75
Acid halides and anhydrides			
Acetyl chloride	M	9.5	71
Succinic anhydride	H	15.4	66.8
Acetic anhydride	H	10.3	94.5
Carboxylic acids			
Formic acid	H	12.1	37.8
Acetic acid	H	10.1	57.1
n-Butyric acid	H	10.5	110

Table 1. Total Solubility Parameters for Polymers and Chemical Agents - Part 3

Compound	Degree of H-bonding*	δ (cal$^{1/2}$cm$^{-3/2}$)	Molar Volume (cm³/mol)
Nitrogen Compounds			
Acetonitrile	L	11.9	52.6
Acrylonitrile	L	10.5	67.1
Propionitrile	L	10.8	70.9
Benzonitrile	L	8.4	102.6
Nitromethane	L	12.7	54.3
Nitroethane	L	11.1	71.5
2-Nitropropane	L	9.9	86.9
Nitrobenzene	L	10	102.7
Ethylenediamine	H	12.3	67.3
2-Pyrrolidone	H	14.7	76.4
Pyridine	H	10.7	80.9
Morpholine	H	10.8	87.1
Aniline	H	10.3	91.5
N-Methyl-2-pyroolidone	M	11.3	96.5
n-butylamine	H	8.7	99
Diethylamine	H	8	103.2
Quinoline	H	10.8	118
Formamide	H	19.2	39.8
Dimethylformamide	M	12.1	77
N-N-Dimethylacetamide	M	10.8	92.5
Hexamethylphosphoramide	H	10.5	175.7
Monohydric alcohols			
Methanol	H	14.5	40.7
Ethanol	H	12.7	58.5
Ethylene cyanhydrin	H	15.2	68.3
Allyl alcohol	H	11.8	68.4
1-Propanol	H	11.9	75.2
2-Propanol	H	11.5	76.8
Furfuryl alcohol	H	12.5	86.5
1-Butanol	H	11.4	91.5
2-Butanol	H	10.8	92
Benzyl alcohol	H	12.1	103.6
Cyclohexanol	H	11.4	106
2-Ethyl-1-butanol	H	10.5	123.2
Diacetone alcohol	M	9.2	124.2
Ethyl acetate	M	10	115
n-Butyl lactate	M	9.4	149
Ethylene glycol monomethyl ether	M	11.4	79.1
Ethylene glycol momoethyl ether	M	10.5	97.8
Diethylene glycol methyl ether	M	8.5	130.9
Ethylene glycol monobutyl ether (EGBE)	M	9.5	131.6
2-Ethyl-1-hexanol	H	9.5	157
1-Octanol	H	10.3	157.7
Diethylene glycol monobutyl ether (DEGBE)	H	12.1	170.6

Table 1. Total Solubility Parameters for Polymers and Chemical Agents - Part 4

Compound	Degree of H-bonding*	δ (cal$^{1/2}$cm$^{-3/2}$)	Molar Volume (cm³/mol)
Phenols			
m-Cresol	H	10.2	104.7
Methyl salicylate	M	10.6	129
Polyhydric alcohols			
Ethylene glycol	H	14.6	55.8
Glycerol	H	16.5	73.3
Propylene glycol	H	12.6	73.6
1,3,-Butanediol	H	11.6	89.9
Diethylene glycol	H	12.1	95.3
Triethylene glycol	H	10.7	114
Water			
water	H	23.4	18

Data points are from Barton 1975 unless otherwise specified.
*Classification as high (H), moderate (M), or low (L) hydrogen-bonding (Barton 1975).
**Data points from D.C. Wright 1996 Table 2.2.

All statements and technical information contained in this table are for informational purposes only. Curbell does not guarantee the accuracy or completeness of any information contained herein and it is the customer's responsibility to conduct an independent review and make its' own determination regarding the suitability of specific products for any given application.

ENVIRONMENTAL CONDITIONS

Regardless of the compatibility between a polymer and a chemical agent, the propensity of any fluid to cause stress cracking will increase with the following factors:

- Strain on plastic part (often the most significant factor)

- Cyclic loading frequency

- Concentration of ESC agent in contact with the plastic part

- Exposure time

- Exposure temperature

An increase in the above factors will shorten the time-to-failure.

Environmental stress cracking occurs in acrylic after repeated contact with common glass cleaners.

Creep rupture occurs in regions of high strain.

POLYOLEFINS (POLYETHYLENE AND POLYPROPYLENE)

The stress-crack resistance of polyethylene increases with molecular weight and decreases with density. Ultra-high molecular weight polyethylene (UHMW-PE) has good ESC resistance. Low-density polyethylene (LDPE) has fair resistance, and high-density polyethylene (HDPE) has poor resistance. Polypropylene is not susceptible to ESC as a practical matter.

Pre-conditioning

If a plastic part is subject to a constant or cyclic stress for a long period of time prior to the environmental exposure, stress cracking typically occurs quickly. On the other hand, if a plastic part is fully immersed in a solvent prior to the stress exposure, significant swelling may reduce the propensity of crazing. Pre-conditioning strategies such as solvent immersion are used in unique situations as a preventative measure.

Material selection

The following considerations should be made when selecting plastic materials for applications where ESC may be of concern.

1. Polymer family
Semi-crystalline polymers like polypropylene and cross-linked polymers like cross-linked UHMW-PE have significantly greater environmental stress cracking resistance (ESCR) compared to amorphous polymers [4, 7, 14].

2. Fiber reinforcement
Fibrous reinforcements such as fiberglass enhance ESCR by bridging surface cracks and crazes [7]. This prevents facile crack propagation across the polymer surface [7]. Note that glass beads and particulate reinforcements have not been shown to provide substantial ESCR due to insufficient fiber length.

3. Molecular weight, crystallinity, and density
Increasing molecular weight increases polymer chain entanglements which reduces the propensity of brittle fracturing and ESC [18, 22]. The ability to bridge crazes and inhibit crack formation has been correlated with molecular weight [17]. Switching to a higher molecular weight grade of a specific polymer can be enough to prevent an ESC failure. For instance, cell cast acrylic sheet with a high molecular weight will have an enhanced ability to contend with mild chemical contact compared to lower molecular weight extruded sheet.

The reduced level of crystallinity in higher molecular weight grades is another factor that increases ESCR. The increased volume of tie-molecules (amorphous domains joining the crystalline domains) improves the elongation and ductility of the polymer [3, 11]. In other words, although crystalline domains provide ESCR, polymers with very high levels of crystallinity are more susceptible to brittle fracture.

TIPS TO AVOID ESC FAILURE IN PLASTIC PARTS

Consider secondary chemical contact

Unanticipated chemical contact, especially from the vapors of volatile compounds, is often the culprit in stress-cracked plastic parts [14]. It is important to evaluate the compatibility of a plastic with adhesives, lubricants, cleaning agents, anti-rust agents, plasticizers, and oils that may contact the part [14].

Here are a few additional tips to decrease the likelihood of ESC when assembling plastic parts:

- Clean all fasteners so that they are free from oil.

- Avoid elastomer washers that may outgas ESC agents.

- Avoid liquid thread lockers.

Minimize stress concentrations

When designing and assembling plastic parts that are susceptible to ESC, it is important to minimize stress. Here are a few tips to reduce the chances of part failure:

- Use round head or pan head screws with flat washers on both sides. Flat head screws or rivets can create a significant hoop stress that can result in stress-cracking.

- Oversize through holes to allow for thermal expansion (CTE) mismatch between the plastic part and the mating material.

- Minimize torque on fasteners.

- Position fasteners as far as possible from the edges of the part.

- Avoid 90-degree internal corners and add generous radii wherever possible.

CHEMICAL RESISTANCE DATA

Chemical resistance charts assign qualitative ratings for the resistance of plastic materials to various chemicals and environments [23]. The ratings typically reflect weight changes, dimensional changes, visual changes, and mechanical property retention for a certain exposure time.

Resistance to environmental stress cracking is one aspect of chemical resistance. Laboratory tests used to develop chemical resistance charts often involve unstressed test specimens. Although a polymer may be labeled as resistant to a chemical, the chemical may still induce ESC given other adverse environmental factors or stress concentrations imposed by the part design or assembly techniques.

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TECHNICAL EXPERTISE

Curbell white papers are intended to provide engineers and designers with basic information about the engineering polymers available as sheet, rod, tube, and film stock from Curbell Plastics. We invite you to contact Curbell via e-mail at **technicalsupport@curbellplastics.com** to discuss applications in detail.

ABOUT CURBELL PLASTICS

For 80 years, Curbell Plastics has been one of the nation's leading providers of plastic sheets, rods, tubes, and films, as well as fabricated parts, adhesives, and prototyping materials. Our customers range from small local businesses to large *Fortune* 500 companies and government agencies. We partner with organizations in dozens of industries, including aerospace, pharmaceutical, machinery manufacturers and sign fabricators. At Curbell, we understand the unique demands of each market and we have the expertise to help you meet your business needs. Whether your objective is to reduce manufacturing costs, improve productivity, or increase product reliability, Curbell can help.

OUR CAPABILITIES

Our branch network includes sales and warehouse locations throughout the United States. We offer a number of value-added services including custom cutting, fabrication, packaging, and kitting, as well as warehousing for just-in-time delivery. With Curbell, you get the plastics you want and the peace of mind you need, from technical support and design assistance at the earliest stages of product design, through production and after-sale support for each product we sell.

PUT US TO WORK FOR YOU

At Curbell, we are committed to providing the highest level of service to our customers. We recognize the urgency of customer needs, and we pride ourselves on providing quick and proactive solutions. Our tag line says it all – we appreciate the opportunity to earn your business and we invite you to *"Put us to work for you!™"*

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