
14 Applications – Environmental Stress Cracking in Polymers

Charles M. Hansen

ABSTRACT

Hansen solubility parameters (HSP) can be used to help predict which chemicals can cause environmental stress cracking (ESC) in polymers. ESC requires tensile stress and correlates when the RED number (relative energy difference in the polymer-solvent interaction) found from HSP considerations is plotted vs. a molecular size parameter, the molar volume, V . There are three distinct regions on this plot. There is a region at low RED including those challenge liquids that dissolve the polymer or are very aggressive, and ESC is not found as such. There is a region at high RED where the absorption is zero or not great enough to matter or else the absorption rate is slow enough to allow relaxation of the polymer in preference to ESC. ESC can occur in an intermediate region where there is some absorption of challenge liquid, although examples are given where ESC takes place without measurable absorption for good matches in HSP at relatively high stress/strain. The ESC region on these plots increases in size with increased tensile stress and/or increased critical strain.

INTRODUCTION

The previous chapter dealt with the chemical resistance of polymers and briefly touched on environmental stress cracking (ESC) as one aspect of chemical attack. This chapter expands the previous discussion of this special type of physical chemical attack on polymers. This form of failure represents at least 25% of all failures in plastics and therefore deserves special attention.¹ A failure by ESC can appear almost immediately, after minutes, after hours, or even after years, and often occurs without prior warning. There is a considerable literature on ESC. An excellent general source of the ESC literature is Wright's encompassing book on failures in polymers in general.¹ The present chapter is in many ways a supplement to this excellent work.

It is now clear that the polymer and the chemical that initiates the stress cracking must have similar or reasonably similar HSP. The ESC initiator need not dissolve the polymer as such. It has generally been assumed that some similarity in HSP is required such that some absorption occurs. More recently it has been recognized that measurable absorption is not always necessary for ESC to occur in some polymers. It is theorized that some physical movement, such as rotation of the polymer chain segments at the contact surface, can initiate the cracking process. In the latter case the similarity of the HSP of the challenge liquid may be to the HSP of an entity in the polymer chain that otherwise might be oriented away from the polymer surface. Under given conditions of strain it may prefer the environment of the ESC initiator once there is contact with the polymer. An understanding of this phenomenon seems to be evolving, but it is not complete as discussed below.

As stated above, the generally accepted mechanism for ESC has been that some absorption of the active chemical weakens the polymer structure locally, such that the tensile stress increases in adjacent regions. The tensile stress must be sufficient to locally pull polymer chains or segments of chains from the bulk. As the structure weakens locally, there is added stress in adjacent regions. This may be sufficient to cause a craze or crack, but in many cases further absorption or further chemical penetration seems necessary to repeat the same process until finally the stress becomes

too high and a craze or crack occurs. The number of chemicals giving ESC in a given polymer increases with increases in the level of stress/strain. The critical strain is that minimum value of strain at which the given challenge chemical will cause crazing/cracking in the given polymer. Any strain levels above this will result in ESC on contact with the given chemical. In some cases absorption of liquid permits stress relaxation, and expected crazing and cracking does not occur. This is presumably for a more or less massive uptake but not enough to completely dissolve the polymer. On the other hand, the polymer is plasticized and/or weakened by the absorption of these chemicals, and there is potentially a different type of problem to cope with.

If a chemical reaction is involved, such as with acids and bases, then the phenomenon is more properly called *stress corrosion cracking* (SCC).

Wright indicates that about 90% of ESC failures involve amorphous thermoplastic polymers with the remaining being found with partly crystalline thermoplastic polymers. Lustiger² lucidly describes the mechanism of ESC in partly crystalline polymers with polyethylene as an example. There are three types of polymer chains to consider in this case. Those with free ends (cilia) extending into the amorphous phase, those with chains extending into the amorphous phase but that loop back into the same lamella (loose loops), and tie-molecules or chains that extend from one lamella and anchor into an adjacent one. It is such tie-molecules that give the ultimate resistance to ESC. One must either break the tie molecules or pull them out of one of the lamella. In a sense these act like strong physical cross-links. Similar considerations are valid for amorphous thermoplastic polymers. Higher molecular weight enhances polymer chain entanglements, and thus reduces the tendency for ESC when solvent is absorbed. There are balances in properties and processing ability that are required for both amorphous thermoplastic polymers as well as partly crystalline polymers in order to achieve maximum ESC resistance and still maintain other desired behavior.

It is beyond the scope of this chapter to discuss models for the fracture mechanics mechanisms of ESC. Emphasis is placed on the consequences of similarity of HSP for the polymer and challenge chemical.

ESC INTERPRETED USING HSP

Wright¹ has discussed ESC data in terms of HSP for polycarbonate (PC), polyvinylchloride (PVC), polymethyl methacrylate (PMMA), and polystyrene (PS). ESC data are discussed for many other polymers including polyethylene (PE), polyamides (PA), polyether ether ketone (PEEK), polytetrafluoroethylene (PTFE), and styrene-acrylonitrile copolymer (SAN). There are many practical examples of how not to do things.

Barton³ has discussed in detail the theory and application of the cohesion (solubility) parameters including HSP for many systems, as witnessed by the 739 pages in his book and hundreds of references. Environment-induced degradation is also discussed with various plots for poly(2,6-dimethyl-1,4-phenylene oxide), PS, PMMA, PVC, and polysulfone. The latter three are found originally in Vincent and Raha⁴. Wyzgoski⁵ constructed several plots to help interpret ESC data for nylon (PA) 6,6 using HSP. Hansen and Just⁶ studied ESC in the COC-type polymer called Topas[®] 6013 from Ticona. [Figure 14.1](#), shows two essentially concentric HSP spheres resulting from this work. The inner sphere encompasses those solvents that dissolve the polymer, whereas the outer sphere encompasses these as well as those giving ESC for the given samples. Additional HSP correlations for ESC in PET, PCTG, and PC were reported for ESC (critical strain) data from Moskala and Jones⁷. HSP correlations for ESC in PEI using data from⁸ were also reported. All of these HSP correlations are included in [Table 14.1](#).

The HSP correlations for ESC reported in [Table 14.1](#) must be considered with care. In the first place there are other factors than HSP that are important, including the size and shape of the given challenge molecule in addition to the state of stress/strain, which is not always well defined. Another point to be remembered is that the RED number (Equation 1.10) refers to the correlation in question. The same solvent polymer pair will have different RED numbers for a HSP correlation of true

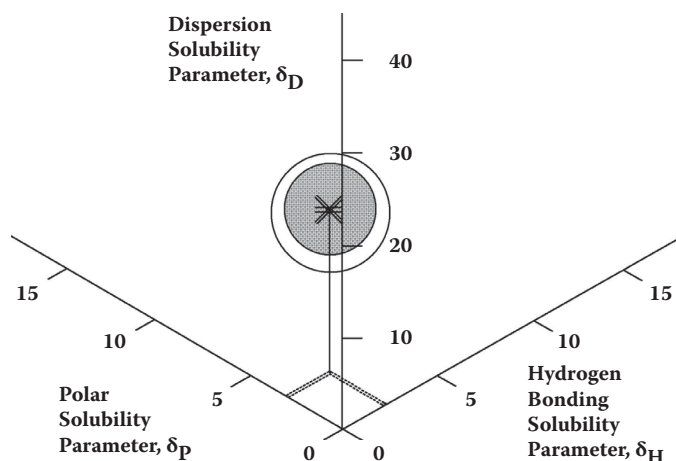


FIGURE 14.1 Three-dimensional HSP plot showing those solvents that dissolve the COC polymer, Topas 6013, Ticona, in the shaded region, and those that induce ESC in the clear shell. The two HSP spheres are almost concentric as can be seen from the data in Table 14.1. (Reprinted with permission from Hansen, C.M. and Just, L., *Ind. Eng. Chem. Res.*, 40(1), 21–25, 2001. Copyright 2001 American Chemical Society.)

TABLE 14.1
HSP Correlations for ESC in Polymers

Polymer	δ_D	δ_P	δ_H	R_0	FIT	G/T ^a
Topas 6013 Solubility	18.0	3.0	2.0	5.0	1.000	8/43
Topas 6013 Sol. + cracks	17.3	3.1	2.1	6.4	0.974	15/43
PC critical strain <0.6% ^b	21.5	9.5	5.1	12.9	0.857	18/47
PVC crit.str. <0.6% ^c	16.0	10.0	5.0	10.7	1.000	5/16
PET crit. str. <0.6%	21.3	4.5	12.3	13.9	1.000	12/19
PCTG crit. str. <0.55%	18.3	9.3	11.3	8.0	1.000	8/19
PCTG crit. str. <0.50%	18.8	8.8	10.8	7.9	0.989	6/19
PC crit. str. <0.31%	18.0	9.0	6.0	10.0	1.000	9/18
PEI Ultem [®] 1000 600 psi	17.3	5.3	4.7	3.3	1.000	3/20
PEI Ultem 1000 1200 psi	17.0	6.0	4.0	4.0	1.000	4/20
PEI Ultem 1000 2500 psi	17.4	4.6	9.0	7.2	0.967	9/20
PEI Ultem 1000 solubility	19.6	7.6	9.0	6.0	0.952	8/45

Note: Units are MPa^{1/2}. All correlations from Reference 6, except as noted. See also Chapter 12; Ultem is a registered trademark of the General Electric Company.

^a G/T is the number of “good” or attacking solvents relative to the total number of solvent data points used in this correlation.

^b Data from Reference 10 through Reference 14.

^c Data from Mai, Y.-W., *J. Mater. Sci.*, 21, 904–916, 1986. With permission.

solubility than it will have for a correlation for ESC where the “good” solvents have critical strains less than, say, 0.6%. HSP correlations can be made with many different types of data (barrier properties, wetting behavior, swelling, solubility, sedimentation rates, etc.) as discussed elsewhere in this book. The term RED number is intimately connected with a given HSP correlation.

Hansen⁹ used data from various sources^{6,10-13} to construct a new type of plot to correlate ESC data. This plot uses the RED number, Equation 1.10, and the molar volume, V , of the test chemicals. Figure 14.2 is such a plot for a large number of liquids in contact with small, injection-molded cylinders of a COC-type polymer called Topas[®] 6013 from Ticona.^{6,9} There are three distinct regions on this plot. There is a region at low RED including those challenge liquids that dissolve the polymer or are very aggressive, and ESC is not found as such. There is a region at high RED where the absorption is zero or not great enough to matter, or else the absorption rate is slow enough to allow relaxation of the polymer in preference to ESC. ESC can occur in an intermediate region where there is some absorption of challenge liquid, although examples are given below for other polymers where ESC takes place without measurable absorption for good matches in HSP. The ESC region on these plots increases in size with increased tensile stress and/or higher values of strain.

Closer study of Figure 14.2 shows that there are several liquids that do not give ESC whereas this would normally be expected from their position on this plot. From Table 14.2, it can be seen that these include methyl isobutyl ketone, acetophenone, and nitrobenzene. These are surrounded on the plot by liquids that do result in ESC including *n*-hexane, *n*-butyl acetate, ethyl acetate, and diethyl ether. The RED numbers and molecular volumes for all seven of these liquids are comparable. The explanation lies in the fact that the four liquids giving ESC have measurable absorption, whereas the three not giving ESC apparently do not absorb at all under the test conditions. It has been determined that 1,4-dioxane, methyl isobutyl ketone, acetophenone, and phenyl acetate do not absorb into this polymer at room temperature.¹⁴ The methyl “side-group” on the methyl isobutyl ketone, and the benzene rings in acetophenone, nitrobenzene, and phenyl acetate, are evidently sufficient to provide the steric hindrance that prevents absorption. Methyl isobutyl ketone does give ESC at higher stress levels.

All of the test liquids causing ESC failure in the immersed COC cylinders had measurable surface resistances retarding absorption, but they did absorb.¹⁴ Surface resistance phenomena may play an important part in the ESC process itself. Delayed absorption can also potentially lead to postponing a catastrophic ESC failure beyond normal testing times. Chapter 16 in this book is therefore dedicated to absorption and diffusion in polymers, and especially emphasizes the frequently overlooked surface resistance. This surface resistance is thought to originate primarily from the rate at which adsorbing molecules can locate a hole in the polymer surface large enough to accommodate them. Larger and more structurally complicated molecules have much more difficulty finding such a suitable hole, so the surface transport coefficient is inversely proportional to the molecular cross-section. Molecules that are too large can simply not enter the polymer. Once an adsorbed molecule locates in a suitable hole, the rate of motion into the bulk is dependent on the local diffusion coefficient. Therefore the surface transport coefficient is directly proportional to the diffusion coefficient. See the discussion in Chapter 16 for more details and examples.

Figure 14.3 and Figure 14.4 use the same parameters, RED vs. V , for correlating ESC in the polymers PC and PVC, respectively. The data used to construct these were taken from references¹⁰⁻¹³, that is, from the older literature. It can be seen that additional liquids will give ESC as the critical stress levels become higher.

Before proceeding to perhaps still more complicated theories and situations in the next section, one should be reminded that there are large variations in the critical strain even for the hexane isomers, which all have very similar total (Hildebrand) or Hansen dispersion solubility parameters. For PC, these isomers have critical strains that increase from 0.85% to 1.68% as branching increases.¹² These data clearly reinforce the need for consideration of shape.

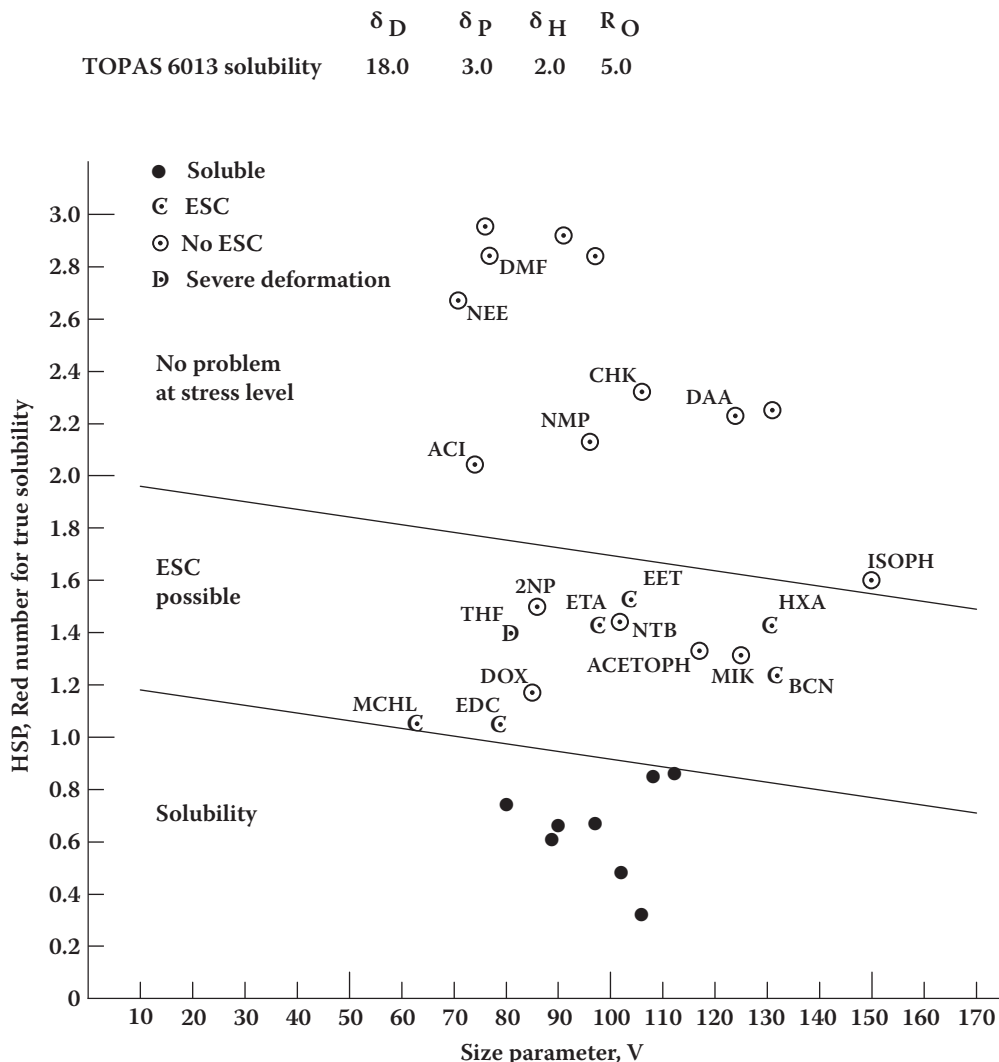


FIGURE 14.2 Plot of ESC and solubility data for injection-molded cylinders of a COC polymer (Topas 6013, Ticona) using RED number vs. molar volume. There is a region of solubility (RED less than 1.0), an intermediate region for ESC, and a region at higher RED where ESC is not found. The ESC solvents all have linear molecular structure. Data from Reference 6. Symbols are explained in Table 14.2. (Reproduced from Hansen, C.M., *Polym. Degradation Stability*, 77, 43–53, 2002. With permission from Elsevier Science.)

ESC WITH NONABSORBING STRESS CRACKING INITIATORS

Recent research has shown that even nonabsorbing chemicals can induce ESC, in some cases very rapidly.^{15–17} It is presumed that there are many additional cases of this kind, but they have not been reported as such. One possible explanation for this is HSP-induced motion of the polymer chain segments in the surface. This phenomenon is called *surface mobility* here and has also been discussed in Chapter 15 and Chapter 18. An example of surface mobility is contact with water converting surfaces like those of peat moss from hydrophobic to hydrophilic. An applied water droplet initially beads up but soon soaks readily in. The surface again becomes hydrophobic when the water is gone. This might be considered as Nature's valve to conserve water within a system. There are other examples given in Chapter 18. Rotation or other form of polymer chain segment

TABLE 14.2
Symbols Used in Figure 14.2

Symbol	Compound
ACI	Acetone
ACETOPH	Acetophenone
BCN	Butyl acetate
CHK	Cyclohexanone
DAA	Diacetone alcohol
DMF	Dimethyl formamide
DOX	1,2-Dioxane
EDC	Ethylene dichloride
EET	Diethyl ether
ETA	Ethyl acetate
HXA	<i>n</i> -Hexane
MCI	Methylene dichloride
MIK	Methyl isobutyl ketone
2NP	2-Nitropropane
NEE	Nitroethane
NMP	<i>N</i> -methyl-2-pyrrolidone
NTB	Nitrobenzene
THF	Tetrahydrofuran

motion may also be sufficient to start the cracking process. All of the ESC cases known to the author where absorption has not been measurable have had relatively high stress/strain imposed on the samples. There have been many other undocumented cases of ESC where one would not suspect absorption of the ESC initiator. These include contact with chemicals in hair spray, deodorants, hand creams, butter, and various kinds of oils including essential oils. In all cases, it is thought that the affinity of the active chemical must be high or moderately high, such that even though it cannot absorb, it is still capable of inducing motion in the polymer chains at the surface.

A related study of surface phenomena by Nielsen and Hansen¹⁸ explored whether ESC could be predicted by the wetting behavior of the challenge chemicals on PC, COC, and ABS type polymers. A large number of challenge chemicals were divided into three groups. Group A included those that spontaneously spread when applied as a droplet. Group B included those that would not spontaneously spread, but which would not retract either, when they were applied as films. Group C liquids did not spontaneously spread and retracted when they were applied as films. It was found that all A and B liquids gave ESC, although the B types had higher critical strains in general. Some type C liquids gave ESC and others did not. Retraction of an applied film is not an indication that ESC will not occur. Contamination of the test surface may also lead to retraction of an applied film, for example, where this would not occur otherwise. Care must be taken, and this test is only an indication of a potential problem. ESC was found for PC polymers with polydimethylsiloxanes having molecular weights of 340 and below but not for those with 410 and above. Exactly why this happens is not known, but surface entry or lack of same (see Chapter 16) and surface mobility of polymer molecules may both be involved.

DISCUSSION

HSP correlations of ESC phenomena have been presented for a number of common polymers. As stated above, the mechanisms for crazing and crack initiation and growth have not been discussed in detail here. The basis of the failures is the pulling of polymer chains from each other in all cases,

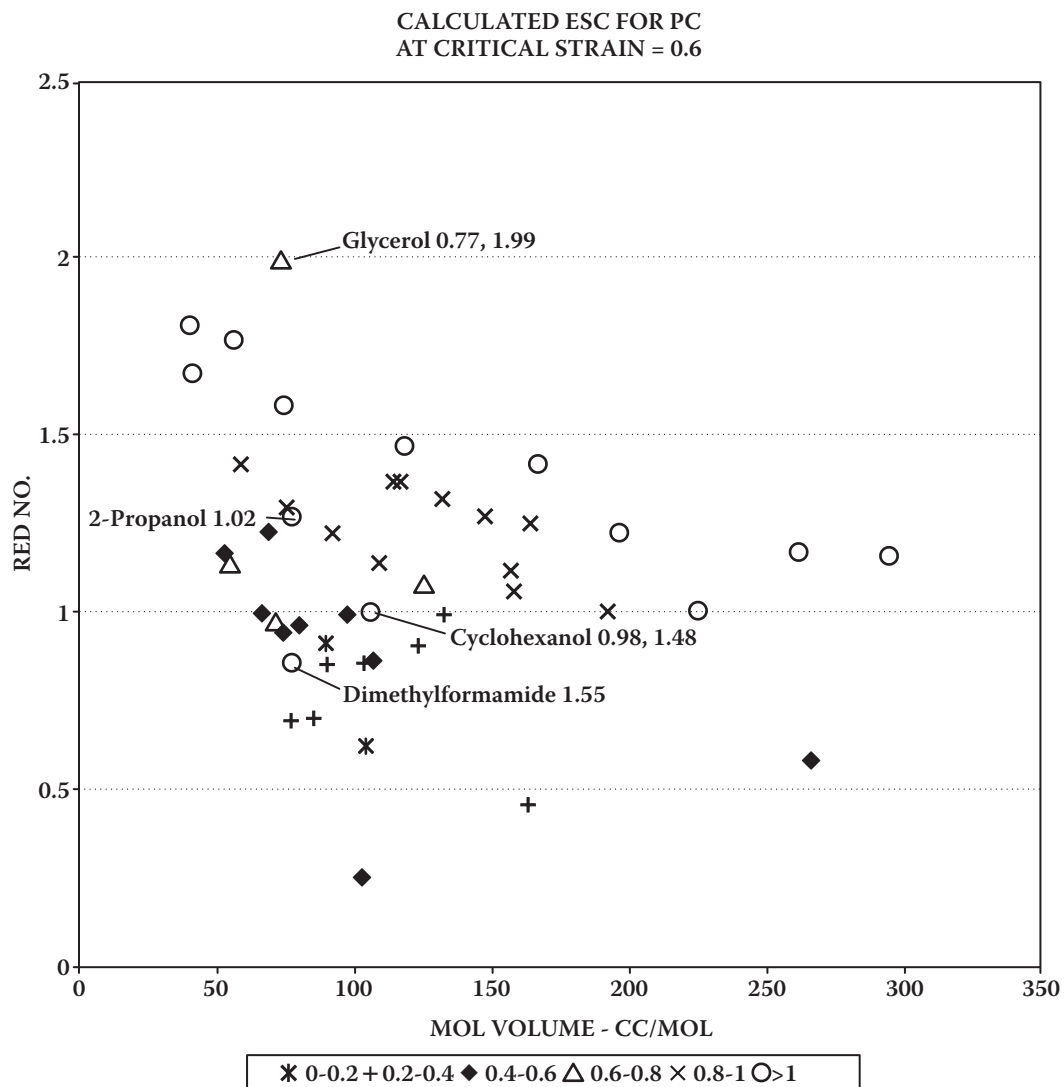


FIGURE 14.3 Plot of ESC data for polycarbonate (PC) using data from Mai¹⁰ and others¹¹⁻¹³ to establish a HSP correlation based on critical strain since true solubility data was lacking. The limit for critical strain was chosen as 0.6%. Liquids with critical strains below this value should have RED less than 1.0, just as liquids with critical strains above this should have RED larger than 1.0. Specific data and a discussion regarding the correlation are included in the text. Higher critical strains lead to larger ESC regions on this plot. The critical strains are indicated in the caption. (Reproduced from Hansen, C.M., *Polym. Degradation Stability*, 77, 43-53, 2002. With permission from Elsevier Science.)

however. A more detailed discussion of the phenomena involved is considered beyond the scope of this chapter. HSP has been used as a correlating parameter, necessarily with other parameters such as molecular size and shape of the challenge chemical and the stress/strain condition of the samples, to provide improved predictability, and to ask new questions regarding ESC.

Figure 14.1 shows that the ESC solvents have RED numbers slightly larger than those required for solubility. The data for this figure are found in.⁶

Figure 14.2 clearly shows that the molecular shape of the challenge molecules is important in addition to V. ESC may occur for a challenge chemical with a linear molecular structure, but not

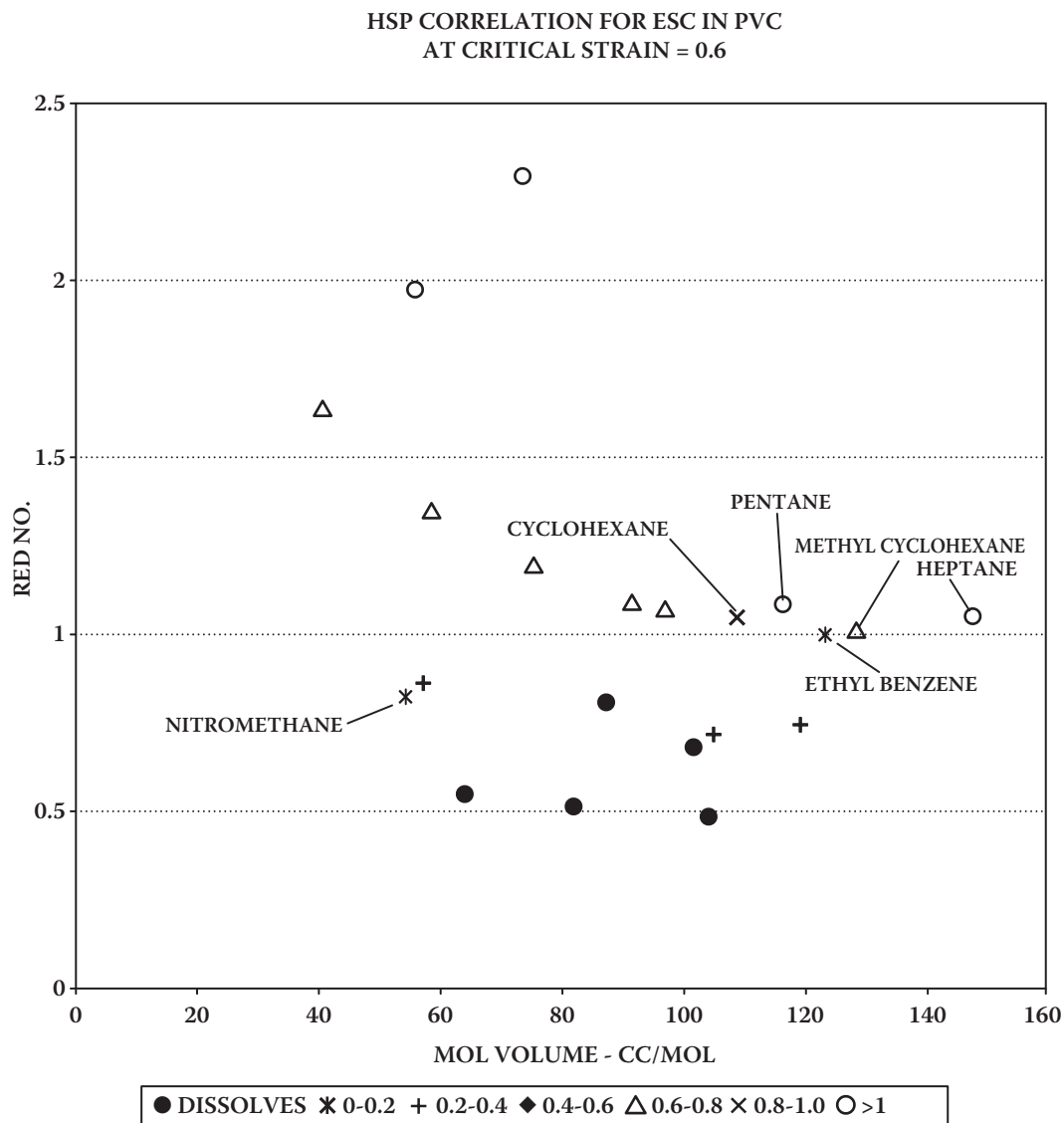


FIGURE 14.4 Plot of ESC data for polyvinylchloride (PVC) using data from Mai¹⁰ to establish a HSP correlation based on critical strain. ESC data were used for the correlation since specific solubility data on these samples were not available. The limit for critical strain was chosen as 0.6%. Solvents with critical strains below this value should have RED less than 1.0, just as solvents with critical strains above this should have RED larger than 1.0. Higher critical strains lead to larger ESC regions on this plot. The critical strains are indicated in the caption. (Reproduced from Hansen, C. M., *Polym. Degradation Stability*, 77, 43–53, 2002. With permission from Elsevier Science.)

for one with the same RED and V, but with a cyclic or more branched structure. The absorption rate of the bulkier molecules is too slow or they may not even be able to absorb altogether. The samples providing the data for this figure were small cylinders, so it was impossible to determine critical strains for the given liquids with these samples.

Figure 14.3 clearly shows larger ESC regions for higher critical strain limits for polycarbonate. More solvents logically give ESC as the strain increases. The data used in this figure were found in.^{10–14}

Figure 14.4 shows the ESC behavior of PVC using data taken from the literature.¹⁰ This figure confirms the ability to use this type of plot to correlate and predict ESC in polymers.

It is not unusual for suppliers of polymers to change compositions without indicating what has been done and to continue to use the general indication of polymer type, such as PC. Thus, the PC data in Figure 14.3 and the PVC data in Figure 14.4 may not be valid for all polymers of these nominal types. This is a significant problem in further research and developing fundamental understanding. Researchers either must work with commercial materials they do not have full knowledge of, or else take the path of making test materials to be certain of what is being dealt with. In the latter case, the information may not apply directly in practice because the practical materials may have added components. This dilemma apparently has no fully satisfactory solution.

CONCLUSION

HSP have been used to develop correlations of ESC. It would appear that testing is still required to ascertain what behavior is to be expected, but these correlations clearly indicate where the problems will be greatest. It is usually the unexpected events that cause the catastrophic failures, but designs or changes in designs that lead to increased tensile stress have also been the causes of ESC in practice. Care is especially required whenever the HSP of the polymer gets too close to the HSP of potential challenge chemicals. The required affinity between active chemical and polymer allows correlations of ESC with HSP, most often with the simultaneous need to consider the size and shape of the active chemical and the stress/strain condition of the polymer.

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