

# Solvent Crazeing as a Stress-Induced Surface Adsorption and Bulk Plasticization Effect

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## SYNOPSIS

In solids with low bulk modulus, like polymer glasses, concentration of stress due to surface defects and other kinds of inhomogeneities can induce substantial surface tension reduction and bulk plasticization in extremely localized regions. This effect becomes important in the presence of organic liquids. As a liquid comes into contact with the polymer surface and as stress is applied, a point is reached when the work to draw new surface area becomes minimal. In addition, at least up to a diffusion limited extent, bulk solvation can also take place locally. At this point, solvent crazing initiates in the presence of a triaxial stress field, and craze fibrils are easily drawn with additional deformation. For van der Waals (WL) interactions between polymer and solvent, two different expressions for solvent craze initiation have been derived. The first is derived assuming interfacial tension reduction (ITR) is the dominant mechanism for solvent craze initiation. The second is derived assuming that flaw tip bulk plasticization (BP) is the main mechanism for solvent craze initiation. Existing experimental data on six different glassy polymers was also examined with respect to the above two expressions. A relatively good functional relation (straight line passing near the origin) was found for a wide spectrum of glassy polymers and apolar (WL) liquids, for both the (ITR) and (BP) cases. Additional assumptions made in this analysis, especially about the stress concentration factor and the bulk modulus of the materials, indicate a better correlation with interfacial tension reduction data, in the case of (WL) liquids. However, better controlled experiments would be necessary to properly identify the mechanisms of environmental crazing, even in the case of (WL) liquids. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Crazing initiation and propagation in glassy polymers is known to be greatly enhanced in the presence of organic liquids and vapors.<sup>1-5,7</sup> The general pattern of the mechanical behavior of polymer glasses in the presence of organic liquids can be summarized as follows:<sup>4</sup>

In weak swelling agents, relatively stable crazes are produced through the application of tensile stress. Crazes formed in this way can maintain stress for a substantial length of time. In moderately strong swelling agents, unstable crazes form with the ap-

plication of tensile stress. After initiation, they turn into cracks in a very short time. Sometimes, even in the absence of external tensile stresses, solvent crazes can initiate as the result of internal residual stresses.

The dramatic drop of critical tensile stress and strain  $\epsilon_c$  for crazing in the presence of various organic liquids is generally attributed to either one of the following: (a) a decrease in surface energy required to form the fibrillar structure of the craze; (b) a decrease in flow stress due to plasticization at the craze tip where fibrils are drawn.

A number of investigators have tried to clarify which of the above mechanisms is dominant in solvent craze initiation.

Kambour et al.<sup>1,2,5,6</sup> measured the critical strain  $\epsilon_c$  for craze initiation of different glassy polymers in

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various organic liquids. They found that correlation between solubility parameter and  $\epsilon_c$  was not acceptable for all of the polymers tested. They also noted that for certain liquids with very low solubility in the polymers tested, crazing action had to be attributed to surface tension reduction effects.<sup>1</sup> However, in other experiments, these authors measured the  $T_g$  of solvent-equilibrated films of the material.<sup>2</sup> They found a good correlation between  $\epsilon_c$  and  $T_g$ . Therefore, they finally concluded that plasticization is the only important, fundamental role of the organic agent in solvent crazing.<sup>2,5</sup>

Vincent and Raha<sup>3</sup> examined the correlation between the solubility parameter of various liquids, and  $\epsilon_c$  for PMMA, PVC, and polysulfone (PSF). They found that crazing and cracking cannot be adequately explained solely by the solubility parameters of the liquids. Hydrogen bonding properties of the liquids were found to be of crucial importance.

Kramer et al.<sup>8</sup> were able to directly measure the change in the normal component of local stress  $\Delta\sigma_{\text{craze}}$  acting on the craze lips. The change in  $\Delta\sigma_{\text{craze}}$  was recorded when various water methanol solutions were introduced into the craze. A good correlation was found between  $\Delta\sigma_{\text{craze}}$  and fibril surface tension reduction  $\Delta\gamma$  after the introduction of the methanol-water solution.

One of the main difficulties in resolving the question of whether it is surface tension reduction or solvent plasticization which is responsible for craze initiation is the fact that most organic liquids that spread on the surface of polymers are also mild to strong solvents. Therefore, the two mechanisms do not exclude one another, but on the contrary, are complementary. Another difficulty comes from the fact that correlation between critical strain for crazing  $\epsilon_c$  and surface tension or solubility parameters of the organic liquids are not expressed in quantitative terms.

In this work, quantitative relations between (1) critical stress for crazing and surface tension, and (2) critical stress for crazing and solubility parameters are derived for van der Waals-Lifshitz (WL) type of interactions.

Gent<sup>9</sup> was the first to make the assumption that hydrostatic tension causes equilibrium swelling in excess of that occurring in the unstressed material. The excess swelling occurring at flaw tips in specimens under tension is expected to reduce the local  $T_g$  and, thus, aid plastic flow of the polymer chains under stress. The hydrostatic tension assumption is also followed in this study. However, here surface and solvent thermodynamic interactions have been both taken into account.

An attempt will be made to demonstrate that materials with low bulk modulus, like polymer glasses, can be very susceptible to polymer-organic liquid interactions under dilational stress, so that, in many cases, crazing initiates before homogeneous yielding takes place. Previous experimental data for six different polymers are also reviewed with respect to the above discussion.

### Stress Concentration Effect

When a tensile stress  $\sigma_{ij}$  is applied to a solid, the negative pressure  $P_o$  produced is given by

$$P_o = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3 \quad (1)$$

However, near surface cracks, defects, etc., negative pressure will, in general, be higher due to stress intensification. Therefore, certain regions of the material are expected to be under a higher negative pressure,  $P > P_o$ . This negative pressure  $P$  will, in turn, change the local molar volume of the material by  $\Delta V$  given by

$$\Delta V = -(-P)V/B \quad (2)$$

where  $B$  is the bulk modulus and  $V$  is the molar volume of the polymer assumed to be constant over the range of pressures considered. Volume creep resulting from the time-dependent bulk modulus  $B(t)$  is expected to affect the local volume changes. In addition, it must be noted that eq. (2) is true for small volume changes.

Also, the density of the polymer, defined as

$$\rho = M/V \quad (3)$$

where  $M$  is the molar weight and  $V$  the molar volume, will change due to the dilational effect of the negative pressure, so that near the stress concentrating regions

$$V_{\text{stress}}^{\text{region}} = V + \Delta V = V(1 + P/B) \quad (4a)$$

and

$$\rho_{\text{stress}}^{\text{region}} = M/(V + \Delta V) = \rho(1 + P/B)^{-1} \quad (4b)$$

The local changes in molar volume and density given from eq. (4) are expected to affect both the surface tension of the polymer and the solubility parameter of the nearby region.

## Surface Tension Reduction

The surface tension  $\gamma_p$  of a polymer in air is a measure of the reversible work per unit area required to increase the surface of the material.

In a polymer glass, both van der Waals Lifshitz interactions (WL), and acid base interactions (AB), will generally exist.<sup>10,11</sup> Present trends favor the summing of all nondispersive forces (polar, hydrogen, etc.) into acid/base terms.<sup>10</sup> The surface tension of a polymer is

$$\gamma_p = \gamma^{\text{WL}} + \gamma^{\text{AB}} \quad (5)$$

where  $\gamma^{\text{WL}}$  and  $\gamma^{\text{AB}}$  are the surface tensions from (WL) and (AB) interactions, respectively.

The surface tension is related to the density  $\rho$  of the material through Macleod's relation:<sup>12</sup>

$$\gamma = \gamma_o \rho^n \quad (6)$$

where  $\gamma_o$  and  $n$  are constants independent of temperature, and  $\gamma_o$  is dependent only on the chemical constitution. The values for  $n$  are:  $n = 3$  for apolar polymers and  $n = 4.5$  for polar polymers.<sup>13</sup> In this work, it is assumed that  $n = 3$  the same for all polymers considered.

Under stress, the surface tension of the polymer will not be the same over the whole surface. At the regions where stress is concentrated, the dilational effect of the negative pressure will eventually change the local density. Thus, from (4b) and (6),

$$\gamma_{p_{\text{stress}}}^{\text{region}} = \gamma_p (1 + P/B)^{-3} \quad (7)$$

where,  $\gamma_{p_{\text{stress}}}^{\text{region}}$  is the surface tension of the polymer near stress-concentrating regions. With increasing tensile stress and negative pressure,  $\gamma_{p_{\text{stress}}}^{\text{region}}$  is expected to decrease. Also, according to eq. (7) the lower the bulk modulus  $B$  of the material, the faster the rate of decrease of  $\gamma_{p_{\text{stress}}}^{\text{region}}$  with respect to tensile stress.

When liquid comes in contact with the polymer, at the point of contact the interfacial tension  $\gamma_{pl}$  will generally be less than  $\gamma_p$ . The interfacial tension  $\gamma_{pl}$  is defined as the reversible work per unit area required to increase the net surface of the polymer in contact with the liquid. According to Girifalco and Good,<sup>11</sup> for an apolar liquid and nonbipolar solid (a solid containing both electron acceptor and donor sites), the following equation is approximately true:

$$\gamma_{pl} = (\gamma_p^{1/2} - \gamma_l^{1/2})^2 \quad (8)$$

where  $\gamma_{pl}$  is the interfacial tension of the polymer in contact with the liquid. Also, according to eq. (8), near stressed regions the interfacial tension of the polymer is as follows:

$$\gamma_{pl_{\text{stress}}}^{\text{region}} = (\gamma_{p_{\text{stress}}}^{\text{region} 1/2} - \gamma_l^{1/2})^2 \quad (9)$$

$\gamma_{pl_{\text{stress}}}^{\text{region}}$  is the polymer interfacial tension and  $\gamma_{p_{\text{stress}}}^{\text{region}}$  is the polymer surface tension, near regions of stress concentration.

From eq. (9) it is evident that  $\gamma_{pl_{\text{stress}}}^{\text{region}}$  becomes zero, when  $\gamma_{p_{\text{stress}}}^{\text{region}}$  takes the value of the surface tension of the liquid  $\gamma_l$ . That is when  $\gamma_{p_{\text{stress}}}^{\text{region}} = \gamma_l$ .

Indeed, with external application of tensile stress, a point will be reached where, near the regions of concentrated stress,  $\gamma_{p_{\text{stress}}}^{\text{region}}$  takes the value of the liquid  $\gamma_l$ , see eq. (7), and  $\gamma_{pl_{\text{stress}}}^{\text{region}}$  will, thus, become zero.

Therefore, there will be a critical value of the tensile stress so that the work per unit area required to form new surface in contact with the liquid, near the regions of stress concentration  $\gamma_{pl_{\text{stress}}}^{\text{region}}$ , will become zero. At this point, the first capillary meniscus<sup>20</sup> for craze initiation and propagation can form easily in the presence of a triaxial stress field.

Thus, from eqs. (9) and (7) for solvent craze initiation in van der Waals liquids, we have

$$\gamma_{p_{\text{stress}}}^{\text{region}} = \gamma_l = \gamma_p (1 + P_{\text{critical}}/B)^{-3} \quad (10a)$$

or, equivalently,

$$P_{\text{critical}} = [(\gamma_l/\gamma_p)^{-1/3} - 1]B \quad (10b)$$

As pointed out previously, besides the surface tension effect, the solubility of the polymer will also be locally affected in a similar way.

## Solubility Effect

In polymers, solubility depends on both endothermic van der Waals and exothermic acid-base interactions. The heat of mixing is, therefore, determined from two terms:

$$\Delta H_m = \Delta H_m^{\text{WL}} - \Delta H_m^{\text{AB}} \quad (11)$$

Mixing will be favored when  $\Delta H_m$  becomes zero or even better, negative (since Gibbs free energy  $\Delta G_m = \Delta H_m - T \Delta S_m \leq 0$ ).

The exothermic acid-base interaction is mainly due to hydrogen bonds, which can be classified as chemical bonds because they involve specific bond distances and bond angles determined by specific orbitals. By contrast, van der Waals forces fall off

smoothly with distance and do not involve bond angles, so they might well be referred to as physical, even though in some cases their magnitudes can exceed the strength of hydrogen bonds.<sup>14,15</sup>

From eq. (11), it is obvious that only in the case of interaction between a van der Waals liquid and a van der Waals polymer solid, acid-base interaction can be ignored.

The endothermic van der Waals–Lifshitz interaction is due predominantly to the London dispersion forces.<sup>16</sup>  $\Delta H_m^{WL}$  is given by Hilderbrand's equation

$$\Delta H_m^{WL} \cong \Delta U_m^{WL} = \Phi_p \Phi_l (\delta_p - \delta_l)^2 \quad (12)$$

where  $U$  the internal energy,  $\Phi_p$ ,  $\Phi_l$ ,  $\delta_p$ ,  $\delta_l$  are the volume fractions and solubility parameters of the polymer and liquid respectively.  $\delta$  is defined as

$$\delta = (E_{\text{cohesive}}/V)^{1/2} \quad (13)$$

$E_{\text{cohesive}}$  is defined as the increase in internal energy per mol of substance, if all the intermolecular forces are eliminated.  $V$  is the molar volume of the substance.

It is obvious from eqs. (11) and (12) that for liquid polymer systems with zero acid-base interactions, there will be mixing, only when  $(\delta_p - \delta_l)$  approaches zero or the ratio  $\delta_l/\delta_p$  approaches unity.

With the application of stress, the molar volume of the polymer will increase, especially in regions of high stress concentration. From eqs. (4a) and (13) we have

$$\delta_{p_{\text{stress}}}^{\text{region}} = \delta_p (1 + P/B)^{-0.5} \quad (14)$$

where,  $\delta_{p_{\text{stress}}}^{\text{region}}$  is the solubility parameter of the polymer in stressed regions. With increasing external stress and negative pressure,  $\delta_{p_{\text{stress}}}^{\text{region}}$  is expected to decrease.

Thus, for solvent craze initiation due to craze tip bulk plasticization, we will have

$$\delta_{p_{\text{stress}}}^{\text{region}} = \delta_l = \delta_p (1 + P_{\text{critical}}/B)^{-0.5} \quad (15a)$$

or, equivalently,

$$P_{\text{critical}} = [(\delta_l/\delta_p)^{-1/3} - 1]B \quad (15b)$$

where  $P_{\text{critical}}$  is the pressure for craze initiation.

The above expression is valid only for van der Waals liquids.

## RESULTS AND DISCUSSION

Two different types of interactions were considered to be important for "solvent" craze initiation: (1) polymer interfacial tension reduction (ITR); (2) polymer bulk plasticization (BP).

These interactions for nonpolar polymers and (WL) liquids were described in terms of eqs. (8) and (12), respectively.

Furthermore, the effect of dilational stress and the accompanying volume change in regions of stress concentration, were considered [see eq. (4)].

Finally, from the general requirement that the free energy for a spontaneous process  $\Delta G_{\text{process}}$  must be  $\leq 0$  (Entropy, effects assumed to be small), eqs. (10) and (15) were proposed as criteria for "solvent" craze initiation in the case of (ITR) and (BP) interactions, respectively. (Interfacial tension can alternatively be defined as the specific free interfacial energy.)

The two mechanisms (ITR) and (BP), as has already been discussed, are not exclusive and can both be active. However, it is expected that surface interactions between polymer and solvent vapor will take place before the bulk polymer is plasticized. This would also be true in the early stages of initiation.

In order to compare eqs. (10) and (15) with available data in the literature, the critical negative pressure near a small region at the tip of a flaw was assumed to be given from

$$P_{\text{critical}} = 1/3K\sigma_{\infty} = 1/3(KE\varepsilon_c) \quad (16)$$

where  $E$  is the modulus of elasticity,  $\varepsilon_c$  is the applied (distant) critical strain for craze initiation and  $K$  the stress concentration factor. It is difficult to make a good estimate for the value of  $K$ , especially near the points of initiation. However, the upper limit in the value of  $K$  for a linearly elastic solid could be 100,<sup>7</sup> where as the lower limit, for a smooth spherical hole<sup>17</sup> is 2. Both of these limits in the value of  $K$  will be considered.

From eqs. (16) and (10), solving for  $\varepsilon_c$  we have

$$\varepsilon_c = \frac{3B}{KE} [\gamma_l/\gamma_p]^{-1/3} - 1 \quad (17)$$

where  $\varepsilon_c$  is the critical strain for craze initiation, assuming (ITR) type of interactions.

Equivalently, from eqs. (16) and (15)

$$\epsilon_c = \frac{3B}{KE} [(\delta_l/\delta_p)^{-2} - 1] \quad (18)$$

where  $\epsilon_c$  is the critical strain for craze initiation, assuming (BP) type of interactions.

The critical strain  $\epsilon_c$  for craze initiation in the presence of various organic liquids has been measured for a number of glassy polymers. In this work, the data used comes from the study of six polymers: poly(2,6-dimethyl-1,4-phenylene (PPO),<sup>1</sup> PMMA,<sup>3</sup> PVC,<sup>3</sup> aromatic copolyether-sulfone (PSF),<sup>2</sup> PS,<sup>5</sup> and polycarbonate (PC)<sup>6</sup>. Table I records the elastic constants, solubility parameter, and surface tension for each polymer. Table II summarizes the data considered for each polymer. Only data for nonhydrogen bonded and mildly hydrogen bonded liquids was considered for reasons already explained.

In Figures 1(a) and (b), the calculated critical strain for craze initiation  $\epsilon_c$ , estimated from eqs. (17) [(ITR) case] and (18) [(BP) case], is plotted against the experimental values for  $\epsilon_c$  listed in Table II, for the two extreme values of the stress concentration factor  $K = 2$  and  $K = 100$ , respectively.

The significant scattering observed in the data can be attributed to the wide variety of sources used. Unfortunately, the elastic constants were not considered relevant and not recorded in the original articles. The recording of critical strain for craze initiation was not very accurate. Different times and ways of exposure to the liquid would add significant error. Finally, and most importantly, not all liquids reported in Table II are pure (WL) liquids. Although scattering for individual polymers would be probably less, plotting all polymers together adds to the statistical confidence.

Linear regression lines through the data are also plotted, and the regression coefficients, as well as the regression indices, are recorded in Figure 1(a) and (b). All lines have a tendency to pass through the origin, with varying slopes. It is obvious from Figure 1(a) and (b) that the slopes for the (BP) case are generally larger than those of the (ITR) case. A good correlation with experimental data (slope of unity) is possible only for the (ITR) case with stress concentration factor  $K = 100$ . Larger values of  $K$ , although they could also give slope unity for the (BP) lines, would be unrealistically high.

The value of  $K = 100$  that was found to show a good correlation between the (ITR) hypothesis and experiment, requires that the local negative pressures vary from approximately zero MPa (strong solvent action) to 1000 MPa in the limiting case of air crazes (no solvent). The value 1000 MPa for dry

**Table I Physical Constants for the Six Polymers**

Polymer	Tensile Modulus (GPa) <sup>a</sup>	Bulk Modulus (GPa) <sup>b</sup>	Critical Surface Tension (mN/m) <sup>c</sup>	Solubility Parameter (cal <sup>1/2</sup> /cm <sup>3/2</sup> )
PC	2.3	5	46	10.2
PS	3.3	5	33	8.76
PMMA	3.2	5.1	39	9.5
PPO	2.3	4.1	38	8.9
PSF	2.5	5.3	41	10.7
PVC	2.6	5.5	39	9.85

<sup>a</sup> Ref. 18.

<sup>b</sup> Ref. 13.

<sup>c</sup> Ref. 19.

craze initiation is unrealistically high, because we know that glassy polymers start to yield at around 100 MPa. Therefore, a more realistic value for the stress intensity factor would have been  $K = 10$ .

There are a number of possible reasons for which the value for  $K$  is found to be larger than expected. Among these, perhaps the most important, are the assumptions made for eq. (2). The volume change given from eq. (2) is the minimum possible, assuming adiabatic conditions, constant bulk modulus  $B$ , small negative pressures, and small volume changes. However, a pressure of 100 MPa can produce a substantial bulk modulus change. For polyvinyl acetate the bulk modulus  $B$  changes from 2.8 GPa to 1.8 GPa when a negative pressure of 100 MPa is applied.<sup>21</sup> In general, due to volume creep effects, the bulk modulus is a function of time, temperature, and pressure. Its limiting values vary from approximately 5 GPa for a glassy polymer to 2 GPa for a liquid like rubber material.<sup>13</sup> Also, entropic effects and nonequilibrium effects from residual stresses have been assumed to be minimal. These considerations, together with the fact that existing residual stresses and microcracks might have resulted in an initial local (BP) of the material well before straining, indicate that the conclusions derived from Figures 1 and 2 should be handled with care.

## CONCLUSIONS

In glassy polymers near regions of stress concentration (due to inhomogeneities and surface flaws), the surface tension and the solubility parameter reduce locally, so that organic and environmental liquids can induce stress crazing and cracking.

In solids with low bulk modulus and low surface tension and solubility parameters, such as glassy

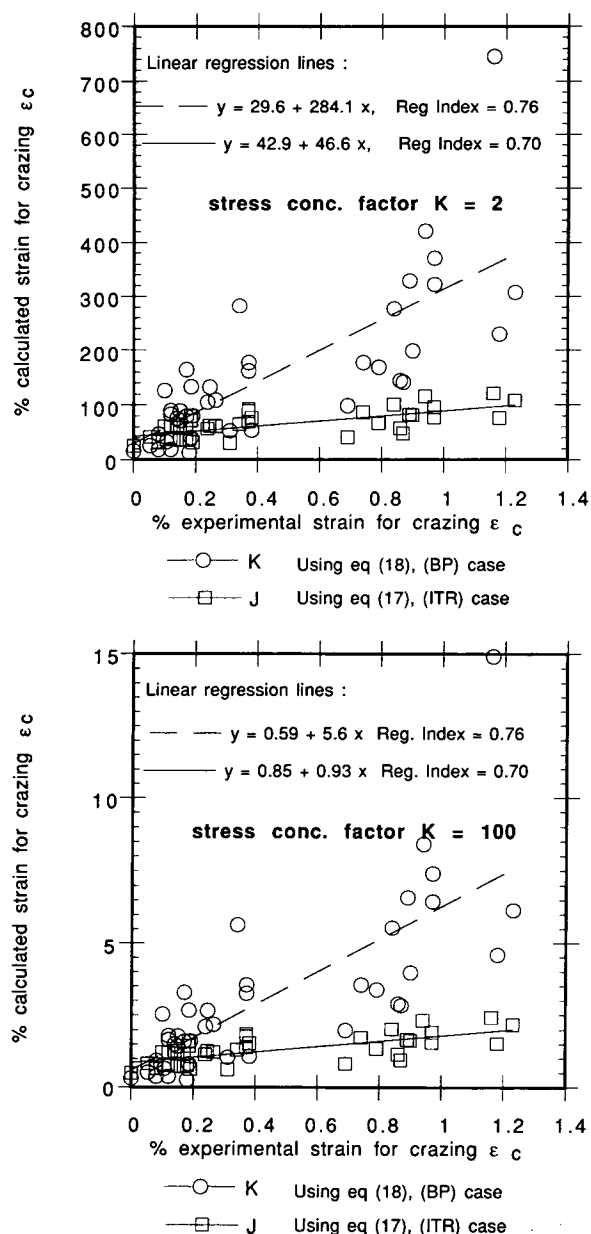
**Table II Critical Strain for Crazeing in van der Waals and Near van der Waals Liquids**

Polymer	Liquid	$\delta$ cal <sup>1/2</sup> /cm <sup>3/2</sup>	$\gamma$ mN/m	$\epsilon_c$ %	
PPO	<i>n</i> -Octane	7.54	21.14	0.238	
	<i>n</i> -Heptane	7.5	20.3	0.264	
	<i>n</i> -Hexane	7.27	18.43	0.185	
	<i>n</i> -Pentane	7.02	16	0.37	
	2-Methylbutane	6.9	15.5	0.37	
	2,2-Dimethylbutane	6.9	16.2	0.74	
	2,2,3-Trimethylbutane	6.9	18.9	0.37	
	Carbon tetrachloride	8.6	26.95	0.08	
	Isoamyl formate	8.5	24.6	0.053	
	<i>n</i> -Butyl acetate	8.6	24.8	0.12	
	Methyl butyl ketone	8.4	25.5	0.107	
	PMMA	Carbon tertachloride	8.6	26.95	0.31
		<i>n</i> -Heptane	7.5	20.3	0.86
<i>n</i> -Hexane		7.27	18.43	0.79	
<i>n</i> -Pentane		7.02	16	0.9	
Benzene		9.2	28.85	0.0001	
PVC	Carbon tertachloride	8.6	26.95	0.69	
	<i>n</i> -Heptane	7.5	20.3	1.18	
	<i>n</i> -Pentane	7.02	16	1.23	
	Cyclohexane	8.19	25.5	0.87	
	Benzene	9.2	28.85	0.08	
	Ethyl benzene	8.8	29.2	0.19	
PSF	Toluene	8.9	28	0.15	
	<i>n</i> -Octane	7.54	21.14	0.97	
	<i>n</i> -Heptane	7.5	20.3	0.89	
	<i>n</i> -Hexane	7.27	18.43	0.97	
	<i>n</i> -Pentane	7.02	16	0.94	
	Acetone	9.62	23.7	0.14	
	Methyl acetate	9.46	24.6	0.15	
	<i>n</i> -Butyl acetate	8.69	24.8	0.17	
	Perfluoromethylcyclohexane	5.85	15.4	1.16	
	Methyl ethyl ketone	9.45	24.3	0.12	
PS	<i>n</i> -Octane	7.54	21.14	0.17	
	<i>n</i> -Heptane	7.5	20.3	0.12	
	<i>n</i> -Pentane	7.02	16	0.1	
	Perfluoromethylcyclohexane	5.85	15.4	0.34	
PC	Acetone	9.62	23.7	0.185	
	Methyl ethyl ketone	9.45	24.3	0.38	
	<i>n</i> -Heptane	7.5	20.3	0.84	
	Carbon tertachloride	8.6	27	0.245	
	<i>o</i> -Dichlorobenzene	10	33	0.18	

polymers, relatively small negative pressures are required to reduce either the local surface tension or the solubility parameter of the polymer to the values of external (environmental) liquids. The tensile stress producing the critical negative pressure for craze initiation, must, of course, be less than the yield stress of the polymer, so that crazing can initiate before homogeneous yielding of the material takes place.

Two independent expressions for "solvent" craze initiation or better "environmental" craze initiation in the presence of (WL) liquids, have been derived for (a) stress-induced interfacial tension reduction, eq. (10); and (b) stress induced local bulk plasticization, eq. (15).

A relatively good functional relation (straight line passing near the origin) has been obtained for a wide



**Figure 1** (a,b) The calculated critical strain for craze initiation  $\epsilon_c$ , estimated from eq. (17), (ITR) case, (open squares) and eq. (18), (BP) case, (open circles), is plotted against the experimental values for  $\epsilon_c$  listed in Table II, for stress concentration factor  $K = 2$  and  $K = 100$ , respectively.

spectrum of glassy polymers and apolar (WL) liquids, for both the (BP) and (ITR) cases.

Further, additional assumptions made in this analysis (especially about the local bulk modulus and the stress concentration factor), indicate that surface tension reduction might be important for

solvent craze initiation in the case of (WL) liquids. However better controlled experiments are necessary to conclusively resolve the question, which one of (ITR) or (BP) is the dominant mechanism.

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