

Mechanism of Solvent Crazing in Unmodified and Rubber-Modified Polystyrenes

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Synopsis

The dependence of critical strain on time was determined at -20° and 20°C with a Bergen elliptical strain device for unmodified and rubber-modified polystyrenes immersed in n -alcohols. Critical strain ϵ_c decreased with time and attained a lower limiting value ϵ_{cl} at long times. The value of ϵ_{cl} decreased with increasing chain length of the n -alcohol and with increasing temperature, while it increased with increasing rubber content. In order to elucidate the mechanism of solvent crazing at longer times, the degree of equilibrium swelling Sv_{eq} and the diffusion coefficient D were also determined by sorption experiment. The lower limiting value of critical stress σ_{cl} was correlated to the value of Sv_{eq} , irrespective of the rubber content. The At , the time necessary to attain ϵ_{cl} , was regarded as the time needed for the thin layer of polymer surface to absorb the liquid to equilibrium for craze formation. The thickness of such a layer was estimated to be about $0.1\ \mu\text{m}$ by using the experimental data of At and D . The predominant mechanism of solvent crazing at longer times appears to be a flow process of absorbed polymer at the craze tip.

INTRODUCTION

The role of solvent in crazing (or cracking) of glassy polymers has been explained in the past years by two major hypotheses, that is, plasticization and surface energy reduction. Recently, Kambour et al.^{1,2} reported that the resistance to solvent crazing of two ductile glassy polymers depends on the degree of swelling and the attendant reduction in T_g . They further suggested³ that organic liquids do not exert a significant role on surface energy reduction in solvent crazing, as a result of the investigation of solvent crazing of "dry" polystyrene and "dry" crazing of plasticized polystyrene.

Andrews and Bevan⁴ measured the minimum surface work τ_0 required to propagate the discontinuity as a function of temperature for the systems of poly(methyl methacrylate) and alcohols. This quantity τ_0 varies with temperature in a consistent manner, decreasing rapidly as the temperature rises to a characteristic temperature T_c and then remaining constant at some value τ_0^* for $T > T_c$. The value of τ_0^* was correlated to the interfacial tension between polymer and solvent, in contrast with the result of Kambour et al.^{1,2}

Time and temperature are vitally important parameters in solvent crazing and should be included as variables in all tests for crazing behavior. Kinetic studies on craze initiation in polystyrene in solvents were done as a function of the chain length of n -alcohol with a Bergen elliptical strain device.⁵ The critical strain decreases with time at shorter times and becomes constant at longer times. It has been concluded that at shorter times where the critical strain decreases with time, the rate of craze initiation is determined by the diffusion of the molecules of liquid into polymer, as the results of the analysis of crazing data in terms of the Eyring model and sorption studies. It was the purpose of this study to

investigate the molecular mechanism of solvent crazing at longer times where the critical strain attains a lower limiting value.

EXPERIMENTAL

The polymers which were used for the experiments were a general-purpose polystyrene, No. 1, and a high-impact polystyrene, No. 3 (HF 77 and HT 88, respectively, Mitsubishi Monsanto Kasei Co., Japan) and a mixture of HF 77/HT 88 = 50/50 No. 2. The liquids were methyl, ethyl, *n*-propyl, and *n*-butyl alcohols. The content of butadiene rubber in HT 88 was determined to be 8.6 wt-% by IR spectroscopy.

Crazing tests were carried out in a Bergen elliptical strain jig⁶ on strips cut from 2.0-mm-thick sheets compression molded at 200°C. In the solvent crazing tests, wicks were used if necessary to avoid crack initiation in the case of a specimen with defective edges.² Before the test, the specimens, the jigs, and the liquids were all placed in the thermostat at the testing temperature for more than 30 min. The jigs with specimens attached were immersed in the thermostated liquid for specific periods. After the jigs were taken from the liquid, the specimens were immediately removed from the jigs and then wiped with absorbent cotton. The critical strain ϵ_c was determined for each case. Five specimens were used in each case so that a reasonably precise value of ϵ_c could be determined. Tests were performed at -20° and 20°C for 0.5, 1, 5, 10, 50, 100, 500, 1000, and 2000 min.

Sorption tests were carried out by using films about 50 μm thick cast from benzene solutions. In a stoppered tube containing several milliliters of alcohol, the films were hung at the top of the tube without touching the liquid. The change in weight of the films was measured for about 3000 hr at room temperature ($20^\circ \pm 2^\circ\text{C}$).

RESULTS

On immersing the jig with the specimen into the liquid, crazes appeared on the specimen surface. The critical strain ϵ_c at which crazes could be detected decreased with time and attained a lower limiting value ϵ_{cl} at long times. Figures 1 and 2 show the average value of ϵ_c plotted against logarithmic time for samples No. 1 and No. 3 immersed in the *n*-alcohols at -20° and 20°C . Table I shows the data of ϵ_{cl} for each system of the polymer and alcohol. The values of ϵ_{cl} decreased with increasing chain length of the *n*-alcohol, with decreasing rubber content and with increasing temperature.

The value of S_v , volume of liquid absorbed per unit volume of polymer, increased rapidly with time and attained an equilibrium value at long times. The equilibrium had reached nearly completion for all systems after about 3000 hr. The rate of sorption decreased with increasing chain length of the *n*-alcohol. On the other hand, the degree of equilibrium swelling $S_{v\text{eq}}$ increased with increasing chain length of the *n*-alcohol. The diffusion coefficient D can be determined from the sorption data according⁷ to

$$S_v = S_{v\text{eq}} \left[1 - \frac{8}{\pi^2} \exp \left(1 - \frac{\pi^2}{l^2} Dt \right) \right] \quad (1)$$

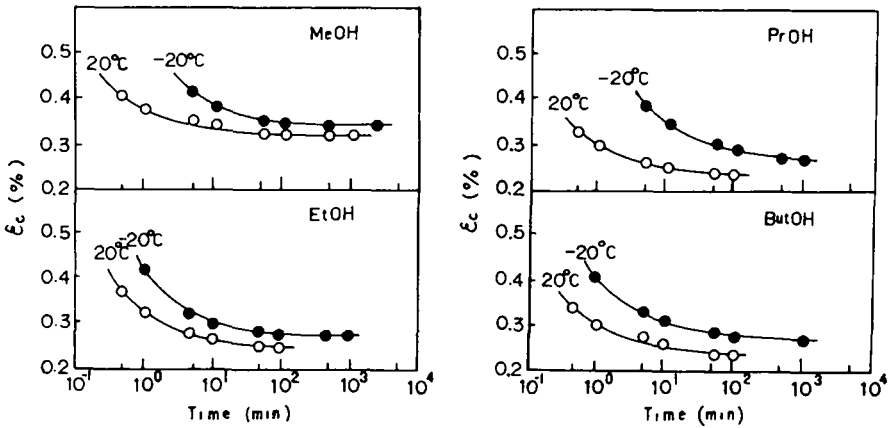


Fig. 1. Dependence on time of critical strain ϵ_c for crazing of sample No. 1 in *n*-alcohols at -20° and 20°C .

where l is the thickness of the specimen and t is the time. In Figure 3 the values of $\log [(Sv_{eq} - Sv)/Sv_{eq}]$ against time at shorter times are plotted for No. 1. The diffusion coefficient was calculated from the slope of the linear plots. Table II lists the values of Sv_{eq} and D for all systems.

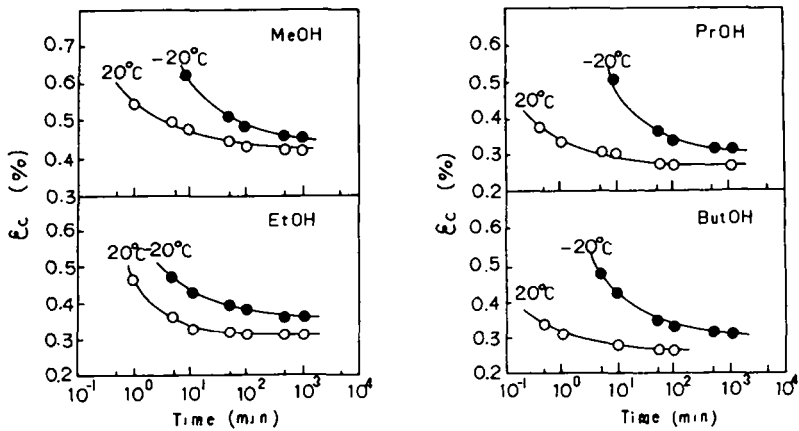


Fig. 2. Dependence on time of critical strain ϵ_c for crazing of sample No. 3 in *n*-alcohols at -20° and 20°C .

TABLE I
Lower Limiting Value ϵ_{cl} (%)

Alcohol	Sample No. 1		Sample No. 2		Sample No. 3	
	-20°C	20°C	-20°C	20°C	-20°C	20°C
Methanol	0.36	0.32	—	—	0.46	0.42
Ethanol	0.29	0.25	0.35	0.31	0.38	0.32
Propanol	0.28	0.24	—	—	0.32	0.26
Butanol	0.28	0.24	—	—	0.32	0.26

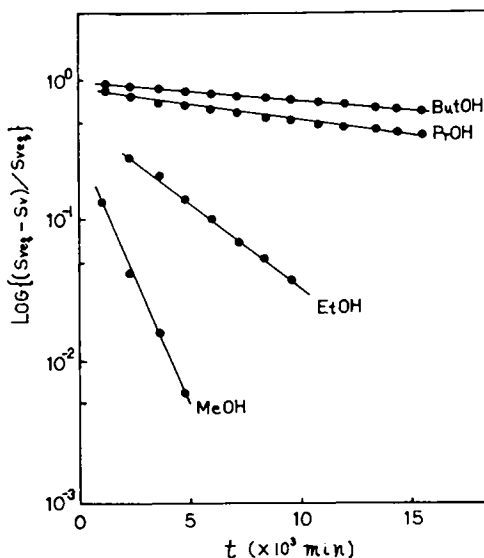


Fig. 3. Dependence on time of swelling characteristics for sample No. 1 exposed to the saturated vapor of each alcohol.

DISCUSSION

Kambour⁸ suggested that the plasticization of polymer is a predominant mechanism for solvent crazing and that critical strain can be correlated to solubility of liquid into polymer. In Figure 4(a) the values of ϵ_{cl} against the solubility parameters δl of each alcohol are plotted. The two curves shown correspond to samples No. 1 and No. 3. The ϵ_{cl} values decrease monotonically with decreasing δl and probably are smallest at the solubility parameters δp of the respective polymers (that is, for No. 1, $\delta p = 8.6$ and for No. 3, $\delta p = 8.1-8.6$). The curve for No. 3 lies above that for No. 1, that is, the former is more resistant to crazing in the same environment than the latter. The solubility parameter does not always predict solubility of liquid into polymer, since the solubility seems to depend on molecular size and shape of the liquid. In Figure 4(b) the values of ϵ_{cl} against Sv_{eq} are plotted. Two curves are again shown, corresponding to No. 1 and No. 3, as well as the curves of ϵ_{cl} versus δl . The above results suggest that the parameters δl and Sv_{eq} serve as correlating ones for ϵ_{cl} , but the respective correlations are not the same for both polymers. Crazing in glassy polymers is attributed to a stress-activated devitrification of a small amount of material at the tip of a flaw to a rubbery state, and subsequently the softened material forms cavities under stress.⁹⁻¹¹ Recently, Kambour et al.³ determined critical strain

TABLE II
Diffusion Coefficients D ($\times 10^{11}$ cm²/sec) and Equilibrium Solubility Sv_{eq} ($\times 10^2$ cm³/cm³)

Alcohol	Sample No. 1		Sample No. 2		Sample No. 3	
	D	Sv_{eq}	D	Sv_{eq}	D	Sv_{eq}
Methanol	6.09	1.82	—	—	2.34	2.00
Ethanol	3.32	1.98	2.10	2.10	1.00	2.64
Propanol	0.91	2.10	—	—	0.63	2.95
Butanol	0.59	2.22	—	—	0.62	2.98

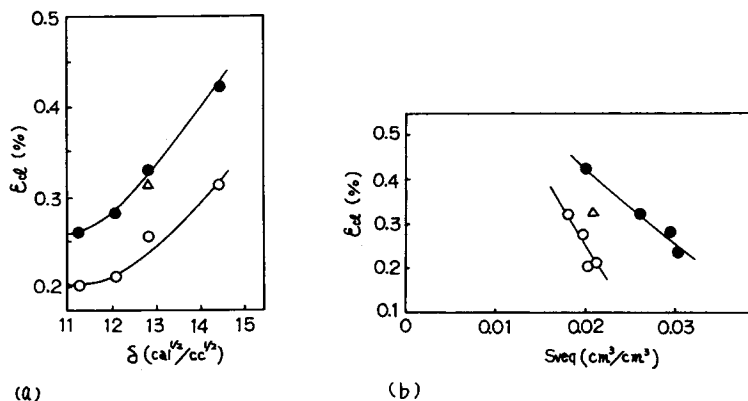


Fig. 4. Lower limiting value of the critical strain ϵ_c for crazing of polystyrenes as functions of (a) solubility parameter δ of *n*-alcohol and (b) equilibrium solubility S_{veq} : O, No. 1; Δ , No. 2; \bullet , No. 3.

ϵ_c from the two kinds of crazing experiments: crazing of polystyrene in each of a variety of organic liquids, and crazing in air by a set of specimens molded from mixtures of *o*-dichlorobenzene and polystyrene. They reported that the values of ϵ_c are correlated identically to the T_g values of the swollen films and of the preplasticized specimens, irrespective of the kind of crazing experiment.³ The T_g of the absorbed polymers was estimated from the data of S_{veq} according to Kelley and Bueche¹²:

$$T_g(\text{system}) = [4.8 \times 10^{-4}cT_g + \alpha s(1 - c)T_g'] / [4.8 \times 10^{-4} + \alpha s(1 - c)] \quad (2)$$

where T_g is the glass temperature of the system, c is the volume fraction of polymer, and αs and T_g' are the thermal expansion coefficient and glass temperature of the solvent, respectively. The parameters used for the calculation are listed in Table III. Here, the T_g' of the alcohols were assumed to be $0.67 T_m'$ (T_m' is the melting temperature of an unsymmetric molecule). The values of T_g were about 80° and 70°C, respectively, for No. 1 and No. 3 in any alcohol. This result indicates that the ϵ_{cl} is not directly related to the T_g , since the polymer having the lower T_g is more resistant to crazing.

Andrews and Bevan⁴ proposed a theoretical equation for the minimum work of craze formation τ_0 . The equation is slightly modified for the work of craze formation under an environment:

$$\tau_0 = 2.42(h\beta_s\gamma/\rho)f^{2/3} + 0.33\beta_p Y\psi hf \quad (3)$$

where h is the craze thickness, β_s is the factor by which the surface energy is reduced by adsorption, γ is the interfacial energy of the voids, ρ is the mean

TABLE III
Parameters Used for the Calculation of T_g^a

Alcohol	T_m' , K	αs , C ⁻¹	T_g' , K
Methanol	178	0.0017	126
Ethanol	169	0.0011	107
Propanol	146	0.00096	98
Butanol	183	0.00093	123

^a The T_g values of No. 1 and No. 3 are 368° and 358°K, respectively.

distance between void centers, f is the void fraction, β_p is the factor by which Y is reduced by the plasticizing effect of the solvent, Y is the shear yield stress, and ψ is a constant of value 4.4. For the present polymers, stress relaxation is not so rapid even at room temperature. It was concluded in the previous report⁵ that the only time-dependent factor in eq. (3) is β_p , which is controlled by the diffusion of the molecules of liquid into polymer, and that the observed dependence of ϵ_c on time results from the time dependence of β_p . Accordingly, ϵ_{cl} is considered to be the critical strain in the case of the β_p at the equilibrium swelling.

The values determined by Andrews and Bevan⁴ were those obtained in the equilibrium state at the temperature of the test. Andrews and Bevan suggested that $Y = 0$ at $T \geq T_c$ and T_c is identified with the glass transition temperature of a solvated zone at the craze tip where the cavitation takes place. The testing temperatures studied here were relatively low compared with the estimated T_g of the polymers swollen to equilibrium, that is, $T < T_c$, and therefore the ϵ_{cl} is considered to be in the temperature region $T > T_c$, which is dependent on shear stress.

Various criteria have been proposed by many investigators⁸ in terms of stress or strain for craze initiation. Much experimental evidence is needed to decide which criterion, stress or strain, is more favorable for craze initiation. Gent¹³ has proposed that the dilatational stress at a flaw tip increases the free volume of the material at the flaw tip and reduces its T_g . He has given the following criterion for craze initiation:

$$\sigma_c/3 = [\beta(T_g - T) + P]/k$$

where σ_c is the critical applied tensile stress, β is the hydrostatic pressure coefficient of T_g , T is the test temperature, P is the applied hydrostatic pressure, and k is the stress concentration factor relating the applied stress to the microscopic stress acting at the flaw tip. In the case of the solvent crazing, the polymeric material at a flaw tip absorbs the solvent to the degree of the equilibrium swelling and softens.

The present crazing data were evaluated according to the stress criterion, taking in consideration the proposed theory by Gent. The ϵ_{cl} data were trans-

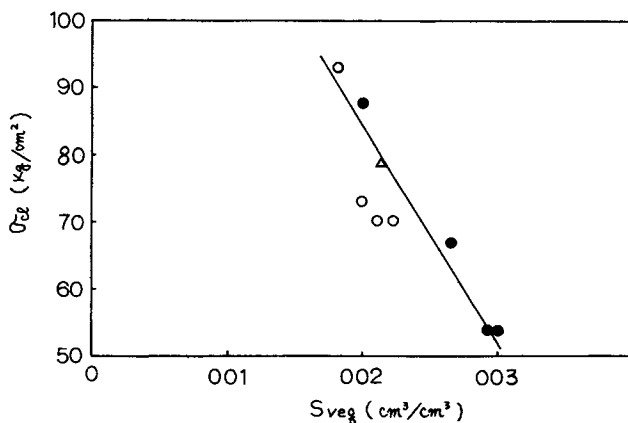


Fig. 5. Lower limiting value of critical stress ϵ_{cl} for crazing of polystyrenes as function of solubility parameter δ of n -alcohol: O, No. 1; Δ , No. 2; \bullet , No. 3.

TABLE IV
The Decreasing Rate of ϵ_{cl} and Y with Temperature^a

Sample no.	$\epsilon_{cl20^\circ C}/\epsilon_{cl-20^\circ C}^c$				$Y_{20^\circ C}/Y_{-20^\circ C}^b$
	M	E	P	B	
1	0.88	0.86	0.86	0.86	0.85
3	0.91	0.83	0.81	0.81	0.77

^a No. 1: $Y_{20^\circ C} = 420 \text{ kg/cm}^2$, $Y_{-20^\circ C} = 490 \text{ kg/cm}^2$. No. 2: $Y_{20^\circ C} = 240 \text{ kg/cm}^2$, $Y_{-20^\circ C} = 310 \text{ kg/cm}^2$.

^b Instron testing data at extension rate of 1 cm/min.

^c M, methanol; E, ethanol; P, propanol; B, buthanol.

formed into those of σ_{cl} through $\sigma_{cl} = \epsilon_{cl} \cdot E$ (Young's modulus $E = 2.9 \times 10^4$ and $2.1 \times 10^4 \text{ kg/cm}^2$ for No. 1 and No. 3, respectively). In Figure 5 are plotted the values of σ_{cl} against Sv_{eq} . The σ_{cl} is correlated to the Sv_{eq} , irrespective of the kind of rubber content in polystyrene. This fact suggests that the solvent crazing can be better described by the criterion of stress than of strain. The values of ϵ_{cl} were observed to be dependent on temperature for all systems. The solubility parameters of the polymer and the alcohol are not so much dependent on temperature. The decreasing rate of Y with temperature is similar to that of ϵ_{cl} (or σ_{cl}), as shown in Table IV. This suggests that the temperature dependence of ϵ_{cl} can be again described in terms of eq. (3). Shear yield stress decreases greatly with volume fraction of solvent in polymer/solvent mixtures.¹⁴ On exposure to liquid, the major part of reduction in ϵ_{cl} (or σ_{cl}) is considered to arise from the Y term in eq. (3).

The time At for the critical strain to attain ϵ_{cl} was about 10 min for each system at $20^\circ C$. The rate of craze initiation on exposure to liquids is controlled by the diffusion of the molecules of liquid into polymer,⁵ and accordingly the time At can be regarded as the time needed for the critical thickness of surface layer on the specimen to absorb the liquid to equilibrium for craze formation. Here, the thickness of the softened material necessary for craze formation can be estimated by using the experimental data of At and D . The critical thickness l_c can be computed from eq. (1), when $Sv/Sv_{eq} = 1/2$. The calculated value of l_c was about $0.1 \mu\text{m}$, comparable to the experimental value of the depth of a craze reported by other investigators.⁴

CONCLUSIONS

Time and temperature are vitally important parameters for solvent crazing. The critical strain ϵ_c , which was determined with a Bergen elliptical strain device, decreased with time and attained a lower limiting value ϵ_{cl} at long times. The solvent crazing at long times can be explained in terms of the stress criterion for craze formation. The predominant mechanism for solvent crazing at long times appears to be a polymer flow process at a critical value ϵ_{cl} of the applied stress.

The liquid molecules need not necessarily penetrate the bulk phase of the polymer. The thickness of the polymer surface to absorb the liquid to equilibrium for craze formation was estimated to be about $0.1 \mu\text{m}$ by using the experimental data of At and D . This value is comparable to the depth of a craze.

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