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Tensile stress increases (ΔS) have been measured in changing the environment of a crazed specimen held at constant extension from methanol, water or their mixtures to air. It is demonstrated that these stress changes are probably due to changes in the interfacial tension between the fibrils and the environment. The observed magnitude of ΔS is in excellent agreement with the theoretical estimates of this quantity.

INTRODUCTION

The technical importance of crazing in polymers induced by action of liquid environments has triggered much interest in, and speculation on, the precise role the environment plays in crazing[1,2]. The enhancement of crazing by the environment usually has been attributed either to (i) a decrease in surface energy requirement for forming the finely divided fibril structure of the craze or (ii) a decrease due to plasticization in the flow (or drawing) stress of the polymer at the craze tip where fibrils are being formed (or at the craze surface where they are being drawn out). Since liquids which wet the polymer surface also tend to plasticize it and *vice versa*, it has not been easy to distinguish between these mechanisms. Kambour *et al.*[2] showed for the *o*-dichlorobenzene–polystyrene system, at least, that plasticization was the more important mechanism. He demonstrated that the decrease in craze stress produced by the environment could be correlated directly with the depression in glass transition temperature caused by the environment (*o*-dichlorobenzene). Identical results were obtained when the environment was applied externally (and T_g measured on a film swollen to equilibrium) and when the environment was applied internally as a plasticizer.

When Andrews and co-workers[3,4] determined the critical strain energy release rate G_c ($2T$ in their notation) to propagate a crack with a craze ahead of it in PMMA immersed in various alcohols however, they found two ranges of behaviour depending on temperature. At low temperatures G_c was high but decreased approximately linearly as T was increased until a value G_c^* was reached at T^*. For temperature above T^*, G_c was constant at G_c^*. They attributed the decrease in G_c with increasing T at low temperatures to a decrease in the plastic work to form a craze, designated T^* as the glass transition temperature of the equilibrium swollen polymer and G_c^* as the residual energy contribution to craze formation. Only when the environmental plasticization is so severe that T_g of the swollen polymers is decreased to the measuring temperature, does the surface energy term become dominant. Direct measurements[5] of the craze fibril stresses by holographic interferometry in one of their systems (methanol–PMMA) for $T<T^*$ tend to bear out their hypothesis.

The object of the present experiments is to determine directly the surface contribution of the crazing stress. We measure directly the normal component of stress S acting on the craze caused by the surface tension of the craze fibrils in the environment. For a single cylindrical fibril of diameter D, length l and surface area A, the equivalent fibril stress σ_f due to the surface tension l of the fibril is given for constant volume deformation by:

$$\left(\frac{\pi D^2}{4}\right)\sigma_f=\left(\frac{\partial A}{\partial l}\right)_v\gamma=\frac{\pi D}{2}\gamma \qquad (1)$$

for long fibrils.

If the volume fraction of these fibrils is v_f and they are all oriented normal to the craze surfaces, the surface stress contribution due to surface tension is

$$S=\frac{2\gamma v_f}{\bar{D}} \qquad (2)$$

where

$$\bar{D}=\frac{\langle D^2\rangle}{\langle D\rangle}$$

and the brackets $\langle\rangle$ denote the average of the quantity within. If a wetting liquid is admitted (or removed) from the craze, there will be a decrease (or increase) in S given by substituting $\Delta\gamma=\gamma_{\text{p-air}}-\gamma_{\text{p-liquid}}$ for γ in Equation 2 where $\gamma_{\text{p-air}}$ is the polymer/air surface tension and $\gamma_{\text{p-liquid}}$ is the polymer/liquid surface tension.

The system chosen for study is polystyrene (PS) using methanol or mehanol/water solutions as the environment. An advantage of this system is that methanol is a weak crazing agent and a very poor solvent for PS. The methanol crazes formed are stable and the non-crazed PS is only swollen slightly by methanol. This system is quite different from the PMMA–methanol system[3–5] for which the environment is a strong crazing agent and swells the bulk considerably.

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EXPERIMENTAL

Tensile specimens were cut from 1 mm thick commercial polystyrene sheet. These were extended to a tensile stress of 18 MN m^{-2} using an inverted loading cage attached to the crosshead of an Instron testing machine. The cage permitted immersion of the specimens into the crazing fluids while these were still under strain. When held at the constant extension corresponding to the above tensile stress the specimens did not craze rapidly in air but crazed rapidly upon immersion in methanol. While the specimens continued to be held at constant extension, different methanol/water mixtures were introduced and then allowed to evaporate. The load was monitored during the introduction and evaporation. The presence of the fluid within the craze was verified independently by small angle X-ray scattering[6]. Methanol/water solutions that are more than 50% volume water enter a dry craze rather slowly, so in these cases, crazed specimens which had been dried were first immersed for a short time in methanol, and then immersed in the methanol/water mixture.

A control experiment was performed in which PS specimens were extended to loads insufficient to cause crazing in methanol. The environments were changed for these samples in the same manner as for the crazed samples in order to measure the effect of methanol absorption in the bulk on the stress change.

After the initial thermal transient only negligible changes in stress were observed over the time scale of the experiments reported for the crazed samples. Very long absorption/desorption times were necessary to observe any bulk effect.

SURFACE ENERGIES

Contact angles between polystyrene and the environments were measured by dissolving some of the polystyrene sheet in toluene and then pulling a glass slide from the solution to form a clean polystyrene surface. Drops of the environment were placed on this surface and photographed. The contact angles, measured to ±2° from these photographs, are tabulated in *Table 1*. For water the contact angle was also measured on a pure polystyrene surface made in the same way. That this contact angle (91°) is larger than the contact angle on the material from the commercial sheet (86°) is not surprising, given the sensitivity of contact angle measurements to small amounts of surface contamination which can come from additives within the polymers.

Table 1 Contact angles on clean surfaces made from the polystyrene sheet

Fluid	Angle
75% CH_3OH–25% H_2O	34°
50% CH_3OH–50% H_2O	52°
25% CH_3OH–75% H_2O	65°
H_2O	86°

The interfacial energies per unit area between methanol/PS and water/PS were estimated using Fowke's method[7] and the data of Owens and Wendt[8]. In this estimation method the surface energy of polymer and solvent are separated into dispersion and hydrogen bonding components γ^d and γ^h. The interfacial tension is given by[7]

$$\gamma_{12}=[(\gamma_1^d)^{1/2}-(\gamma_2^d)^{1/2}]^2+[(\gamma_1^h)^{1/2}-(\gamma_2^h)^{1/2}]^2 \qquad (3)$$

where component 1 is the liquid environment and component 2 is polystyrene. *Table 2* shows the values[7,8] used for γ_1^d, γ_1^h, γ_2^d and γ_2^h as well as the γ_{12}'s derived from these for the methanol/PS and methanol/water surfaces. Also shown in *Table 2* are γ_2, the surface tension of a PS/air surface[9] as well as γ_1's, the surface tension of the various liquid/air interfaces[10].

For a solution in contact with a solid the Young/Dupre equation takes the form

$$\gamma_{12}=\gamma_2-\pi_2-\gamma_1\cos\theta \qquad (4)$$

where θ is the contact angle and π_2 is the film pressure of the solid–vapour interface[11]. Since π_2 is not known for solutions γ_{12} cannot be determined from contact angles. However if π_2 in Equation 4 is set equal to zero the γ_{12} so computed from the observed contact angle will be an upper limit. These upper limit γ_{12}'s for the methanol/-water solutions are also shown in *Table 2*. Also displayed in *Table 2* are the computed $\Delta\gamma$ $(=\gamma_2-\gamma_{12})$ values, corresponding to the change in surface energy of polystyrene on removing the various environments.

RESULTS AND DISCUSSION

The change in tensile stress on a crazed polystyrene sample is measured as a function of time after it is removed from various environments as its crazes are

Table 2 Various surface energies (mJ m^{-2})

	γ^d	γ^h	γ_1	γ_2	γ_{12}	$\Delta\gamma=\gamma_2-\gamma_{12}$	$\Delta\gamma_{exp}$[d]
Polystyrene	41.4	0.6	–	42	–	–	–
CH_3OH	22	1	21.8	–	3.0	+39	74.2
75% CH_3OH–25% H_2O	–	–	28.1	–	17.1[c]	24.9[c]	49.6
50% CH_3OH–50% H_2O	–	–	34.8	–	20.3[c]	21.7[c]	35.8
25% CH_3OH–75% H_2O	–	–	45.6	–	22.2[c]	19.8[c]	24.8
H_2O	21.8	51	72.0	–	43.5 (43.2[a], 37[b])	–1.5 (–1.2[a], +5[b])	

[a] Computed from contact angle of solvent cast film of 91° assuming $\pi_2 = 0$

[b] Computed from θ of commercial sheet of 86° assuming $\pi_2 = 0$

[c] Computed from measured contact angle on solvent cast PS film assuming $\pi_2 = 0$. As explained in the text this is an upper limit on γ_{12} and thus a lower limit on $\Delta\gamma$

[d] Computed assuming $\bar{D} = 11$ nm

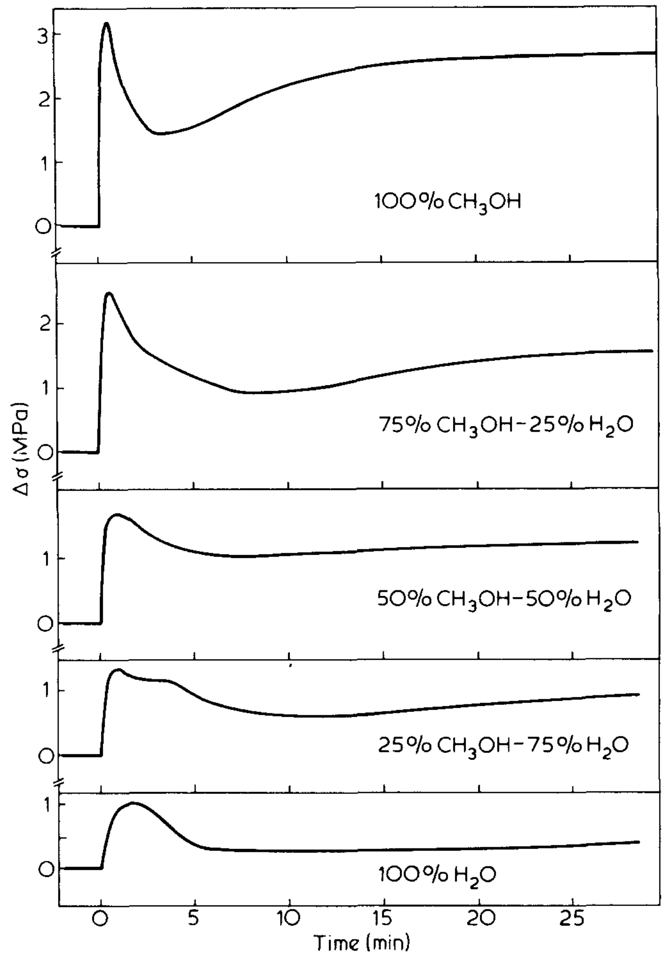

Figure 1 Tensile stress changes of crazed specimens held at constant extension v. Time after removing them from various liquid environments

allowed to dry. Stress–time curves are displayed in *Figure 1* for methanol, water and various solutions of the two. In all cases the qualitative shape of the curve is the same, a rapid stress pulse increase superimposed on a stress which rises gradually to a new, constant value. The uncrazed specimen showed a similar transient stress pulse, which is due to the thermal contraction of the specimen due to the cooling effect of liquid evaporation, but very little long-term increase in stress ($\Delta S < 0.2$ MPa). The long-term increase in stress is clearly caused by loss of the enviroment from the crazes. Although one might argue there would be a small component of stress change due to loss of methanol absorbed in the bulk of the specimen immediately adjacent to the crazes, the small equilibrium swelling of PS in methanol ($<2.5\%$) and the small methanol diffusion distance (<1 μm) during the time of these experiments (15–30 min) makes this component negligible. These long-term changes, caused by exchanging each of the environments for air, are shown in *Table 3*. These changes are reversible in that the crazes can be rewet and the same change observed on redrying. The changes are also independent of the applied tensile stress as long as it is not so high as to cause additional crazing or so low as to cause the crazes to be compressed by elastically-strained polymer surrounding the craze[6]. This stress change has all the attributes one would expect if it were caused by the change in surface tension of the craze fibrils.

According to Equation 2 the change in stress across the craze on removing the enviroment should be

$$\Delta S = \frac{2\Delta\gamma v_f}{\bar{D}} \tag{5}$$

We recently demonstrated[6] that $\bar{D}$ can be determined by small angle X-ray scattering and obtained values of 6 nm for air crazes in PS with some evidence that wet methanol crazes were similar. Dried methanol crazes gave a value of 11 nm when using a value v_f of 0.2 from transmission electron microscopy[12]. From the $\Delta\gamma$ data in *Table 2* one can compute the ΔS expected from fibril surface tension changes on removing methanol ($\Delta S = +1.4$ MPa if $\bar{D} = 11$ nm and $+2.6$ MPa if $\bar{D} = 6$ nm) and water ($\Delta S = -0.05$ to $+0.17$ MPa if $\bar{D} = 11$ nm and -0.09 to $+0.32$ MPa if $\bar{D} = 6$ nm). These values are the same order as the measured stress changes shown in *Table 3* and agree very well if the lower value of $\bar{D}$ is used. It is not obvious which value to use as the fibril clumping on drying[6] might be partly reversible. As expected methanol/water solutions produce ΔS's monotonically increasing from low values for the water-rich solutions to larger values for the methanol-rich ones.

Another way to demonstrate this agreement is to compute $\Delta\gamma$ values from the stress change data and Equation 5. These $\Delta\gamma$ experimental values obtained, assuming $\bar{D} = 11$ nm, are also shown in *Table 2* where they can be compared with estimates of $\Delta\gamma$ for the solutions. The agreement is reasonable considering the experimental and theoretical uncertainties.

One might argue that some portion of these stress changes are caused by the fibril volume changes (deswelling) resulting from the removal of methanol. Since these were typically 4 crazes per millimetre along the specimen and since such isolated methanol crazes are of the order of 1 μm in thickness[12], the change in strain in the craze must be ~ 250 times the nominal strain ($\sim 10^{-3}$) that produces the ΔS of 2.7 MPa. The change in craze strain $\Delta\varepsilon$ required is 0.25 whereas the equilibrium change in volume of PS on swelling with methanol is less than 0.025. The fibril shrinkage on deswelling is too small.

From the large changes in craze strain required in response to the changes in fibril surface tension it also appears that the fibrils have a considerably higher compliance than bulk glassy PS. It seems possible that the small size of the fibrils makes them more rubbery than the bulk polymer and we have observed other evidence of large fibril retractions on fracture[13,14]. The question of polymer chain mobility in small diameter craze fibrils is an important one for fibril stability and deserves to be investigated further.

Finally it is worth comparing the magnitude of these ΔS's to the total stress required for craze growth. Stress

Table 3 Long-term stress increases on removing crazed specimens from various liquid environments

Methanol/water solution composition (vol % methanol)	ΔS (MPa)
100	2.7
75	1.8
50	1.3
25	0.9
0	0.2

measurements of air crazes in PS reveal that the total stress across the craze is within 15% of the applied stress[15] and preliminary measurements on methanol crazes in PS[12] reveal similar results. (T_g in the fibrils is only depressed to 90°C by methanol.) Thus the total stress across these crazes is close to the applied stress, 7–10 MPa. The stress change due to change in surface tension is only a small part of this stress and thus the major effect of the methanol environment in enhancing craze growth to reduce the flow stress of the polymer by plasticizing it. These observations thus confirm the contentions of Kambour and others to this effect. If the fibril diameter D and volume fraction v_f were to remain constant as the temperature is raised toward T_g the flow stress would decrease (the current evidence is that D increases[16] but v_f decreases[12]) the change in surface tension would become more important as claimed by Andrews *et al.* It will be quite important therefore to make measurements of the relevant quantities as a function of temperature.

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