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Plasticization effects on environmental craze microstructure

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Environmental crazes were grown in thin films of polystyrene (PS) using the homologous series of alcohols, CH_3OH, C_2H_5OH, n-C_3H_7OH and n-C_4H_9OH. The films were bonded to copper grids, strained to below the minimum crazing strain in air and exposed to the vapour of the various alcohols. The craze microstructure, as measured quantitatively by transmission electron microscopy, varies significantly along the series. The craze fibril volume-fraction, v_f, decreases monotonically from 0.25 for methanol, which depresses the glass transition temperature, T_g, of PS to 91° C, to 0.09 for n-butanol, which depresses T_g of PS to 71° C. All these slowly-growing vapour crazes thicken by drawing more fibrillar material from the craze surfaces rather than by fibril creep. The large decrease in v_f along the series of alcohols cannot be due to a change in the chain-entanglement molecular weight, as a result of swelling by the alcohols, but must result rather from an easier slippage of molecular entanglements in the drawing glassy fibrils. The large decrease in v_f from methanol to butanol crazes must also enhance the nucleation of cracks within these crazes, as evidenced by the ten-fold decrease in the environmental fatigue life of PS along the series from methanol to butanol.

1. Introduction

A characteristic feature of the fracture of glassy polymers is the appearance of crazes in the specimen prior to actual fracture. These crazes, which have the appearance of fine cracks in the naked eye, upon microscopic examination are found to contain oriented fibrillar polymer material interspersed in a continuous matrix of voids [1–5]. Transmission electron microscopy of crazes in thin films reveals that the oriented polymer fibrils, approximately 10 nm in diameter, are drawn across at normal incidence from one craze matrix interface to the other [6–10]; this picture is confirmed by the results of small-angle X-ray scattering experiments on crazes in bulk specimens [11–14]. In the absence of an aggressive environment (e.g. in air) fracture is initiated by the break-down of the fibrillar microstructure, usually at the midrib of the craze (a slab of low fibril volume-fraction in the craze centre), to form voids which grow slowly until one reaches a critical size beyond which it can propagate catastrophically as a crack [3, 4, 15, 16].

In the presence of certain environments, crazes can grow at much lower applied stresses than in air [3, 17, 18]. The fracture initiation stress appears to be similarly depressed [5]. Most attention has centred on the depression of the critical tensile strain, ϵ_c, for craze initiation by the environment. The results strongly indicate that plasticization of the craze–matrix interface (or the craze fibrils) by the environment is primarily responsible for the ϵ_c depression [17, 18] although when the glass transition temperature, T_g, is depressed to, or below, the ambient temperature there is evidence that changes in surface tension of the solid on wetting by the environment may also be important. Logically, the plasticization can be expected to affect the craze fibrillar microstructure as well as the break-down of the fibrils to form cracks. Apart from a qualitative comparison of the craze microstructures produced by a weakly-plasticizing environment (methanol) and a strongly-plasticizing environment (n-heptane) in polystyrene, in which large differences in microstructure [19] (and craze mechanical properties [20]) were observed, there

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has been no systematic investigation of the effect of environment on craze microstructure.

In this paper, the results of just such an investigation are reported using as environments the homologous series of alcohols, methanol, ethanol, *n*-propanol and *n*-butanol. The decrease in solubility parameter, δ, from $\delta = 14.5\,\mathrm{cal}^{1/2}\,\mathrm{cm}^{-3/2}$ for methanol to $\delta = 11.4\,\mathrm{cal}^{1/2}\,\mathrm{cm}^{-3/2}$ for *n*-butanol [21] suggests that increasing alcohol solubility and increasing depression of T_g of PS ($\delta = 9.1\,\mathrm{cal}^{1/2}\,\mathrm{cm}^{-3/2}$) in equilibrium with alcohols of increasing molecular weight should be observed. This expectation is demonstrated to be correct and the resulting environmental craze microstructures are shown to depend strongly on only rather modest changes in T_g depression.

2. Experimental procedure

To ensure that the craze microstructure is faithfully revealed by transmission electron microscopy (TEM) a method must be found for straining thin PS films (not more than 1 μm in thickness), exposing these films to the environment, removing the environment without damaging the craze microstructure and then examining any crazes in the film in the TEM, all whilst maintaining the applied strain. A ductile copper grid, of grid squares 1 mm × 1 mm, was cut into rectangular strips (5 mm × 50 mm). The grid bars of the strips were coated with PS by dipping in a 2 wt% solution of PS in toluene and were then set aside to dry. Polystyrene films were cast from another, more concentrated, PS–toluene solution onto glass slides by pulling the slides at a uniform rate from the solution. The polystyrene had a number average molecular weight of $\bar{M}_N = 97\,800$, and a weight average molecular weight of $\bar{M}_W = 314\,000$. Film thicknesses, which were between 0.5 μm and 1 μm, were measured using an optical interference microscope. After drying, the PS film was floated off the glass slide onto the surface of a water bath and was picked up on the PS-coated copper grid. The film and grid were then exposed for 2 to 3 min to toluene vapour. This treatment softens the film and the coating on the grid just enough so that a good bonding between the film and the grid is achieved.

After drying, the film is subjected to a tensile stress, ϵ, by straining the copper grid in tension to a value, $\epsilon = 0.25\%$, which is below the critical strain for crazing in air. The copper grid deforms plastically and holds the polymer film under tension even when the applied force on the grid is removed. After straining, the film is examined in the optical microscope to ensure that no air crazes had formed. The film is then placed in the vapour 2 to 3 cm above the surface of a bath of the appropriate alcohol environment and allowed to craze for between 2 and 24 h. Crazing the samples in the vapour environment eliminated distortions of the fibrillar microstructure that can occur due to the action of the liquid–air meniscus that can occur when drying a craze which has been immersed in liquid [5, 14].

After viewing the film again with the optical microscope, representative crazed grid squares were cut from the grid for examination in the TEM at 100 kV. Care was taken to use minimum exposures to reduce radiation damage, even though changes in craze microstructure due to radiation damage in PS have been shown to be minimal [22]. Measurements of the volume fraction, v_f, of fibrils in the craze were made from micrographs of the craze. Optical densities, ϕ, of the electron image plate were determined in regions of the plate corresponding to the solid film, the craze and a hole through the film. The fibril volume fraction may then be computed [23, 24]

$$v_f = 1 - \frac{\ln(\phi_{\mathrm{craze}}/\phi_{\mathrm{film}})}{\ln(\phi_{\mathrm{hole}}/\phi_{\mathrm{film}})}\,. \tag{1}$$

Glass transition temperatures, T_g, were measured using a simple technique developed by Krenz [25]. A 5 μm thick film of PS was soaked at room temperature in each of the solvents until equilibrium was achieved. The film was then wedged between two metal blocks and a small weight was applied to the protruding end. The film was stiff enough when glassy to deflect only slightly as a rigid cantilever beam. The entire assembly was placed on a hot-plate and a thermocouple was attached to one of the blocks to monitor the temperature. Since the Young's modulus of the film decreases abruptly at T_g, heating the blocks causes the film to become limp and bend over the point-of-contact with the blocks. By measuring the temperatures at which the various plasticized films made a 60° angle to the horizontal and calibrating these temperatures with a known glass transition temperature of a plasticized PS, appropriate values of T_g were obtained. Methanol-plasticized PS was chosen as the standard against which all of the glass transition temperatures of the other samples

TABLE I Correlation between the glass transition temperature of the swollen polymer, craze microstructure and fatigue life of PS in the environment

Environment	Glass transition temperature, T_g (° C)	Craze fibril volume-fraction, v_f	Fatigue life (Number of cycles to failure), N_f (from [32])
Methanol	91	0.25	11 900
Ethanol	85	0.18	7 530
n-Propanol	81	0.12	1 230
n-Butanol	71	0.09	1 170

were calibrated, since the T_g of methanol–PS has been well documented to be 91° C [17–19]. The glass transition temperatures measured in this way are shown in Table I and decrease as expected as higher alcohols are reached along the homologous series.

3. Results and discussion

Figs 1 to 4 show, respectively, the fibrillar microstructures typical of methanol, ethanol, *n*-propanol and *n*-butanol crazes in PS. Methanol crazes show a dense network of fine fibrils and appear rather similar to air crazes in PS, a conclusion confirmed by small-angle X-ray scattering studies of methanol crazes [14]. While no drastic change in fibril diameter occurs on traversing the series from methanol to butanol (the individual fibril diameter is anyway notoriously difficult to measure from an image of overlapping fibrils [9, 10]), the visibility of individual fibrils improves dramatically for the higher alcohols. Whereas it is difficult to pick out individual fibrils in the strongly overlapping fibril microstructure of the methanol craze, shown in Fig. 1, it is quite easy to pick out individual fibrils in the *n*-butanol craze (in the same thickness PS film) shown in Fig. 4. The increased fibril visibility suggests that the craze fibril volume fraction, v_f, decreases as the PS is crazed by progressively higher alcohols. This hypothesis is borne out by quantitative measurement of v_f using microdensitometry. As shown in Table I, v_f decreases monotonically along the series from 0.25 for methanol crazes (almost identical to air crazes in PS [24]) to 0.09 for *n*-butanol crazes.

It seems reasonable to suppose that this decrease in v_f is due to the increasing T_g depression produced by the higher alcohols. Other evidence for plasticization of the fibrils comes from the substantial fibril retraction behind crack tips in vapour environments of the higher alcohols. Fig. 5 shows the craze ahead of a crack tip in a PS film exposed to *n*-propanol. The crack developed by fibril break-down during exposure to the environment. It is obvious that fibrils behind the craze tip have retracted to approximately a third of their original unbroken length. While air-craze fibrils in PS broken by cracks also undergo retraction, it is usually to no more than half of the original fibril length.

Measurements of the fibril volume-fraction v_f along these crazes reveal that it is roughly constant over most of the craze, decreasing only just behind the craze tip and in the craze midrib, a slab of less-

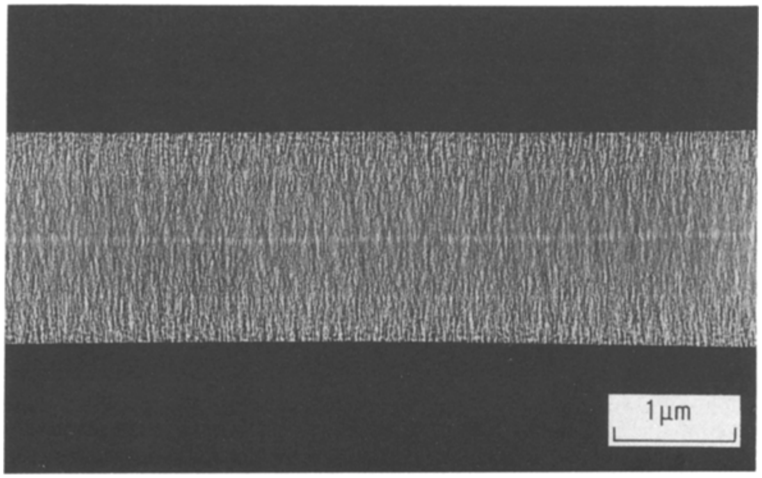

Figure 1 Transmission electron micrograph of the methanol–PS craze fibril microstructure.

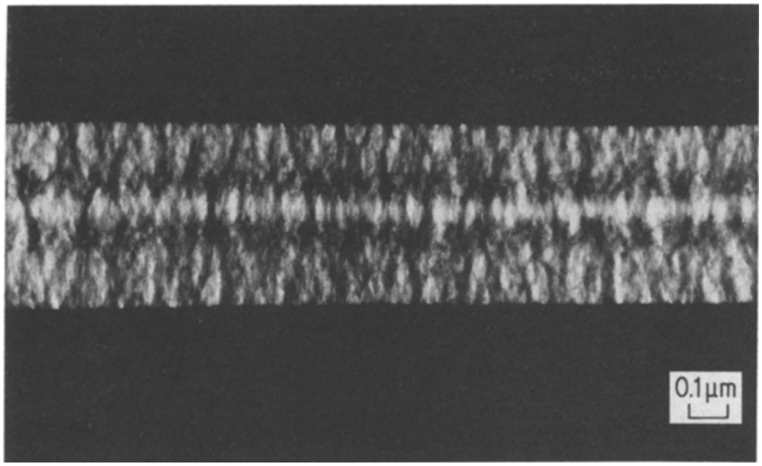

Figure 2 Transmission electron micrograph of the ethanol–PS craze fibril microstructure.

dense fibrillar material midway between the two craze surfaces. The presence of the midrib in these vapour crazes (it can be plainly seen in Figs 1, 3 and 4) is in marked contrast to previous observations on methanol and n-heptane crazes in PS films produced by exposure to the liquids [19]. The variation of v_f along all the vapour crazes is very similar to that observed in air crazes. Since it has been proved in air crazes that this v_f profile and the midrib is a consequence of the fact that the craze thickens as it grows in length by drawing new fibril material from the craze surfaces, and since the decrease in v_f in the midrib and just behind the craze tip is due to the higher craze surface stress behind the craze tip, it seems reasonable to attribute the v_f profile observed in the vapour crazes to a similar mechanism of craze thickening. Even though the thickening of environmental crazes by surface drawing could, in principle, be limited by diffusion of the environment into the craze surfaces [5], it appears that at the low stresses and low craze-growth rates ($< 10^{-5}$ cm sec^{-1}) of these experiments diffusion is fast enough that the predominant mechanism of craze thickening can be surface drawing rather than fibril creep.

It is commonly believed that the craze fibrils are stabilized against failure by plastic flow (creep) by chain entanglements in the glass. This view is strongly supported by the observed instability of craze fibrils in polymer whose molecular weight is below the chain-entanglement molecular weight, M_c, computed as the break in the shape of the low-shear-rate melt viscosity against molecular weight curve. (In PS, $M_c \simeq 35\,000$ [26].) Since the

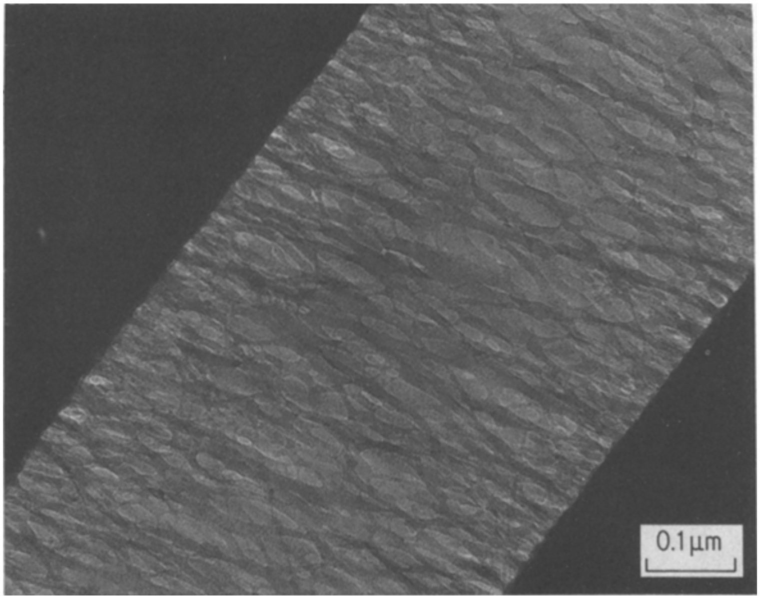

Figure 3 Transmission electron micrograph of the n-propanol–PS craze fibril microstructure.

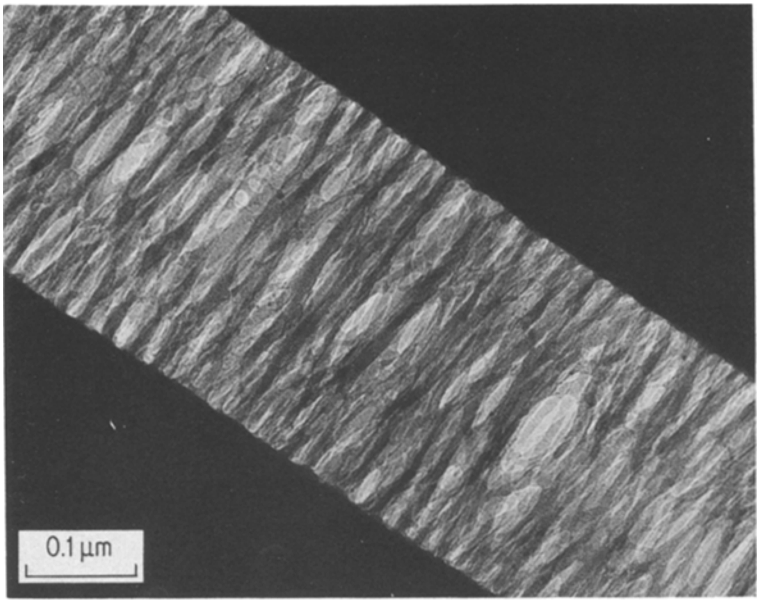

Figure 4 Transmission electron micrograph of the *n*-butanol–PS craze fibril microstructure.

root mean square end-to-end distance of a molecule of such a molecular weight in the glass, as well as the fully extended length of such a chain, is known from neutron scattering experiments [27–29], one can compute the maximum extension ratio, λ_m, that can be achieved for PS without the slipping of entanglements (i.e. treating the entanglements as permanent cross-links) [24] to be,

$$\lambda_m = 0.03(M_c)^{1/2}. \quad (2)$$

Using the M_c value for PS, λ_m is approximately 5.7 [24]. The actual λ values measured for air crazes in PS ($\lambda = 1/v_f$, since the fibril deformation occurs at constant volume) are 4 to 5 in reasonable agreement with the hypothetical limiting value [24].

It is known that diluting the polymer with a molecular-weight diluent increases the entanglement molecular weight as [26]

$$(M_c)_s = M_c/\Phi_2, \quad (3)$$

where $(M_c)_s$ is the entanglement molecular-weight in the concentrated polymer solution and Φ_2 is the polymer volume fraction in the solution.

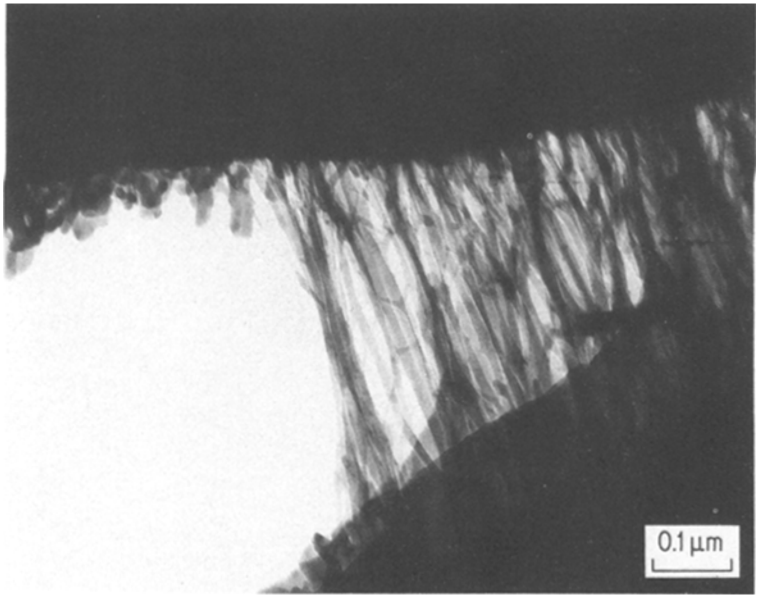

Figure 5 Transmission electron micrograph of a partially-cracked *n*-propanol–PS craze. Note the large fibril retraction behind the crack tip.

Hence it might be postulated that the maximum fibril extension ratio in the swollen polymer glass, $(\lambda_m)_s$, plasticized by the alcohols, would be given by

$$(\lambda_m)_s = 0.03(M_c/\Phi_2)^{1/2}, \qquad (4)$$

or the minimum fibril volume-fraction $(v_f)_{\min}$, be given by

$$(v_f)_{\min} = \left(\frac{1}{\lambda_m}\right)_s = 33(\Phi_2/M_c)^{1/2}. \qquad (5)$$

At first glance it might appear that this hypothesis would account for the decrease in v_f with increasing alcohol molecular weight, since Φ_2 decreases along the series. (Φ_2 for *n*-butanol is 0.95 whereas Φ_2 for methanol is about 0.99.) However, the decrease in $(v_f)_{\min}$, so predicted, is only 2.5% from methanol to butanol, much less than the 65% decrease in v_f actually observed. Moreover, the lowest v_f value of 0.09 for butanol corresponds to a fibril extension ratio of 11 which, from Equation 2, would require a chain molecular-weight between entanglement cross-links of more than 130 000 which is much larger than is physically reasonable (it would require $\Phi_2 < 0.27$). Therefore it must be concluded that the main effect of the environment diluent in the fibrils is not to change the entanglement molecular weight but to allow more extensive slippage of entanglements (for example by molecular reptation [30]).*

It is also worth noting that the observed changes in craze microstructure in the homologous series cannot be due to changes in surface energy of the fibrils. The interfacial energy, γ_{12}, of a methanol–PS interface is only 3 mJ m^{-2}, whereas that of an air–PS surface is 42 mJ m^{-2}. Increases in tensile stress of the magnitude appropriate to being the result of changes in surface tension are actually observed on drying methanol crazes in PS [31]. However, the methanol craze microstructure is very similar to that of the air craze; even if γ_{12} decreases further from methanol to butanol, the small magnitude of the decrease that is possible relative to that from air to methanol implies that the resultant changes in craze microstructure due to this decrease would be negligible.

Whatever the reason for the decrease in fibril volume-fraction with increasing depression of T_g of the swollen polymer by the series of alcohols, it would be expected that this decreased fibril content would enhance the probability of the nucleation and growth of cracks within the craze. A sensitive test of this hypothesis would be measurements of the fatigue life, N_f, (N_f is defined as the number of cycles to failure) of smooth polymer samples exposed to these environments at a low and constant stress amplitude.

Under these conditions most of the fatigue life of the polymer is spent in the nucleation of the initial crack within a craze. Fortunately, such measurements have been made on PS in all four alcohol environments by Warty, Morrow and Sauer [32]. The fatigue lives of their specimens are also tabulated in Table I. As the craze fibril volume-fraction decreases along the series there is a corresponding decrease in the fatigue life, with the fatigue life in *n*-butanol being only one tenth of that in methanol. The evidence seems quite convicing that decreasing the craze fibril volume-fraction by crazing in a more strongly plasticizing environment has the adverse effect of enhancing the nucleation and growth of cracks within the craze. A major reason for this behaviour is undoubtedly the fact that at constant applied stress the true stresses in the fibrils are much higher in low fibril volume-fraction crazes than in higher fibril volume-fraction crazes. (The true stress in the fibrils of an *n*-butanol craze will be approximately 2.8 times that in a methanol craze.) In addition, the enhanced entanglement slippage that we postulate leads to the low v_f values will make the final fibril break-down process by viscous flow of one molecule past another more rapid. Both factors will lead to a more rapid nucleation and growth of cracks within the craze.

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*Similar effects might be produced if the environment which swells the fibrils promoted chain scission, but there is no evidence to suggest that the alcohols play this role in polystyrene.

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