polymer reports

The effect of water on the tensile yield of polystyrene

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When PS is tested in tension but immersed in water the yield stress is unchanged and the crazing stress is increased, as compared with tests conducted in air. The crazing pattern is otherwise unchanged. If the PS is first equilibrated with water and then tested under water, both crazing stress and yield stress are reduced. A very large number of small crazes are generated which result in a 23% increase in the fracture strain.

Keywords Polystyrene; water; yield; crazing; fracture surface

INTRODUCTION

The effect of solvents and swelling agents upon the mechanical properties of glassy thermoplastics is a matter of continuing scientific and practical interest. Changes in the conditions to bring about crazing or shear yielding can result in brittle to ductile transitions in impact loading and in dramatic changes in fatigue life[1]. Results have been correlated with physical parameters of the polymer and liquid, especially the solubility parameter[2]. An important distinction is drawn between tests in which the polymer is simply immersed in the liquid (and may not be in sorption or swelling equilibrium with it) and tests in which the polymer is first equilibrated with the liquid and then tested. In the case of polystyrene (PS) and *O*-dichlorobenzene, Kambour[2] produced evidence which indicated that the critical strain to craze the polymer was the same whether the polymer was plasticized at the surface only, or throughout its bulk. In this study we show that as compared with simple immersion, PS responds quite differently after soaking in water. The difference may be due to the special mist-like pattern ('water pattern') which appears in extruded PS in hot water[3].

EXPERIMENTAL

A heat-resistant grade of PS was used, having $M_w = 2.74 \times 10^5$ and $M_n = 1.0 \times 10^5$ and hence $M_w/M_n = 2.74$. The material was commercially extruded into 12.7 mm diameter rods from which flat tensile test specimens were milled. The specimens were cut with their tensile axes colinear with the extrusion axis of the rod. The waisted gauge section measured approximately (12.5 × 6.4 × 3.1) mm. The specimens were carefully polished by hand to a highly reflective finish and were then washed in water and dried at 50°C in a vacuum for 6 h. They were stored in a desiccator over fresh silica gel until immediately prior to testing. A number of these specimens were heated in distilled water at 60°C for 103 h during which time their weight increased slightly ($<0.05\%$): on cooling to room temperature a water pattern appeared. These were stored in water and tested in tension while surrounded in water. The test gauge was uniformly birefringent; the birefringence was estimated to be $\sim -(6 \times 10^{-5})$, a low value typical of weakly oriented or stressed PS[4].

Tensile tests were conducted on an Instron TTM machine at room temperature and a strain rate $\sim 6.7 \times 10^{-4}\ \mathrm{s}^{-1}$. The specimen was illuminated by an intense beam of light directed at about 75° to its axis. Crazing was observed with a low power microscope. The yield stress recorded is the nominal stress obtained from the peak load and is the mean of two tests. Dry specimens were exposed to ambient conditions for a period not exceeding 10 min during testing: it is believed that the moisture absorption during this period was negligible. Specimens tested whilst immersed in water were exposed to air for only a minute whilst being fixed in the grips.

RESULTS AND DISCUSSION

The tensile yield stress (σ_y) and the crazing stress (σ_c) were determined at 25°C and $6.7 \times 10^{-4}\ \mathrm{s}^{-1}$ on three groups of samples. Schematic load displacement graphs are shown in *Figure 1*. *Figure 1a* shows the result for dry specimens tested in ambient conditions, *Figure 1b* for the dry specimens immersed in water and *Figure 1c* for the water-soaked specimens immersed in water. The crazing and yield stresses are given in *Table 1*. As compared with tests in air, when dry PS is immersed in water, neither the tensile yield stress nor the strain to fracture are much affected. If the PS is first soaked in water, the yield stress is decreased by about 5%, the material shows a typical crazing yield (with no change of cross-section), and the fracture strain is increased by 23%. Bigger changes occur in the crazing stress than in the yield stress. σ_c is *increased* by 13% on simple immersion in water, and *decreased* by

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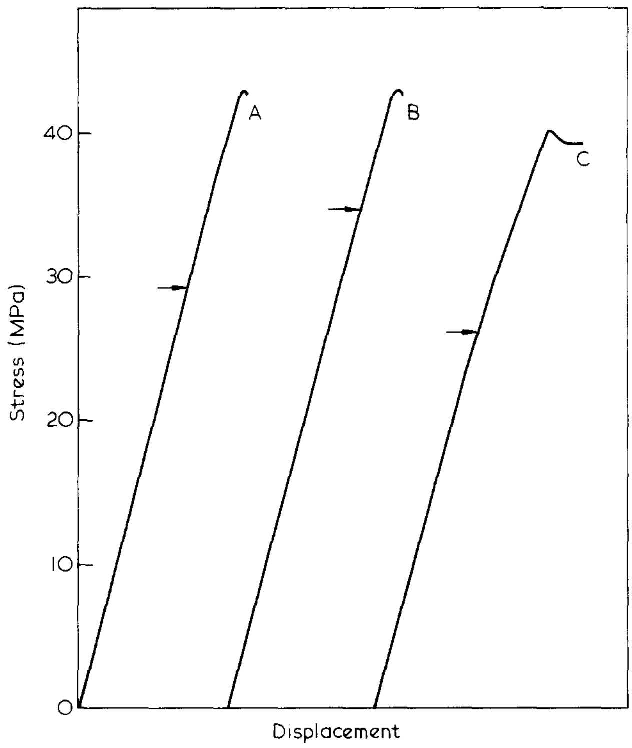


Figure 1 Schematic load displacement graphs: the arrow indicates the onset of crazing or micro-crazing (A) dry specimen tested in air (B) dry specimen tested in water (C) water-soaked specimen tested in water (crosshead speed 0.02 in/min)

Table 1 Crazing stress and tensile yield stress of extruded PS

Condition	Crazing stress (MPa)	Yield stress (MPa)
Dry, tested in air	31 ± 1	43.0 ± 0.3
Dry, tested under water	35 ± 1	43.3 ± 0.3
Wet, tested under water	26 ± 1	40.7 ± 0.3

16% when the water soaked specimen is tested under water, as compared with results obtained in air.

If we assume that crazes grow very rapidly to become visible and then more slowly before fracture[5] we can equate the crazing stress (σ_c) with the craze initiation stress. The yield stress (σ_y) in these tests must also be close to the stress to fracture the most stressed craze. The results here indicate that simple immersion of dry PS in water raises the craze initiation stress, an effect which has been reported in fatigue[1] and creep[5]. Simple immersion, however, does not alter the craze breakdown stress because water does not wet fresh PS surfaces and probably does not reach the tip of the growing craze which is still dry[6]. Dissolved water has been shown to have a mild plasticizing action on poly(methyl methacrylate) and reduces the yield stress in plane strain compression by 20–40%[7,8].

The same mild plasticizing action in water saturated PS would account for the 16% decrease in the craze initiation stress and the 5% reduction in the stress for craze failure.

The size and number of crazes formed are illustrated in *Figure 2*. The dry specimen, whether tested in air or immersed in water, produces a pattern of large well-spaced crazes as shown by the optical micrograph of *Figure 2a*. However, the water soaked specimen produced a dense field of micro-crazes as shown in *Figure 2b*, in appearance very much like the 'stress-whitening' of high impact PS (HIPS). The test gauge became opaque. The accumulated elongation of these micro-crazes resulted in a tensile yield-drop, and an increased failure strain as shown in *Figure 1c*.

The water soaked specimens were also internally etched with a water pattern which has been shown to be characteristic of water-etched extruded PS[3]. In the present case, the pattern appeared after treatment with water for about 12 h at 60°C followed by quenching in cold water. *Figure 3* illustrates the water pattern in these tensile test specimens, formed about 40°C below T_g after 15 days of water immersion and subsequent quenching in cold water. An earlier study[3] suggested that the pattern would

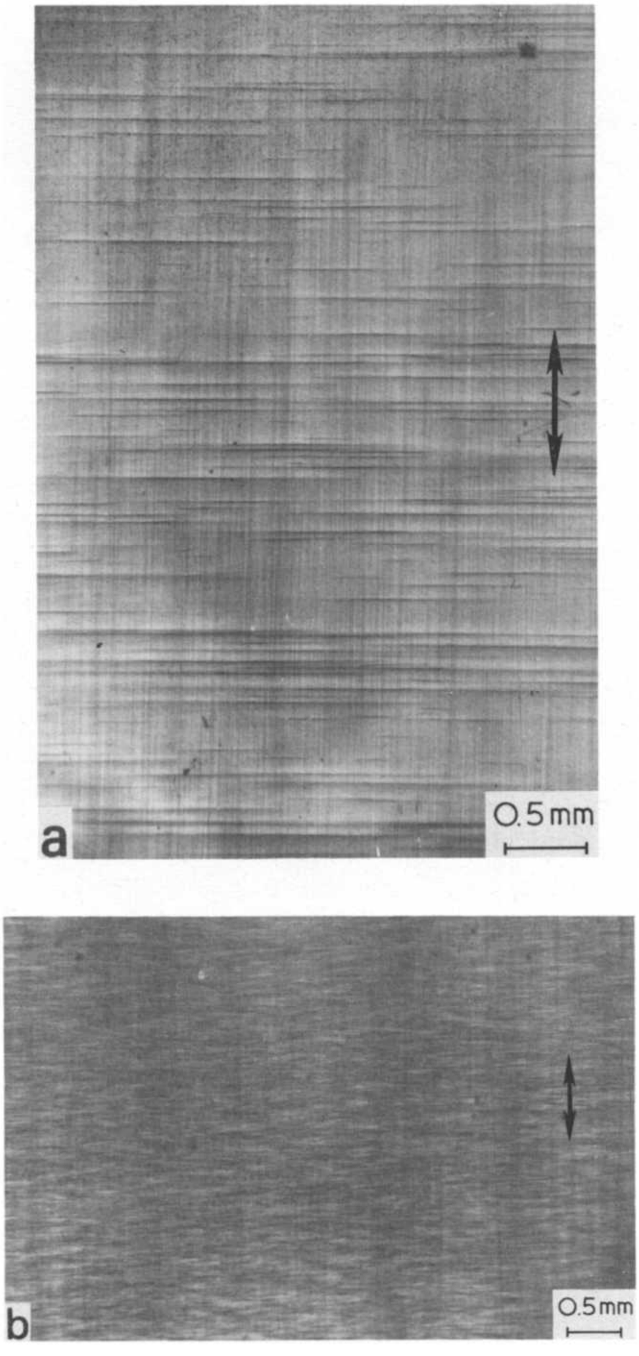


Figure 2 Photographs of individual portions of the gauge length of fractured specimens (a) dry specimen tested in air (b) water-soaked specimen tested under water

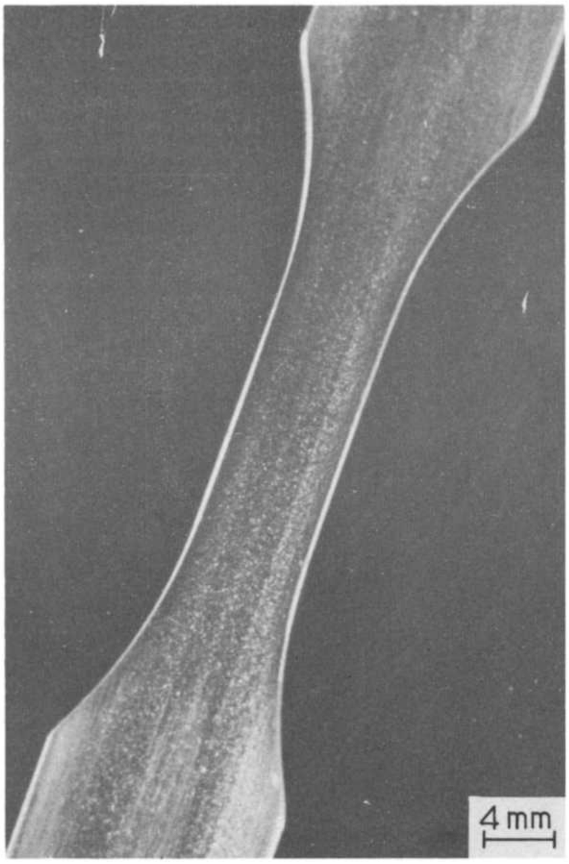
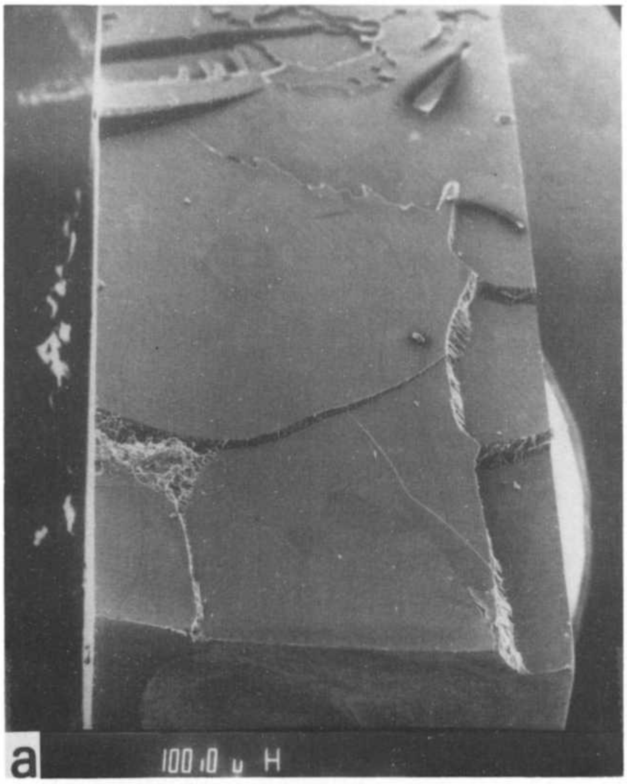


Figure 3 Photograph of test specimen after immersion in water at 60°C for 15 days followed by quenching in cold water: the 'water pattern'

form only if the PS were immersed in an aqueous environment, (a) at or above T_g, (b) for a sufficient period of time, (c) followed by quenching to 20°C. The first requirement is now seen to be unnecessary, and the idea that rubbery segmental chain motion is involved needs to be reviewed. Whatever the state of the water in these specimens, the results suggest that it reduces the stress to initiate crazes and produces a large number of internal craze nucleation sites.

The fracture surface morphology, as well as the craze pattern, is also significantly different for the water-soaked sample than for the dry sample. For the dry sample, whether tested to fracture in water or in air, the fracture surface, as depicted in *Figure 4a*, is highly reflective. This is an indication that large crazes have developed prior to craze breakdown and subsequent rapid crack propagation. The tensile fracture surface for the water-soaked sample is shown in *Figure 4b*. There is a relatively smooth region extending inward from the four sides of the specimen and a less reflective core area indicative of crack jumping from one small craze to another nearby one. The smooth edge region probably represents the extent of craze growth prior to crack initiation and propagation. Somewhat similar features are also seen upon tensile testing PS specimens coated with a low viscosity silicone oil[9].

A higher magnification view of a portion of the fracture surface near to a specimen edge is shown in *Figure 5*. At this magnification, many small voids are visible, as well as some secondary fracture parabolas (upper right corner). These voids are not present on the fracture surface of the dry samples so their presence is probably related to the 'water pattern' shown in *Figure 3*. They may be the result of water clustering or water vapour condensation at localized sites of excess free volume.



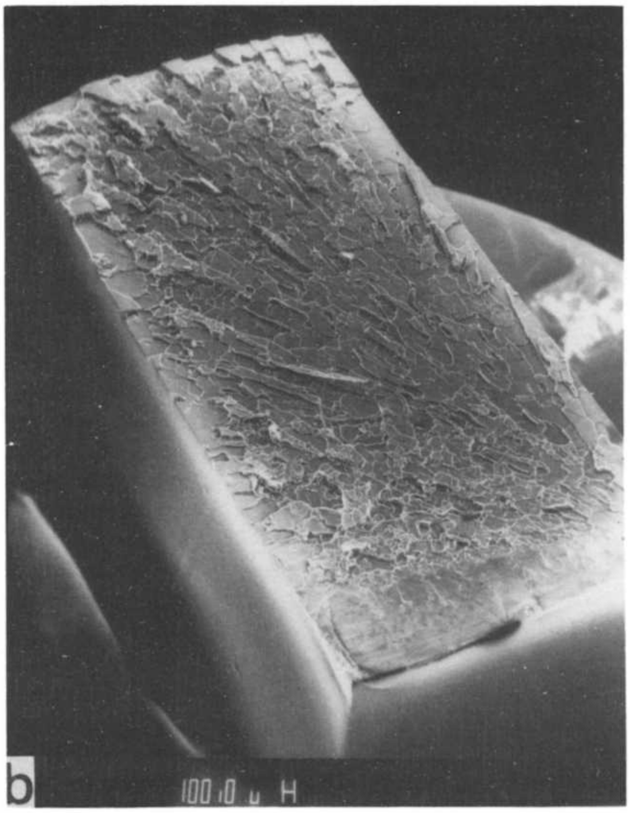


Figure 4 SEM micrographs of tensile fracture surfaces (a) dry specimen tested in air (b) water-soaked specimen tested in water

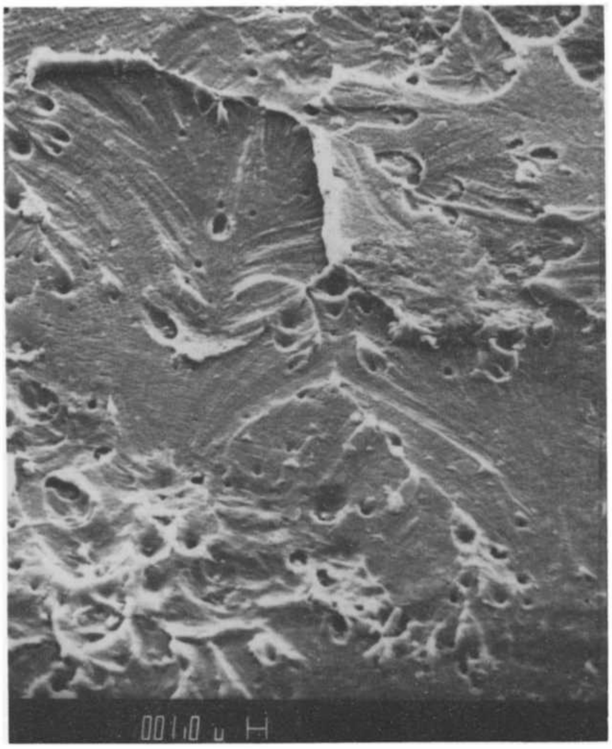


Figure 5 High magnification SEM micrograph of portion of fracture surface near edge of water-soaked sample

CONCLUSION

Small quantities of water enter the structure of extruded PS at temperatures well below T_g. The response to tension is consistent with a mild plasticizing action by the absorbed water. Microcrazes result in a crazing yield somewhat similar to the stress whitening of HIPS.

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Miscibility of SAN with polyacrylates and polymethacrylates

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Styrene–acrylonitrile copolymers, SAN, are known to be miscible with poly(methyl methacrylate). Based on the presence of a single composition dependent glass transition and lower critical solution temperature behaviour, it is shown that SAN is also miscible with poly(ethyl methacrylate). However, the SAN does not appear to be miscible with other polymethacrylates or polyacrylates.

Keywords Blends; miscibility; glass transition; lower critical solution temperature; poly(ethyl methacrylate); styrene–acrylonitrile copolymer

INTRODUCTION

It has been known for some time that styrene–acrylonitrile copolymers, SAN, and poly(methyl methacrylate), PMMA, are miscible[1–4]. Recently, it was observed in this laboratory that poly(α-methyl styrene-co-acrylonitrile), αMSAN, is miscible with PMMA and PEMA, poly(ethyl methacrylate), but not with higher homologues[5]. This raises the question of whether SAN might be miscible with PEMA or other related polymers. To answer this, two polyacrylates, PMA and PEA, four polymethacrylates, PEMA, PnPMA, PiPMA and PCHMA, as well as PVAc, which has reversed carbonyl group position to PMA, were blended with SAN. The appearance of the cast films and glass transition temperature behaviour were used to judge miscibility. Further measurements of density, the change in heat capacity at the glass transition, and lower critical solution temperature, *LCST*, behaviour were made for miscible blends.

EXPERIMENTAL

The source of the polymers used in this work are listed in *Table 1*. Blends containing different weight percentages of SAN were prepared by solution casting from tetrahydrofuran, THF. Each polymer was first dissolved in THF at the 5 to 10% level and then mixed in proper proportions. After vigorous stirring for a few hours, the mixture was poured into aluminium pans wrapped by aluminium foil punched with pin-holes to evaporate the solvent slowly. The resulting films were dried in vacuum at room temperature for one day and then at 60°C and 110°C for 3 days at each temperature.

The glass transition temperature of the polymers and

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