

NOTES

Dynamic Mechanical Properties of Solvent-Crazed Polystyrene

It is well-known that crazes often occur when polymers are strained in an "active environment," while no craze is observed for unstrained samples in the same environment.¹ At present, two mechanisms have been proposed to rationalize the solvent crazing. One is the plasticization theory, which appears to be consistent with data on a number of glassy polymers. Extensive studies have been carried out for polystyrene in the presence of several alcohols, aprotic polar and nonpolar agents both for solvent equilibrated²⁻⁴ and preplasticized films.⁵ The other theory is the internal surface energy hypothesis. Wieser⁶ has demonstrated its usefulness for poly(methyl methacrylate) in a series of alcohols and alcohol-water mixtures. In this note, we wish to report on the dynamic mechanical properties of solvent crazed polystyrenes in order to gain some insight into the mechanism of the solvent crazing process.

Polystyrene was purchased from Polysciences, Inc. Gel permeation chromatography measurements indicate that the average molecular weight of the material is 10^5 . The polymer was dissolved in benzene, and thin films were cast from the solution by means of spin casting.⁷ The polymer film was kept *in vacuo* at 50°C for 24 hr, and then at 100°C for 2 to 3 days to remove all solvents. Rectangle strips of the sample were deformed in the presence of a number of liquid organic environments (Table I) by a specially constructed creep instrument.⁸ The amount of deformation was maintained up to the critical strain values (ϵ_c). As soon as the crazes have formed, the sample was removed from the creep instrument and surface dried. It was then immediately transferred to the sample chamber of a Rheovibron DDV-IIB Viscoelastometer. In order to minimize solvent loss during measurements, the sample chamber was modified to contain the liquid at the bottom of the chamber away from the sample.

Table I shows the relevant characteristics of solvents used in this study, along with the T_g values of solvent-plasticized polystyrene and the critical strain values. For ethylene glycol and diethylene glycol, presumably due to their large differences from the solubility parameter of polystyrene (Table I), crazing took 15 hr to complete. For 1-pentanol and triethylene glycol, only 4½ and 10 min were required, respectively. Because of the extensive crazing, samples were very fragile and great care must be taken during the experimentation. Only one frequency (3.5 Hz) was found to be most suitable to work with, without fracturing the sample. Data were taken to the maximum possible temperature before rupture.

Figure 1 shows the loss tangent data for uncrazed polystyrene and for those crazed in ethylene glycol and diethylene glycol, separately. The loss curves are almost identical, with slightly higher values of $\tan\delta$ for crazed samples at temperatures below 70°C. It is of interest to note that the glass

TABLE I
Some Properties of Polystyrene and The Organic Liquids Used

	Molecular weight	Boiling point (°C)	δ^a (cal/cm ³) ^{1/2}	T_g^b (°C)	ϵ_c^a (%)
Polystyrene	10^5	—	9.1	105	0.36
Triethylene glycol	1.5×10^2	290	10.7	(n.a.) ^c	0.27
1-Pentanol	8.8×10	138	11.1	63	0.21
Diethylene glycol	1.06×10^2	244	14.2	63	0.21
Ethylene glycol	1.02×10^2	197	17.1	14.2 ^d 102	0.36

^a From Kambour et al. (ref 6). Other data were taken from Lange's *Handbook of Chemistry and Physics*.

^b Except the first, which is the data for pure polystyrene, all others represent T_g values of solvent plasticized polystyrene.

^c (n.a.) = not available.

^d From Vincent et al. (ref 10).

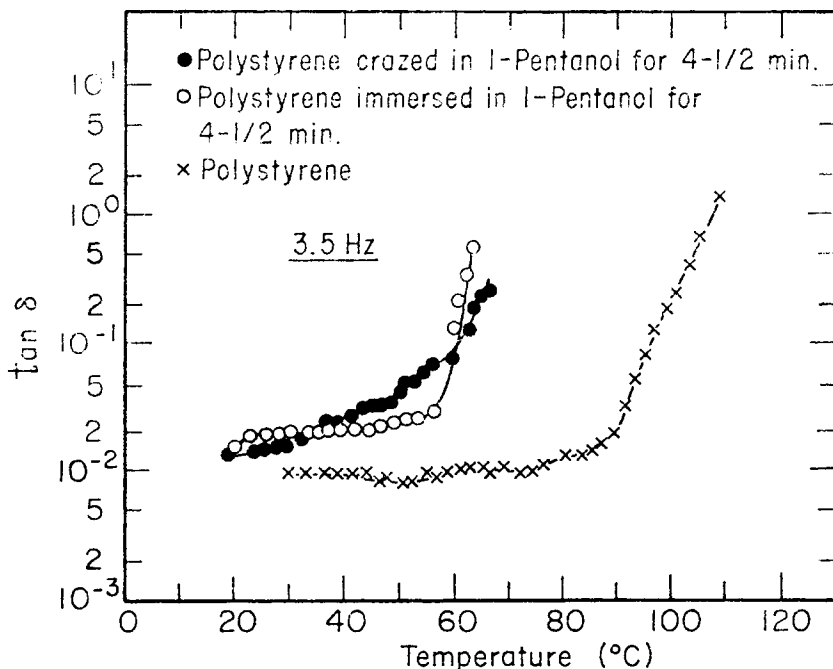


Fig. 1. Loss tangent vs. temperature curves for (●) uncrazed polystyrene, and for (○) polystyrene crazed in ethylene glycol, and (×) diethylene glycol.

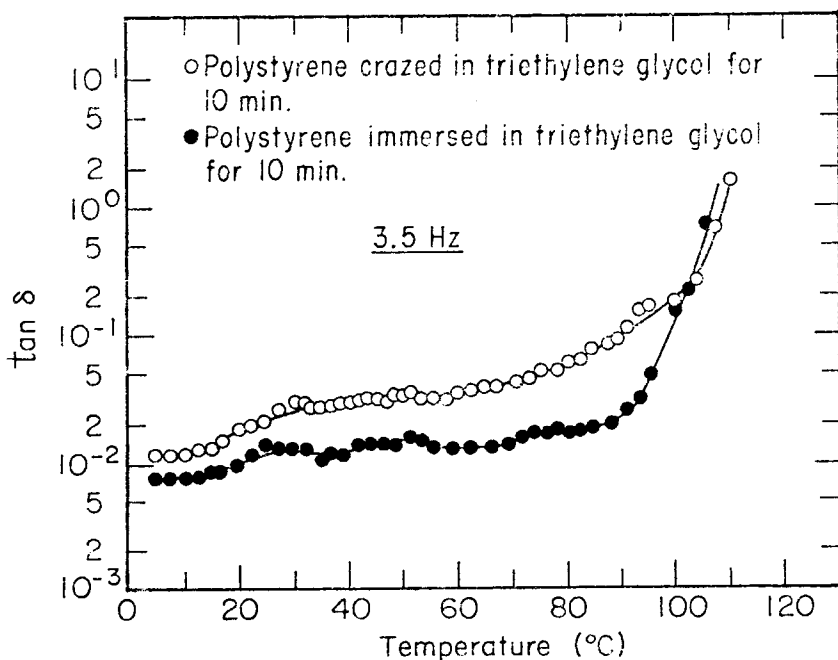


Fig. 2. Loss tangent vs. temperature curves for polystyrene crazed in triethylene glycol and immersed in the same solvent.

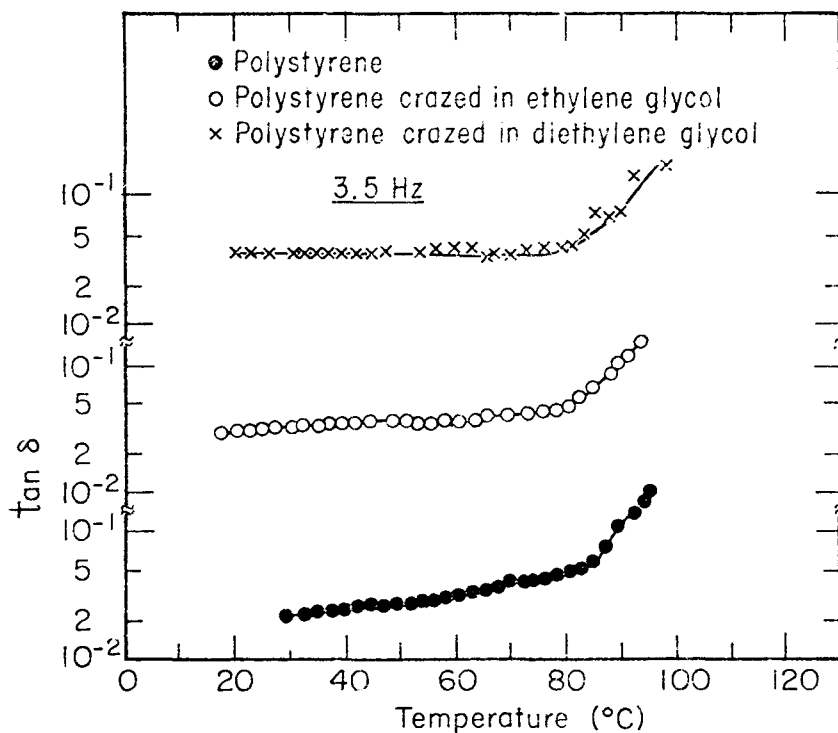


Fig. 3. Loss tangent vs. temperature curves for polystyrene crazed in 1-pentanol and immersed in the same solvent.

transition observed for polystyrene crazed in diethylene glycol environment (100°C) in Figure 1 is quite different from that of a plasticized sample (6°C) given in Table I.

To examine if any solvent loss has taken place during the transfer of sample from the creep instrument to Rheovibron and during subsequent measurements, we compare in Figure 2 the loss curves of polystyrene crazed in triethylene glycol with an unstressed sample immersed in the same solvent for the same length of time. Again, the loss curves are very similar in shape, and the loss strength is higher for the crazed sample. The upswings of the loss curves are near the glass transition temperature of unplasticized polystyrene (105°C). However, the loss curves of polystyrene crazed and immersed in 1-pentanol are very different (Fig. 3). Here the upswing in $\tan \delta$ occurs around 60°C , which is near the glass transition temperature of the plasticized polystyrene (Table I). The transition for the crazed sample is not as sharp as the polystyrene and noncrazed-immersed samples.

The 1-pentanol data appear to favor the plasticization mechanism of solvent crazing. For the other solvents, the interpretation is less clear. It is possible that plasticization took place on a thin surface layer of the polymer only, and the observed primary glass transition processes are due to the core materials only. It has been shown⁹ that several months were required for unstressed polystyrene to reach swelling equilibrium in glycols. However, Kambour found that the rate of swelling increases with increasing levels of stress.¹⁰ Even so, it does not appear likely that the equilibrium has been reached in the relatively short time that it took to craze the polymer in this study. Thus in the case of glycols the data seem to favor the surface stabilization hypothesis. It is possible that both kinds of mechanisms could be operative in solvent crazing. Whether one predominates over the other may depend on the nature of the interaction between the solvent and the polymer.

The very similar dynamic behavior of the immersed and crazed samples appear to indicate a uniform plasticization. If plasticization only occurred in the craze matter, then the polymer would have become a heterogeneous system and two glass transition processes should have been observed.

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