Calorimetric and neutron scattering studies of mixtures of polystyrene with poly(2,6-dimethyl-1,4-phenylene oxide) and its brominated derivatives

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(Received 13 December 1979)

Mixtures of polystyrene (PS) and poly(2,6-dimethyl 1,4-phenylene oxide), also known trivially as poly(xylenyl ether) (PXE), are thought to be miscible in that each exhibits a single, composition-dependent T_g[1,2]. A solution calorimetry study of PXE/PS mixtures has shown that the heat of mixing of the two polymers is exothermal by a few cal/g[3]. Copolymers of styrene and *p*-chlorostyrene are no longer miscible in PXE when the content of the latter comonomer in the styrenic polymer is greater than about 65 mol%[4].

The addition of bromine to solutions of PXE results in rapid substitution on the aromatic ring, no catalyst being needed[5]. As a result of ring deactivation, the use of less than stoichiometric amounts of bromine results in no more than one bromine on any given ring (attached at the 3 or 5 position). In this way 'copolymers' containing 2,6-dimethyl-1,4-phenylene oxide and 3-bromo-2,6-dimethyl-1,4-phenylene oxide repeat units are easily produced across the whole composition spectrum starting from a single PXE resin. At 1 bromine per ring (PBr_1XE), the T_g of the polymer is 280°C.

We have begun a study of the compatibility properties of mixtures of PS with PXE brominated in chloroform solutions to various levels up to one Br per ring ($PBr_{\bar{x}}XE$, $\bar{x}$ = 0 to 1). Preliminary results are reported here.

Phase behaviour of mixed films

PXE itself crystallizes partially when cast from chloroform solution. Cast films of $PBr_{\bar{x}}XE$, $\bar{x} \geqslant 0.25$, are clear and amorphous (i.e. no evidence of melting by scanning calorimetry). T_g rises linearly with Br content. A cast film containing 30 to 50 wt % PS is clear and exhibits only one T_g as long as $\bar{x} < 0.8$ to 1.0. The critical value $\bar{x}_c$ required for two-phase behaviour has been found to depend on the molecular weights of both the PS and the PXE used. For the polymers used in the neutron scattering part of this work $\bar{x}_c \approx 0.87$.

Neutron scattering studies

Neutron scattering studies have been initiated using mixtures containing 9 parts by volume of PS and 91 parts by volume of $PBr_{\bar{x}}$ XE,$\bar{x}$ = 0 to 0.80. In order to measure the radius of gyration, R_g, of the polystyrene a number of samples with different concentrations of perdeuteropolystyrene (PS-d_8) were prepared keeping the total polystyrene content the same, i.e., the concentration of hydrogenous PS plus the concentration of PS-d_8 was 9 parts by volume in all specimens.

Both PS samples were obtained from Polymer Laboratories Ltd, Church Stretton, Shrewsbury. For the PS-d_8 $\bar{M}_w$ = 29 000 and $\bar{M}_w/\bar{M}_n \leqslant 1.1$; for the PS-$h_8$ $\bar{M}_w$ = 33 000 and $\bar{M}_w/\bar{M}_n < 1.05$. For the *PXE* $\bar{M}_w$ = 35 000 and $\bar{M}_n \approx$ 15 000. Polymer mixtures were prepared by co-dissolving the requisite materials in chloroform, coprecipitating fibrous powders in methanol and drying the product in vacuum at temperatures up to 140°C for 24 h. Discs were cold-pressed first and then compression moulded in a closed steel mould at temperatures up to 300°C. The resultant mouldings were about 1 mm thick.

Low-angle neutron scattering studies were carried out at the Institut Laue–Langevin at Grenoble using the D17 small-angle diffractometer with a detector distance of 2.8 m and a wavelength of 15 Å.

A Zimm plot is shown in *Figure 1* for specimens of PS in PXE all moulded at 260°C and cooled slowly. The derived radius of gyration R_g of the PS is 48 ± 4 Å, which is the same within experimental error as the value expected for the bulk homopolymer[6]. The value of the second virial coefficient A_2 derived from *Figure 2* is 3.7×10^{-4} compared with zero for PS-d_8 of the same molecular weight[6]. This value of A_2 suggests a modest expansion of the PS chain. Data from a few specimens quenched from various temperatures above T_g suggest a positive temperature dependence of both R_g and A_2.

Results from specimens containing $PBr_{\bar{x}}XE$ moieties of $\bar{x}$ = 0.30 and 0.55 indicate that A_2 decreases with increasing bromine content. Quantitative A_2s have not yet been obtained.

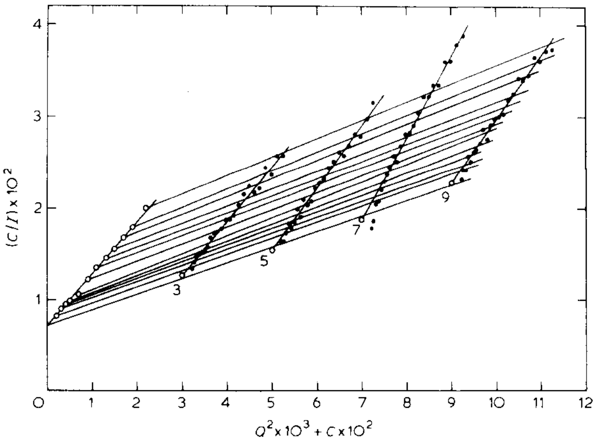

Figure 1 Zimm plot for perdeuteropolystyrene in 9/91 PS/PXE mixtures. $Q = (4\pi/\lambda) \sin \theta/2$ where λ = wavelength and θ = scattering angle. Numbers 3 to 9 indicate percentages of PS-d_8

0032–3861/80/020133–02$02.00
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Discussion

The results reported here confirm that PS properly mixed with PXE is dispersed on a molecular scale*. The positive value of A_2, moreover, indicates a favourable free energy of mixing. The trend in A_2 with partial bromination also accords with expectation, given that higher levels of bromination cause phase separation.

The precise interpretation of the A_2 derived from *Figure 1* is hampered by the fact that the matrix compositions (i.e. the material other than the deutero PS) differed from each other by small degrees (i.e. 0 to 9% hydrogenous PS). Finally the indication that A_2 and R_g may both increase with temperature suggests an endothermal heat of mixing, which appears inconsistent with the exothermal heat of mixing derived from the solution calorimetry study.

These studies are continuing with the goal of determining quantitatively the thermodynamics of mixing of PS with PXE and its brominated derivatives.

Acknowledgements

We are indebted to D. M. White and J. W. Verbicky Jr, for synthesis guidance; to C. A. Williams and P. E. Donahue for copolymer analysis by nuclear magnetic resonance; to J. M. Caraher for moulding assistance; and to G. Allen, J. T. Bendler and A. R. Shultz for extensive discussions of experimental design and results.

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* Subsequent to the carrying out of the work described above, we became aware of neutron scattering work of Wignall (*Polymer* 1980, **21**, 131) on the system PS/PXE from which a value of R_g for PS consistent with that for bulk polymer has also been found

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The uptake of water vapour by an epoxide adhesive formed from the diglycidyl ether of bisphenol-A and di-(1-aminopropyl-3-ethoxy) ether

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(Received 1 October 1979)

Introduction

We have previously reported[1] the results of uptake from liquid water at temperatures between 25° and 100°C for a series of six epoxide adhesives based on the diglycidyl ether of bisphenol-A (DGEBA). One of these adhesives was selected for a more detailed study involving uptake from water vapour at 48°C, and we report the results here. We wanted to investigate more thoroughly the mechanism of water diffusion and the thermodynamics of the water–epoxide equilibrium. A parallel objective was to use the same adhesive in single lap joints with aluminium adherends and attempt to relate the loss of joint strength upon exposure to wet air to the diffusion coefficient of water in the adhesive. Results of this latter investigation are available, and will be published later.

Experimental

The adhesive consisted of 100 g 'Shell Epikote 828' and 32.5 g di-(1-aminopropyl-3-ethoxy) ether (DAPEE). The former is based on the diglycidyl ether of bisphenol-A (DGEBA). Thin films of the adhesive were prepared by casting on tin foil using a method we have previously described[1]. Films were 50–170 μm thick, and pieces used were approximately 10 mm x 40 mm. Cure of the adhesive was for 3 h at 80°C. To investigate the effect of varying the amount of hardener, some hardener-rich and hardener-lean films were prepared which were respectively 10% rich or deficient in DAPEE.

Uptake from water vapour at 48° ± 0.2°C was undertaken using a C. I. Electronics Vacuum Microbalance, contained within an air thermostat. The microbalance could be evacuated via its connection to a vacuum line pumped by a mechanical pump and a mercury diffusion pump. A mercury manometer, connected to the microbalance and contained within the air thermostat, could be read using a travelling microscope external to the thermostat. A flask containing water or a water-glycerol mixture was also connected to provide water vapour at a static pressure. Prior to experimentation, liquid in the flask was degassed by freezing and thawing under vacuum.

The adhesive film was suspended from one arm of the microbalance, and if necessary a small piece of wire provided a counterweight on the other arm. A 'Zerostat Gun', sold for discharging static electricity on gramophone records, was found useful in assembling the apparatus. A chart recorder with full scale deflection set at 4 mg continuously recorded the mass of the sample.

Initially, the same piece of film was used for several sorption–desorption cycles at different activities, but the scatter in the results suggested that a permanent change in the properties of the film might be taking place, even though after desorption the film always returned to its original weight. This effect was investigated by subjecting films to several sorption–desorption cycles; values of water activity were 1.0 or 0.66 during the sorption stages. In other cases a fresh film was used for each sorption experiment.

Epoxide adhesives are widely used against suitably treated

0032–3861/80/020134–05$02.00
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