Polymeric Systems for Acoustic Damping. III. Blends of Poly(vinyl Chloride), Segmented Poly(ether Ester), and Poly(methyl Acrylate)

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Synopsis

A solution blend of poly(vinyl chloride) and a segmented poly(ether ester) and blends containing these two polymers plus poly(methyl acrylate) were investigated by dynamic mechanical analysis and electron microscopy. The binary blend, which contained 75% by weight of the poly(ether ester), showed only one loss peak, but also evidence of some phase separation. It is believed that the polyether sequences of the poly(ether ester) are extensively mixed with poly(vinyl chloride). Poly(methyl acrylate) was added to spread the damping range and produce a material of potential use as an acoustic damper. It is evident from both electron microscopy and dynamic mechanical analysis that poly(methyl acrylate) is substantially incompatible in the other polymers.

INTRODUCTION

In earlier papers^{1,2} mention was made of the use of polymers in acoustic damping applications. Briefly, the objective is to develop materials with significant damping over a fairly wide temperature range centered at about 20°C.

Blends of poly(vinyl chloride) and a segmented poly(ether ester) (Hytrel)^{3,4} have been shown to be compatible¹ in the sense that the poly(vinyl chloride) and the poly (tetramethylene ether) glycol terephthalate soft segments of the polyether ester show extensive mixing. This is true at least up to poly(ether ester) contents of around 50% by weight. At 75% by weight of poly(ether ester) the tan δ -temperature dispersion shows⁵ a shoulder (Fig. 1) indicating that at least partial phase separation has occurred. Blends of segmented poly(ether ester) with nitrile rubber⁶ and with chlorosulphonated polyethylene⁷ have also been investigated.

In this work ternary blends were prepared with 10 parts and 20 parts (9.1 and 16.7 wt %), respectively, of poly(methyl acrylate) per hundred parts of a poly-(ether ester)/poly(vinyl chloride) blend containing 75% by weight of the poly-(ether ester). By adding poly(methyl acrylate) (Tg is 32° C at 110 Hz), which is reported by Krause⁸ to be incompatible with PVC, the transition region of the ternary blends may be broadened by the partial overlap of separate relaxation processes. These blends were investigated using electron microscopy and dynamic mechanical analysis.



Fig. 1. Tan δ vs. temperature plots for poly(methyl acrylate) (O), the poly(ether ester)/poly(vinyl chloride) binary blend containing 75% by weight of the poly(ether ester) (---) and the ternary blends containing 9.1 wt % (\bullet) and 16.7 wt % (\bullet) of poly(methyl acrylate). Frequency, 110 Hz.

EXPERIMENTAL

The poly(vinyl chloride) (Corvic—grade D60/11) was an unplasticized grade which was kindly supplied by I.C.I., Ltd. and the segmented poly(ether ester) (Hytrel—grade 4055) was donated by Du Pont Ltd. The poly(methyl acrylate) was prepared by an emulsion polymerization technique.⁹ See Table I for characterization data.

The blends were prepared by mixing solutions (2-3% w/v) of poly(ether ester) and poly(methyl acrylate) in chloroform and poly(vinyl chloride) in tetrahydrofuran and by precipitating the blends by the addition of an excess of methanol. They were then dried under vacuum at room temperature for at least 10 days prior to the fabrication of sheet by hot pressing (1651°C). See Table II for blend compositions.

The dynamic mechanical measurements were made using a Rheovibron dynamic viscoelastometer (model DDV-II-B) at a frequency of 110 Hz. The temperature range scanned was covered at a rate of $1-2^{\circ}$ C/min.

| TABLE I Characterization Data | | | | |
|----------------------------------|--------------------------------|----------------------------------|----------------------------|--|
| Material | $\overline{M}_n 	imes 10^{-3}$ | $\overline{M}_v 	imes 10^{-3}$ a | Density, kg/m ³ | |
| Poly(vinyl chloride) | 80 | | 1420 | |
| Poly(ether ester) | 30 | | 1150 | |
| Poly(methyl acrylate) | | 790 | 1230 | |

^a See M. Baer, J. Polym. Sci., 2(A), 417 (1964).

| TABLE II Blend Compositions | | | | |
|--------------------------------|----------------------------|--------------------------------|--|--|
| Poly(vinyl chloride), wt % | Poly(ether ester), wt % | Poly(methyl acrylate), wt % | | |
| 22.7 | 68.2 | 9.1 | | |
| 20.8 | 62.5 | 16.7 | | |

RESULTS AND DISCUSSION

Figure 1 shows the tan δ vs. temperature dispersions for poly(methyl acrylate), the poly(ether ester)/poly(vinyl chloride) binary blend containing 75% by weight of the poly(ether ester) and also the two ternary blends. The poly(methyl acrylate) homopolymer shows only the glass transition at about 32°C. As previously reported,⁵ the binary blend containing 75% by weight of poly(ether ester) shows a slight shoulder indicating that at least some phase separation has occurred. The main transition for this blend is at around 48°C, while the glass transitions for the poly(ether ester) and poly(vinyl chloride) homopolymers, at this frequency, are -32°C and 97°C, respectively.



Fig. 2. Electron micrograph of the ternary blend containing 9.1 wt % of poly(methyl acrylate). The sample was stained using osmium tetroxide. Scale mark represents $1 \mu m$.



Fig. 3. Dynamic storage moduli (E') vs. temperature plots for poly(methyl acrylate) (O), the poly(ether ester)/poly(vinyl chloride) binary blend containing 75% by weight of the poly(ether ester) (---) and the ternary blends containing 9.1 wt % (\mathbf{O}) and 16.7 wt % (\mathbf{O}) of poly(methyl acrylate). Frequency, 110 Hz.



Fig. 4. Dynamic loss moduli (E'') vs. temperature plots for poly(methyl acrylate) (O), the poly-(ether ester)/poly(vinyl chloride) binary blend containing 75% by weight of the poly(ether ester) (---) and the ternary blends containing 9.1 wt % (\mathbf{O}) and 16.7 wt % (\mathbf{O}) of poly(methyl acrylate). Frequency, 110 Hz.

Figure 2 shows an electron micrograph of the ternary blend which contains least poly(methyl acrylate). This material is clearly heterogeneous. From Figure 1 it is seen that both of the ternary blends show three transition regions centered at around -23° C, 35° C, and 70° C, respectively. The transition at 35° C is believed to be associated with the glass transition of a pure poly(methyl acrylate) phase which is dispersed as domains in a matrix of the other two polymers. This transition increases in magnitude as the poly(methyl acrylate) content is increased. The transitions at -23° C and 70° C are thought to result from poly(ether ester)/poly(vinyl chloride) domains which are, respectively, rich in poly(ether ester) and poly(vinyl chloride).

The dynamic storage moduli (E') and the dynamic loss moduli (E'') vs. temperature plots are shown in Figures 3 and 4, respectively. The E' curve for poly(methyl acrylate) is typical of an amorphous polymer. The poly(ether ester)/poly(vinyl chloride) blend shows a much broader transition region with the poly(ether ester) hard segment^{1,5} crystallites resulting in a moderately high rubbery modulus. As far as the E'' vs. temperature data are concerned the results for poly(methyl acrylate) are again as expected for an amorphous homopolymer. The essentially two-phase nature of the binary blend is clearly seen by the presence of a well-developed shoulder at approximately -14° C.

From the point of view of acoustic damping, the E''-temperature cures for the ternary blends show desirable, broad transition regions in more or less the correct position on the temperature scale. As frequency is increased, these materials will improve as dampers because the transition region will shift to higher temperatures. However, as the blends have a coarse morphology, the individual components of the blend transitions may well have different frequency dependences, which could result in the individual transitions becoming more separated.

I.D.H. wishes to thank the Science Research Council for a Research Studentship.

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Received September 29, 1980 Accepted April 22, 1981