Binary and Ternary Blends of Poly(vinyl Chloride), Hytrel, and a Polyurethane

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Synopsis

Binary blends of poly(vinyl chloride) and a poly(ether urethane) containing 20 and 40 weight percent, respectively, of poly(vinyl chloride) have been prepared by solution blending from tetrahydrofuran and their degree of mixing investigated using dynamic mechanical analysis. In the polyurethane, transitions were found at −19°C and −119°C. The former was attributed to the glass transition and the latter to a Schatzki type of motion of the polyether sequences. This latter transition occurred at a temperature which is higher than the literature value for the low temperature transition in poly(tetrahydrofuran), which is equivalent to the polyether sequence in the polyurethane. This discrepancy is attributed to the influence of neighboring hard segments present because of incomplete segmental phase separation of the polyurethane. For the blends only one very broad transition was observed, indicating that there was substantial mixing of these two polymers. Three ternary blends were prepared, also by solution blending, containing poly(vinyl chloride), Hytrel, and the polyurethane in the ratios 1:1:1, 1:2:1, and 2:1:1, respectively. In the first two blends there was clear evidence of phase separation. It was only in the 2:1:1 blend that an apparently significantly compatible material resulted.

INTRODUCTION

Many polymer blends (alloys) have been investigated[1-3] in which one component is poly(vinyl chloride). In this paper we are concerned with both binary blends of poly(vinyl chloride) and a segmented polyurethane and with ternary blends of poly(vinyl chloride), Hytrel—a copolyether ester—and the same polyurethane. Previous papers[4-7] have reported, in detail, on the morphology and consequent mechanical properties of binary blends of poly(vinyl chloride) and Hytrel.

It is evident from the literature that poly(vinyl chloride)–polyurethane systems have not been studied in such detail. Bonk et al.[8] have reported that a range of apparently compatible blend compositions, covering a wide range of hardness values, can be prepared from the molten state. In the patent literature[9] it has been reported that ethylene/n-butyl urethane and ethylene/n-methyl urethane yield transparent moulded films when blended with poly(vinyl chloride). More recently Piglowski et al. have reported on the properties[10] of poly(vinyl chloride) modified with thermoplastic polyurethane elastomers and on the thermal stability[11] of poly(vinyl chloride)–polyurethane blends.

No previous work has been reported on the ternary blends, which were investigated here as possible acoustic damping materials. Earlier papers[6,12] have discussed the use of certain polymer blends for this application. The basic requirement is the existence of a large, broad loss transition in the desired temperature/frequency region.

EXPERIMENTAL

The unplasticized poly(vinyl chloride) (Corvic D60/11) was donated by I. C. I. Ltd., while the Hytrel (grade 4055) was kindly supplied by Du Pont. The linear polyurethane was synthesized[13] by reacting a prepolymer (Adiprene L-100), supplied by Du Pont, with an equimolar amount of 4,4'-methylene-*bis*-2-chloroaniline. The reaction temperature was kept below 8°C to preclude allophanate formation. Both 2,4-dihydroxybenzophenone and 2-naphthylaniline were added (2.5% by weight of polymer) to act as stablizers. See Table I for characterization data.

Blending

The binary blends were made by mixing solutions (approximately 2% w/w) of each polymer in tetrahydrofuran, casting into trays, and allowing the solvent to evaporate relatively slowly. The sheets were placed under vacuum at 20°C for at least a week prior to use.

The ternary blends were also prepared by solution blending. Solutions of the same concentrations as before were prepared with the Hytrel in methylene chloride and the other two polymers again in tetrahydrofuran. The three solutions were carefully mixed and the blends precipitated by the addition of an excess of methanol. The precipitated blend was centrifuged and then vacuum dried at 20°C for several days before sheeting on a hot press at 165°C.

Measurements

The dynamic mechanical measurements were conducted using a Rheovibron dynamic viscoelastometer (model DDV-II-B) at a frequency of 110 Hz and a heating rate of 1°–2°C/min.

RESULTS AND DISCUSSION

Poly(vinyl Chloride)–Polyurethane Blends

Figure 1 shows the tan δ vs. temperature dispersions for the poly(vinyl chloride) and polyurethane homopolymers, plus two blends containing 20% and 40% by weight, respectively, of poly(vinyl chloride).

The unplasticized poly(vinyl chloride) homopolymer has two transitions. There is a broad, minor transition centered at 5°C and the glass transition is at 97°C. These PVC transitions have been discussed by Pezzin et al.[14]

The polyurethane homopolymer, whose soft segments are poly(tetramethylene ether) blocks, exhibits transitions at −19°C and at −119°C. Ferguson et al.,[15]

TABLE I
Characterization Data

	Poly(vinyl chloride)	Hytrel	Polyurethane
$\overline{M}_n \times 10^{-3}$	80	30	—
Density (23°C) (kg/m³)	1420	1150	1120
$[\eta]^a$ (dL/g)	—	—	1.03

a Intrinsic viscosity in N,N'-dimethyl acetamide at 25°C.
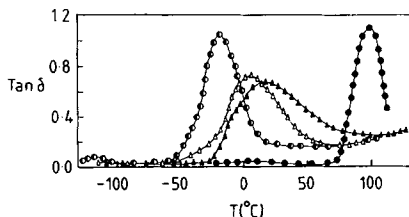
Fig. 1. Plots of tan δ vs. temperature for poly(vinyl chloride) ($\bullet$), polyurethane ($\circ$), and binary blends containing 20% ($\triangle$) and 40% ($\blacktriangle$) poly(vinyl chloride). The frequency was 110 Hz.

in a study of a series of linear polyurethanes, also based on Adiprene L-100, observed transitions (110 Hz) at about $-20°C$ (β) and $-130°C$ (γ). It is clear that these β and γ transitions[15] are in reasonable agreement with the data in this study. They interpreted the β (glass) transition as arising from motions of the polyether soft segments. It was argued[15] that the γ-transition also had its origin in the Adiprene L-100 residues, and probably resulted from some kind of Schatzki[16] motion associated with the polyether segments. In this study the low-temperature transition, which had an activation energy of 38 kJ/mol, occurred at a somewhat higher temperature than either the γ-transition of Ferguson et al.[15] or the low temperature transition (110 Hz) for polytetrahydrofuran ($-140°C$) reported[17] by Takayanagi et al. Kajiyama and MacKnight[18] have studied this γ transition in detail.

In a segmented polyurethane, it is unlikely that the phase separation of the hard and soft segments will be complete. Hence, the glass (β) transition probably arises from segmental motions located[19] in regions composed of mixtures of hard and soft segments. Further evidence for this interpretation comes from the value of half-peak width (Table II) of the tan δ-temperature curve which is larger than that usually found for a homopolymer. With this interpretation in mind, an explanation for the somewhat higher γ relaxation temperature may be proposed. The Schatzki[16] mechanism may be hindered in this particular polyurethane by the presence of hard segments in the immediate environment of the relaxing polyether sequences.

Figure 1 also shows the tan δ-temperature data for two blends containing 20% and 40% by weight, respectively, of poly(vinyl chloride). It is evident that the blends are at least significantly compatible as they exhibit only one major glass transition whose position on the temperature scale is raised with increasing levels of poly(vinyl chloride), and, which can be predicted, to a good approximation, by the Wood[20] equation. It is, however, clear (Fig. 1 and Table II) that addition of poly(vinyl chloride) to the polyurethane homopolymer results in a lowering of peak height acompanied by a substantial increase in the widths of the tan δ

TABLE II

Dynamic Mechanical Properties of Poly(vinyl Chloride)–Polyurethane Blends and Homopolymers

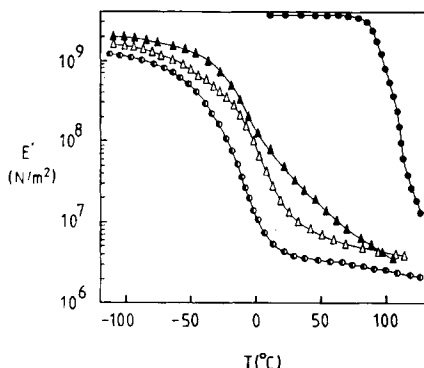| Composition [wt % poly(vinyl chloride)]	T_g, °C	tan δ_{max}	Half-peak width, °C
0	−19	1.05	35
20	5	0.75	48
40	19	0.67	78
100	97	1.10	27

Fig. 2. Plots of dynamic storage modulus (E') vs. temperature for poly(vinyl chloride) (●), poly-urethane (◐), and binary blends containing 20% (△) and 40% (▲) poly(vinyl chloride). The frequency was 110 Hz.

dispersions, which have values of tan δ in excess of 0.1 over the entire temperature range between the polyurethane and poly(vinyl chloride) glass transitions. This behavior suggests that mixing on the segmental scale is not achieved.

Figure 2 shows the dynamic storage modulus, E', vs. temperature curves for the blends and constituent homopolymers. Note that the transitions are broadened, but not dramatically so, in the case of the blends. The dynamic loss modulus, E'', vs. temperature curves for the blends (Fig. 3) show single peaks, but there is more evidence of peak broadening than in the E'-temperature plots.

There is strong evidence[4-7] to suggest that for blends of poly(vinyl chloride) and Hytrel it is the poly(tetramethylene ether) sequences in the Hytrel which, over a certain composition range, are miscible with the poly(vinyl chloride) segments. It seems, therefore, reasonable to propose that the same is true for poly(vinyl chloride)–polyurethane blends.

Piglowski et al.[10,11] have investigated poly(vinyl chloride)–thermoplastic polyester urethane blends. The polyurethanes were synthesized from poly-ethylene adipate and diphenylmethane-4,4′-diisocyanate with propane-1,3-diol, butane-1,4-diol or hexane-1,6-diol as chain extender. Dynamic mechanical
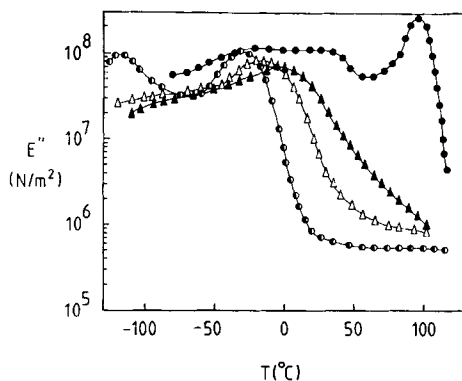

Fig. 3. Plots of dynamic loss modulus (E'') vs. temperature for poly(vinyl chloride) (●), poly-urethane (◐), and binary blends containing 20% (△) and 40% (▲) poly(vinyl chloride). The frequency was 110 Hz.
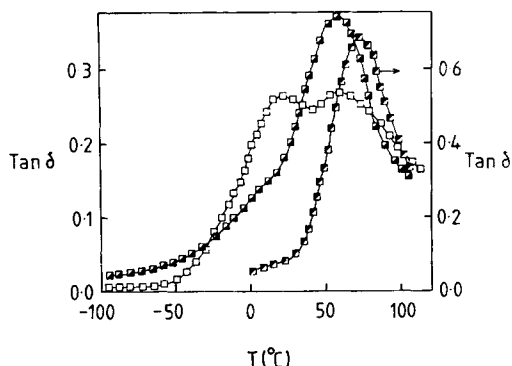
Fig. 4. Plots of tan δ vs. temperature for ternary blends containing the following ratios of polyvinyl chloride:Hytrel:polyurethane. 1:1:1 (□), 1:2:1 (◪), and 2:1:1 (◪). The frequency was 110 Hz.

analysis[10] indicated that these blends, which contained 87.5 weight percent poly(vinyl chloride), were significantly incompatible as the polyurethane transition showed clear evidence of two maxima. As the poly(vinyl chloride) Tg was shifted to a somewhat lower temperature, some slight mixing was postulated. Clearly the poly(ester urethane) is very much less compatible than the poly(ether urethane) used in this work.

Poly(vinyl Chloride)–Hytrel–Polyurethane Blends

As there is evidence for both poly(vinyl chloride)–poly(ether urethane) and poly(vinyl chloride)Hytrel[4-7] compatibility, is it possible to prepare compatible ternary blends?

Figure 4 shows the tan δ versus temperature dispersions for three ternary blends. The weight ratios refer to poly(vinyl chloride), Hytrel, and polyurethane, respectively. The blend containing equal weight ratios of the components shows two peaks while the 1:2:1 by weight blend exhibits a single maximum, but has a pronounced shoulder on the low temperature side of this dispersion. Thus, both the 1:1:1 and 1:2:1 blends are heterogeneous. The 2:1:1 blend has only a single peak in the tan δ-temperature spectrum with no evidence of even a low temperature shoulder. It is quite clearly the most compatible of the three ternary blends.
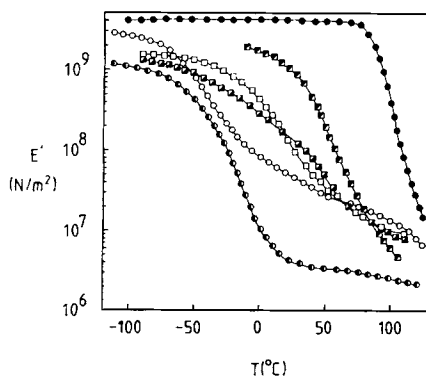

Fig. 5. Plots of dynamic storage modulus (E') vs. temperature for polyvinyl chloride (●), Hytrel (○), and polyurethane (◒) and for ternary blends containing the following ratios of poly(vinyl chloride):Hytrel:polyurethane: 1:1:1 (□), 1:2:1 (◪), and 2:1:1 (◪). The frequency was 110 Hz.
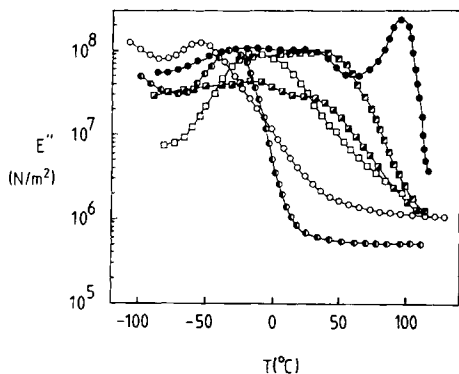
Fig. 6. Plots of dynamic loss modulus (E'') vs. temperature for polyvinyl chloride (●), Hytrel (○), and polyurethane (◐), and for ternary blends containing the following ratios of poly(vinyl chloride):Hytrel:polyurethane: 1:1:1 (□), 1:2:1 (◪), and 2:1:1 (◩). The frequency was 110 Hz.

The E' and E'' vs. temperature plots for the three homopolymers and the three ternary blends are shown in Figures 5 and 6, respectively. The E' curve for the 1:1:1 blend shows a broad, but single transition, while the 1:2:1 blend has two transitions, indicating that probably both materials are incompatible. The relatively sharp drop in dynamic storage modulus of the 2:1:1 blend is highly suggestive of the fact that this is a substantially compatible system. For the E''-temperature curves the high, broad β transition of the PVC makes interpretation of the behavior of the blends difficult, but it is clear at least that the 1:2:1 blend is incompatible. In these ternary blends it is thought that the poly(tetramethylene ether) soft segments from both the Hytrel and the polyurethane are capable of plasticizing poly(vinyl chloride). However, more information is necessary in order to deduce, with any confidence, the compositions of the phases which give rise to the observed transitions in the 1:1:1 and 1:2:1 blends.

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