polymer report

Binary and ternary blends from poly(vinyl chloride), segmented poly(ether ester) and chlorosulphonated polyethylene

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INTRODUCTION

Chlorinated and chlorosulphonated polyethylene have both been used for a number of years. The former, in particular, has been employed in the modification of rigid poly(vinyl chloride)[1] to produce a variety of flexible and semi-rigid compounds with useful properties. Locke and Paul[2] by means of dynamic mechanical sepectroscopy, in conjunction with other techniques, have shown that the polymers are actually incompatible, but that increased interfacial adhesion of the phases may result in improved properties. Zitek and Zelinger[3] have investigated the dynamic shear moduli of poly(vinyl chloride)–chlorinated polyethylene blends and have found that the modulus–composition relation proposed by Uemura and Takayanagi[4] for two phase materials is obeyed up to moderate concentrations of chlorinated polyethylene.

As far as is known no work has been reported on blends of segmented poly(ether ester) and chlorosulphonated polyethylene, but a number of papers[5–8] have been published on the properties and morphology of poly(vinyl chloride)–segmented poly(ether ester) blends. It has been proposed[7] that, at certain compositions the polyether soft segments of the poly(ether ester) are miscible with poly(vinyl chloride).

In this study binary blends of chlorosulphonated polyethylene with poly(vinyl chloride) and with a segmented poly(ether ester) as well as a ternary blend, have been prepared and investigated using dynamic mechanical spectroscopy.

EXPERIMENTAL

Materials

Both the poly(ether ester) (Hytrel, grade 4055) and the chlorosulphonated polyethylene, which had chlorine and sulphur contents of 21.9 and 0.9%, respectively, were kindly supplied by Du Pont Ltd. The poly(vinyl chloride) (Corvic, grade D60/11) was unplasticized and donated by ICI Ltd. See *Table 1* for characterization data.

Blends

The binary and ternary blends were prepared by solution blending. Solutions (2–3% w/v) of chlorosulphonated polyethylene and poly(vinyl chloride) in tetrahydrofuran and the poly(ether ester) in methylene chloride were mixed and the blend precipitated by the addition of an excess of methanol. The resulting materials were dried under vacuum at room temperature for at least ten days prior to the manufacture of sheets by hot pressing.

Dynamic mechanical spectroscopy

The dynamic mechanical measurements were performed using a Rheovibron (model DDV-II-B). The temperature range covered was scanned at a rate of about 1°C min^{-1}. The uncertainty in the temperature readings is believed to be ±1°–2°C.

RESULTS AND DISCUSSION

Figure 1 shows the tan δ *versus* temperature dispersion for chlorosulphonated polyethylene at a frequency of 3.5 Hz. Two transition regions are discernible for this homopolymer occurring at −16°C and −112°C. The transition at −16°C is the glass transition and has an activation energy of approximately 179 kJ mol^{-1}. The transition at −112°C is believed to correspond to the γ transition[9] found in polyethylene and also in chlorinated polyethylene by Locke and Paul[2]. This transition is believed to result from a crankshaft type of motion[10] of short methylene sequences.

Figures 2 and *3* show the dynamic storage modulus (E') and the dynamic loss modulus (E'') *versus* temperature plots for the chlorosulphonated polyethylene homopolymer. The E' *versus* temperature curve shows a marked drop in the storage modulus at about −30°C which corresponds to the onset of the glass transition. The rubbery plateau is poorly defined with flow occurring at about 40°C. This

Table 1 Characterization data

Material	$\bar{M}_n \times 10^{-3}$ a	Density^b (kg m^{-3})
Chlorosulphonated polyethylene	30	1080
Poly(ether ester)	30	1150
Poly(vinyl chloride)	80	1420

a by membrane osmometry
b at 23°C

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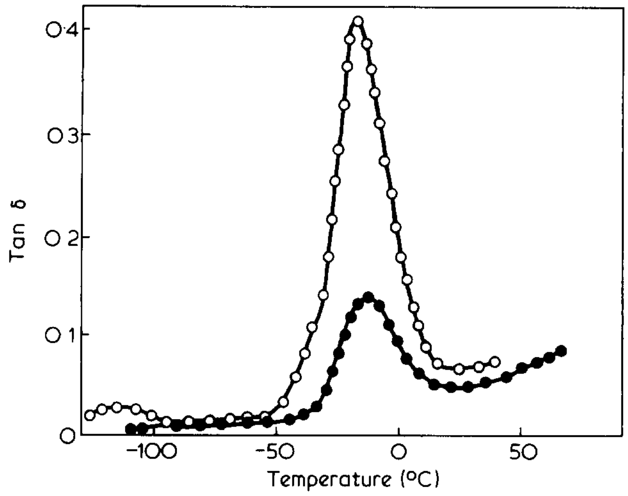

Figure 1 Tan δ *versus* temperature plots for chlorosulphonated polyethylene (○) and a blend of chlorosulphonated polyethylene and poly(vinyl chloride) (●) containing 50% by wt of chlorosulphonated polyethylene. Frequency, 3.5 Hz

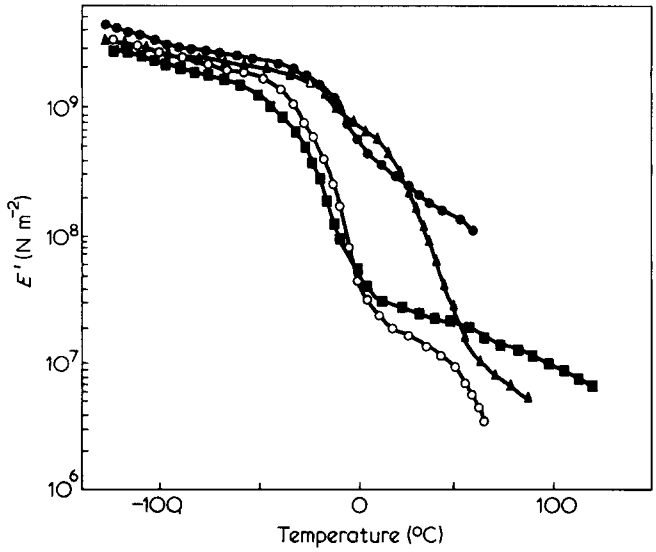

Figure 2 Dynamic storage moduli (*E'*) *versus* temperature plots for chlorosulphonated polyethylene (○) and the binary and ternary blends. Binary blend containing 50% by wt of chlorosulphonated polyethylene with poly(vinyl chloride) ●; binary blend containing 50% by wt of chlorosulphonated polyethylene with segmented polyether ester, ■; ternary blend containing equal weights of chlorosulphonated polyethylene, poly(vinyl chloride) and segmented poly(ether ester), ▲ Frequency, 110 Hz

behaviour is consistent with that of an amorphous polymer of relatively low molecular weight (*Table 1*). The *E''* *versus* temperature plot (*Figure 3*) shows both the glass transition and the secondary relaxation

The dynamic mechanical behaviour of the 50% by wt blend of chlorosulphonated polyethylene with poly(vinyl chloride) shown in *Figures 1–3* presents evidence of substantial incompatibility. The tan δ *versus* temperature dispersion (*Figure 1*) shows a transition centred at –12°C which is only marginally higher than the glass transition of the homopolymer. The glass transition of poly(vinyl chloride)$^{7-9}$ in the blend is not resolvable by this dynamic mechanical technique because of the softness of the sheet. The basically incompatible nature of this blend was confirmed by thermal mechanical analysis when two transitions corresponding closely to the constituent homopolymer transitions were observed.

Figures 2 and *3* show the *E'* and *E''* *versus* temperature plots for this binary blend of chlorosulphonated polyethylene and poly(vinyl chloride). The *E'* *versus* temperature plot shows the blend transition as being somewhat broader than that of the glass transition of the modified polyethylene homopolymer and it is shifted (about 10°C) to a slightly higher temperature. The *E''* *versus* temperature plot shows the blend transition and the chlorosulphonated polyethylene low temperature transition at about –100°C. This is in good agreement with the observed value for this homopolymer at the same frequency (110 Hz). The blend transition is about 6°C higher than the glass transition temperature of the homopolymer.

It is concluded that this blend is largely incompatible, but the small temperature shifts in all the blend dynamic mechanical data indicate that there is, perhaps, a very slight amount of mixing.

Figure 4 shows the tan δ *versus* temperature dispersion for a binary blend containing 50% by wt of chlorosulphonated polyethylene with segmented poly(ether ester). This binary mixture exhibits only one major transition at –19°C which is very close to the glass transition temperature of the chlorosulphonated polyethylene. At 3.5 Hz the glass transition temperature of chlorosulphonated polyethylene (*Figure 1*) is –16°C and that of the segmented poly(ether ester) may be calculated from published data[7] to be –46°C. However, for the blend at a frequency of 3.5 Hz, a shoulder on the low temperature side of the tan δ peak is discernible, which suggests that the material is at least partly phase separated.

Figures 2 and *3* show the *E'* and *E''* *versus* temperature plots for this blend. The blend shows only one quite sharp transition region in the storage modulus spectrum at a some-

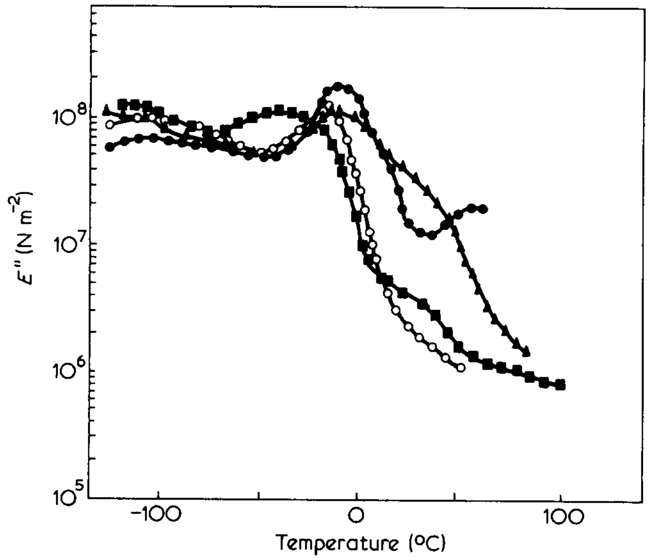

Figure 3 Dynamic loss moduli (*E''*) *versus* temperature plots for chlorosulphonated polyethylene ( ) and the binary and ternary blends. Binary blend containing 50— by wt of chlorosulphonated polyethylene with poly(vinyl chloride), ●; binary blend containing 50— by wt of chlorosulphonated polyethylene with segmented poly(ether ester), ■; ternary blend containing equal weights of chlorosulphonated polyethylene, poly(vinyl chloride) and segmented poly(ether ester), ▲. Frequency, 110 Hz

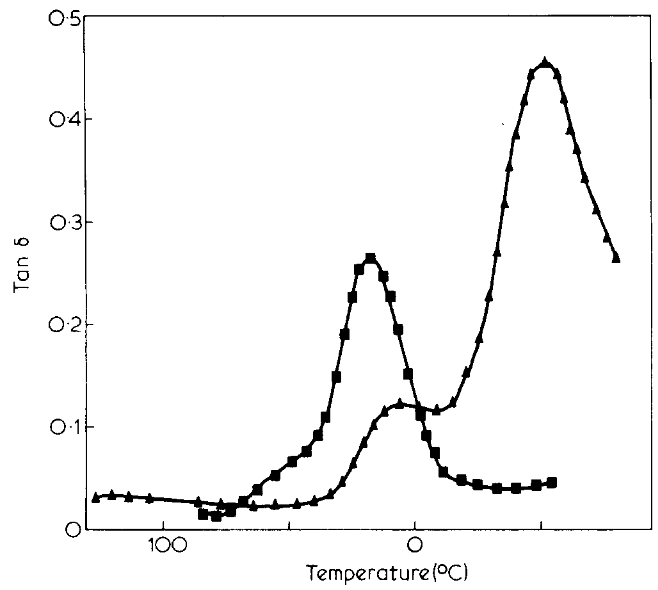

Figure 4 Tan δ *versus* temperature plots for a blend of chlorosulphonated polyethylene and segmented poly(ether ester), ■, containing 50% by wt of chlorosulphonated polyethylene and for a blend containing equal weights of chlorosulphonated polyethylene, poly(vinyl chloride) and segmented poly(ether ester), ▲. The binary blend data were obtained at a frequency of 3.5 Hz and those for the ternary blend at 110 Hz

what lower temperature than the glass transition of chlorosulphonated polyethylene. The well-developed rubbery region reflects the influence of the segmented poly(ether ester) crystallite tie-points[7,8]. The E'' *versus* temperature plot shows a broad loss maximum intermediate with those of the two homopolymer[7] transitions.

From the above evidence it is deduced that there is some mixing of the chlorosulphonated polyethylene and the segmented poly(ether ester), but that there is also a pure poly(ether ester) phase and poly(ether ester) hard segment[7] crystallites.

The tan δ *versus* temperature dispersion for the ternary blend containing equal parts of chlorosulphonated polyethylene, poly(vinyl chloride) and segmented poly(ether ester) (*Figure 4*) reflects the basic incompatibility of poly(vinyl chloride) and chlorosulphonated polyethylene. At a frequency of 110 Hz, two relaxation regions are discernible, at –6°C and 52°C. The higher temperature transition is believed to result from an essentially compatible phase of poly(vinyl chloride) and at least the poly(tetramethylene ether) glycol terephthalate soft segments[7] of the segmented poly(ether ester). The temperature of this transition is in good agreement with the observed[7] glass transition, at the same frequency, of an equal weight blend of the poly(ether ester) and poly(vinyl chloride). The lower temperature transition at –6°C is believed to result from essentially pure chlorosulphonated polyethylene regions which are embedded in a poly(ether ester)–poly(vinyl chloride) matrix.

The E' *versus* temperature plot (*Figure 2*) shows two distinct slope changes corresponding to the observed maxima in the loss tangent spectrum. The higher temperature transsition is accompanied by a substantial decrease in the storage modulus which suggests that this is the glass transsition of the continuous phase. In contrast, the fall in E' associated with the glass transition of the chlorosulphonated polyethylene phase is much less pronounced.

The E'' *versus* temperature plot shown in *Figure 3* has two distinct transition regions. The first occurs at virtually the same temperature as that of the chlorosulphonated polyethylene homopolymer. On the high temperature side of this loss peak the glass transition of the mixed poly(vinyl chloride)–segmented poly(ether ester) phase is observed as a pronounced shoulder.

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