Poly(vinylidene fluoride) - poly(methyl methacrylate) blends

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A dynamic mechanical study of four blends of PVdF and PMMA plus the constituent homopolymers indicates that these two polymers are partly compatible, but that a crystalline PVdF phase also exists. The pure PVdF sample showed four transitions at −95°, −25°, 75° and 100°C which are ascribed to a restricted chain motion of the Schatzki type, to a crystalline phase transition, to the glass transition and to premelting of poorly formed crystallites respectively. A longitudinal sonic velocity *versus* composition plot is interpreted in terms of the overall morphology of the blends whilst differential scanning calorimetry measurements are used to study crystalline melting.

INTRODUCTION

In this study, four blends of poly(vinylidene fluoride) (PVdF) and poly(methyl methacrylate) (PMMA) were prepared principally in order to investigate both the dynamic mechanical and sonic velocity behaviours of such systems. The sonic velocity results are discussed in terms of the blend morphology. Compatibility in this system following melt blending has been reported by a number of authors[1–5]. It is believed[4,5] that PVdF crystallizes in the blend if its weight fraction exceeds 0.5. Recent work on this system by Nishi and Wang[6] has shown that the two polymers are compatible above the PVdF melting point of 170°C[5], but that the PVdF can crystallize when a blend is held at any temperature between the glass transition temperature (T_g) and the crystalline melting temperature. Patterson *et al.*[7] have used Brillouin scattering to study crystalline melting in such blends.

Mandelkern *et al.*[8] have reported a T_g value for PVdF of about −35°C. Paul and Altamirano[5] have discussed dynamic mechanical studies of annealed PVdF and PVdF–PMMA blends. Some analogous dielectric relaxation investigations of PVdF have also been reported[9–12]. Kabin and coworkers[9] observed two relaxation regions. One was ascribed to the T_g of PVdF and the second mechanism was thought to have its origin in the crystalline phase. Ishida *et al.*[10], over a certain temperature range, found a single relaxation which corresponded to the glass transition found by Kabin *et al.*[9]. They also found that at temperatures below −39.5°C the single peak resolved into two components. They assigned this second low temperature mechanism to restricted chain motion. From dielectric studies, Peterlin and (Holbrook) Elwell[11] have discussed the effects of rolling and annealing on the relaxation mechanisms exhibited by PVdF whilst Yano[12] has commented on the origins of three such transitions.

EXPERIMENTAL

Materials

The PVdF used in this work was a sample (Kynar) kindly donated by the Pennwalt Corporation, whilst the PMMA was also a commercial sample (BDH). Characterization data for the homopolymers are given in *Table 1*.

Preparation of blends

Both the slow rate of dissolution of PVdF in any solvent common for PMMA and the desire to avoid plasticization by traces of casting solvent led to the preparation of the blends by melt blending and pressing in a hot press at 185°C. Four blends containing 75, 50, 40, and 33% respectively by wt of PVdF were prepared. The PVdF and PMMA samples were hot-pressed into sheets at 185° and 165°C, respectively.

Sonic velocity studies as well as visual inspection showed that an apparently homogeneous and isotropic sheet resulted.

Techniques

The dynamic mechanical measurements were made using a Rheovibron dynamic viscoelastometer (model DDV-II) at a heating rate of about 1°C/min. The sonic velocity measurements utilized a Morgan pulse propagation meter (model PPM-5R) supplied by H. M. Morgan, Cambridge, Massachusetts, USA. This instrument operated at a resonant frequency of about 15 kHz. A Perkin–Elmer differential scanning calorimeter (model DSC-2) was used for the thermal studies.

RESULTS AND DISCUSSION

Dynamic mechanical properties

Figures 1 to *4* show plots of tan δ, dynamic storage modulus (E') and dynamic loss modulus (E'') *versus* temperature for both the homopolymers and for all four blends. All dynamic mechanical experiments were performed at a frequency of 110 Hz. *Figure 1* shows evidence for three transitions in PVdF at about 75°, −25° and −95°C. These transition regions will be referred to as the α-, β- and γ-regions, respectively. The E' *versus* temperature curve in *Figure 3*

Table 1 Homopolymer characterization data

Property	PVdF	PMMA
$\overline{M}_n \times 10^{-3}$ a	–	66
[η] (dl/g)b	2.12	–

a Number-average molecular weight (membrane osmometry)
b Intrinsic viscosity in dimethylformamide at 18°C

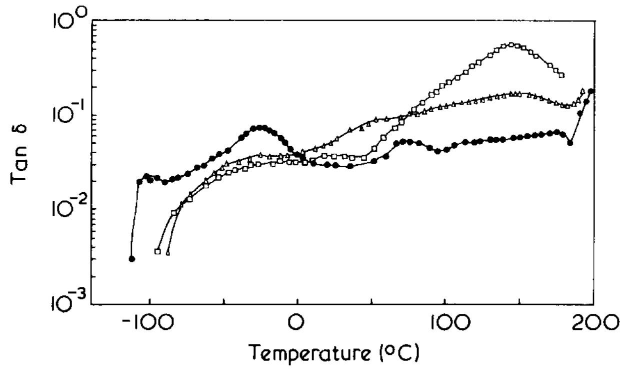

Figure 1 Tan δ *versus* temperature plots of PVdF (●) and blends of PVdF and PMMA containing respectively 75 (△) and 50% (□) of PVdF by wt. Frequency, 110 Hz

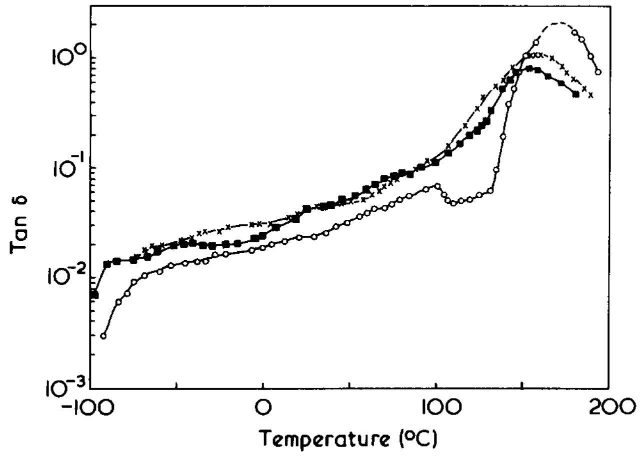

Figure 2 Tan δ *versus* temperature plots of PMMA (○) and blends of PVdF and PMMA containing respectively 40 (■) and 33% (X) of PVdF by wt. Frequency, 110 Hz

clearly shows the β PVdF transition as does the E'' *versus* temperature plot in *Figure 4*, but it also shows quite distinct transitions at about 60°C and around 100°C. Paul and Altamirano[5] also noted three transitions which they also referred to in order of decreasing temperature as the α-, β- and γ-transitions. These transitions occurred for a frequency of 110 Hz in the 60° to 80°C, the −20° to −40°C and the −70° to −80°C temperature ranges, respectively. The first two regions agree very well with the observed α- and β-transitions in the tan δ *versus* temperature data of this work. Our γ-transition is observed at a temperature around 20°C lower than the γ-transition of Paul and Altamirano[5].

There is a difference of opinion in the literature about the mechanisms of these transitions. Yano[12] has stated that the α-transition is concerned with molecular motions in the crystalline regions and their defects, that the β-transition is the glass transition whilst the γ-mechanism is associated with local chain motion in the amorphous phase. Peterlin and Holbrook[11,13] disagree. They have suggested that the α-mechanism is the glass transition and that the β-mechanism is the result of dipole rotation in crystal defects. They also found a premelting transition. They further reported T_g values of 13° and 27°C by calorimetric and dilatometric studies[11,13].

Paul and Altamirano[5] found that the tan δ and E'' peaks shift in the following way when PMMA is blended with PVdF. The β-peak decreases in size and eventually disappears at about the composition where they believe that the PVdF crystallinity vanishes. They also have some evidence to suggest that this peak shifts to lower temperatures as the PMMA content rises. They speculate that this latter effect is probably caused by the increase in importance of the partly overlapping γ-transition. They think that the α-transition increases in size and moves to higher temperatures as PMMA is added. They also note that after all crystallinity has been lost this peak no longer increases in size as the PMMA content of the blends is further increased, but the transition does continue to shift to higher temperatures. Clearly these trends would be more readily explicable if the views of Peterlin and Holbrook[11,13] were accepted.

As in the work of Paul and Altamirano[5] our β-relaxation mechanism decreased in size with the addition of PMMA, but unlike the work of the above authors, the transition was still clearly visible (*Figure 4*) in a blend containing only 33% by wt of PVdF. If this transition does have its origin in the crystalline phase, then differences in the method of sample preparation could account for this. It is also clear from *Figure 4* and *Table 2* that the position on the temperature

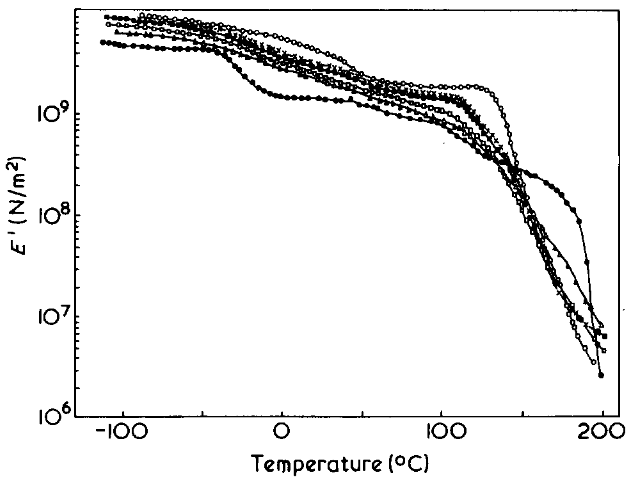

Figure 3 Dynamic storage modulus (E') *versus* temperature plots of PVdF (●), PMMA (○) and blends of PVdF and PMMA containing respectively 75 (△), 50 (□), 40 (■) and 33% (X) PVdF by wt. Frequency, 110 Hz

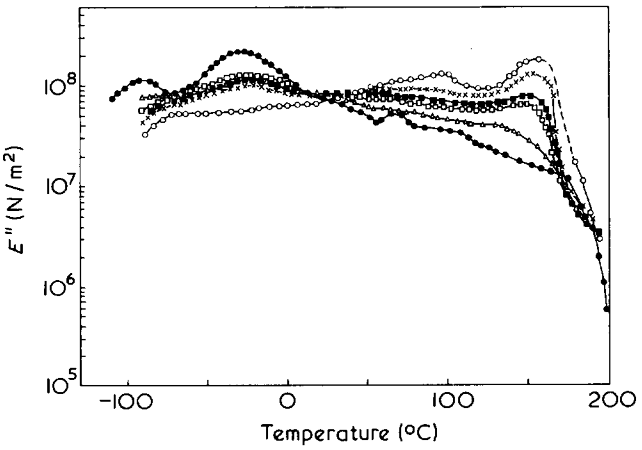

Figure 4 Dynamic loss modulus (E'') *versus* temperature plots of PVdF (●), PMMA (○) and blends of PVdF and PMMA containing respectively 75 (△), 50 (□), 40 (■) and 33% (X) PVdF by wt. Frequency, 110 Hz

Table 2 Transition temperatures and sonic velocities of the homopolymers and the blends

Composition (wt% PVdF)	β-transition^b (°C)	Major transition (°C) Method 1^a	Major transition (°C) Method 2^b	V_L (km/sec)
100	−26	–	–	1.44
75	−26	145	–	1.45
50	−26	145	148	1.76
40	−25	155	151	2.22
33	−25	159	156	2.20
0	–	170	–	2.29

^{a} Measured from the tan δ *versus* temperature dispersion.
^{b} Measured from the E'' *versus* temperature dispersion

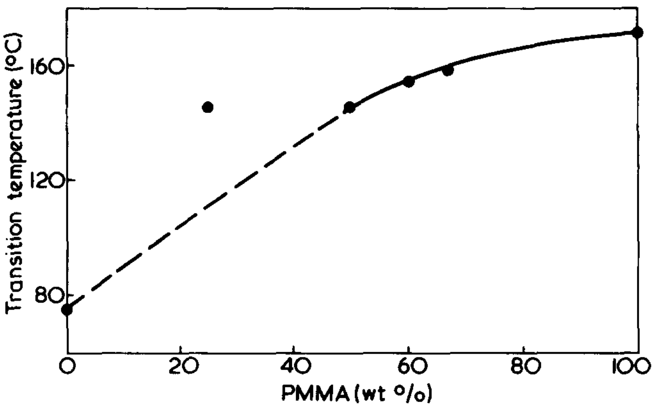

Figure 5 Temperature of the major high temperature transition *versus* blend composition

scale of the β-relaxation mechanism is not sensitive to the addition of PMMA as would be expected for compatible or partly compatible blends if this transition were in fact the PVdF glass transition. The shift to lower temperatures reported by Paul and Altamirano[5] was not observed.

The PVdF homopolymer α-transition is small, which is not unreasonable if the sample is highly crystalline. However, it is plain from *Figures 1, 2* and *4* as well as *Table 2* that the glass transition of PMMA is influenced by the addition of PVdF, being diminished, broadened and shifted progressively to lower temperatures as the PVdF content increases. Both this dramatic broadening and the shift of the high temperature transition in the blends to lower temperatures indicate that there is some mixing of the homopolymers, but the breadth of this tan δ/temperature dispersion shows that in these blends this pair of polymers are not highly compatible.

A plot of the temperature of this transition *versus* blend composition (*Figure 5*) seems to indicate a trend which if extrapolated gives a PVdF glass transition temperature in our α-transition region. It is noted that for the blend containing 75% by wt of PVdF the transition temperature is the same as for the 50% blend. This is explicable in terms of crystallization becoming increasingly important at higher PVdF levels[4,5].

Thus, it is concluded, in agreement with Paul and Altamirano[5], that the Peterlin and Holbrook[11,13] interpretation of the α- and β-transitions in PVdF seems to be correct.

As already stated, the γ-transition at around −95°C (*Figure 4*) is about 20°C lower in temperature than the value reported by Paul and Altamirano[5]. At a frequency of 110 Hz, polymers containing methylene sequences often exhibit a minor transition at approximately −110°C which Schatzki[14] has ascribed to a crankshaft type of motion of short sequences of methylene units. It does not seem improbable that amorphous regions of PVdF could exhibit a similar mechanism, but at a higher temperature as a result of the higher bond rotational energies involved.

Figure 3 shows a fall in E' *versus* temperature at around 100°C which is thought likely to be the result of the melting of some small, imperfect PVdF crystallites. In the d.s.c. thermogram for PVdF shown in *Figure 6*, there is a very small endotherm at 109°C which is ascribed to the same mechanism. Peterlin and Holbrook[11,13] have observed such premelting.

The dynamic mechanical behaviour of isotactic PMMA has been extensively studied[15]. Taking into account the frequency differences the tan δ/temperature dispersion in *Figure 2* showing the α-transition (T_g) at about 170°C and the β-relaxation at 98°C is in good agreement with the results of Heijboer[16]. In the experiments reported here, the temperature was not taken low enough to detect the two now well established[14] transitions arising from methyl group rotation on the backbone and on the ester side chain.

Longitudinal sonic velocity studies

Figure 7 shows a plot of longitudinal sonic velocity (V_L) *versus* blend composition. As the frequency of the applied sonic pulses is about 15 kHz and the average sonic velocity is approximately 2 km/sec, the effective wavelength is around 13 cm. Such a pulse is not sensitive to small scale morphological features, but is influenced by both the composition and the overall distribution of the phases[17].

A possible interpretation of the V_L *versus* composition curve (*Figure 7*) is to consider the blends as consisting of a crystalline PVdF phase and an amorphous PVdF/PMMA mixed phase such that between about 30 and 60% by vol of PMMA, both phases are continuous. Below 30% by vol of PMMA, the crystalline PVdF phase is continuous, but this becomes the discrete phase above about 60% by vol of PMMA. In fact, it is likely that at high PMMA levels the system is behaving essentially as an amorphous blend.

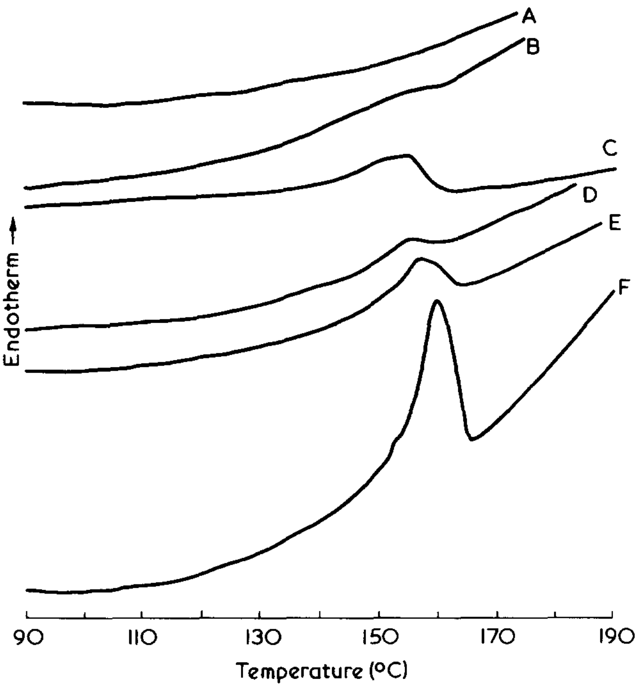

Figure 6 D.s.c. thermograms of PMMA (A), PVdF (F) and blends of PVdF and PMMA containing respectively 33 (B), 40 (C), 50 (D) and 75% (E) PVdF by wt

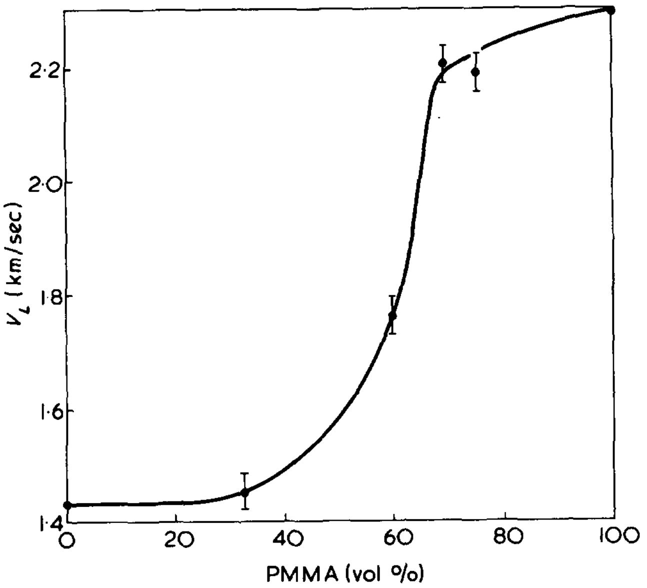

Figure 7 Longitudinal sonic velocity (V_L) *versus* vol % PMMA

Table 2 gives a summary of the sonic velocity data for both the homopolymers and the blends.

Differential scanning calorimetry

Nishi and Wang[6] have shown d.s.c. thermograms for solution cast PVdF/PMMA blends and homopolymers. A very similar set of thermograms are shown in *Figure 6* for both the homopolymers and the melt blended samples. One significant difference between these results and those of Nishi and Wang[6] is the relative constancy of the melting temperature (T_m). Over the entire composition range T_m fell by only 5°C whereas, over the same range, Nishi and Wang[6] observed a drop of about 17°C. The PVdF thermogram, but not those of the blends, showed very minor endotherms at 109° and 153°C which are thought to represent premelting of small, imperfect crystallites. However, there is also some evidence in *Figure 1* that there is a phase change prior to the d.s.c. melting transition at 160°C.

The T_g of the PMMA sample was found to be 114°C.

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