Dynamic mechanical relaxations of poly(vinylidene fluoride)–poly(vinylpyrrolidone) blends

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Dynamic mechanical measurements on blends of poly(vinylidene fluoride) (PVDF) and poly(vinylpyrrolidone) (PVP) over the whole composition range are reported from −150 to 220°C. The results provide evidence of miscibility of PVDF with PVP. Two ranges of compositions are identified. When the PVP content is higher than 40%, crystallization of PVDF is inhibited and single-phase, homogeneous mixtures are obtained. At lower PVP concentrations, three phases coexist: a homogeneous blend of quasi-constant composition, crystalline PVDF and a pure amorphous PVDF phase, the so-called 'interphase' evidenced by a relaxation at about −40°C. For the partially crystalline blends, the viscoelastic spectrum is shown to depend strongly on thermal history.

(Keywords: poly(vinylidene fluoride); poly(vinylpyrrolidone); polymer blends; dynamic mechanical relaxations)

INTRODUCTION

A number of polymer blends containing poly(vinylidene fluoride) (PVDF) mixed with an amorphous component, in most cases poly(acrylates) or poly(methacrylates), have been investigated[1–17]. PVDF has been shown to be highly compatible with such oxygen-containing polymers, the blends with methyl and ethyl esters being reported as miscible in the amorphous state over the whole concentration range[18,19].

Also for blends of PVDF with poly(vinylpyrrolidone) (PVP) complete miscibility in the melt has been found[20–22]. D.s.c. measurements showed a strong depression of the melting point of the crystalline component in blends cast from dimethylformamide solution[22]. When PVP in the mixture exceeds a given amount, crystallization of PVDF is prevented and fully homogeneous amorphous blends are obtained. The minimum amount of PVP needed to inhibit PVDF crystallization depends on PVP molecular weight, being smaller the higher the molecular mass of the amorphous component. At high PVDF contents, the blends are partially crystalline and—as previously suggested for PVDF–PMMA[15]—are composed of a crystalline phase as well as of two amorphous phases: a homogeneous PVDF–PVP mixture and a pure PVDF amorphous phase, denoted as 'interphase'.

The present paper provides additional insight into the phase behaviour of the PVDF–PVP system, by examining the viscoelastic spectrum of the mixtures over a wide temperature range.

EXPERIMENTAL

PVDF used in this investigation was either a Ugine Kuhlmann product (Foraflon 1000 HD) or a Solvay commercial sample (Solef 2010).

PVP was purchased from Serva (PVP 350) and characterized by g.p.c. ($M_n = 170\,000$, $M_w = 498\,000$)[22].

Blends were prepared by dissolving both polymers in dimethylformamide, casting on polypropylene plates and drying as previously described[22]. The same blends were investigated, except for those containing low-molecular-weight PVP, which were too brittle to be subjected to dynamic mechanical measurements. Films about 500 μm thick covering the whole range of composition were prepared.

Dynamic mechanical measurements were carried out by means of a Dynamic Mechanical Thermal Analyser (Polymer Laboratories) operated in the tensile mode, at a frequency of 3 Hz and a heating rate of 3°C min^{-1}. The temperature range investigated was from −150 to 220°C. To avoid sample drawing in the softening region, the instrument was equipped with a force-reducing device that automatically changes the pretensioning force depending on the decrease of modulus that occurs at the glass transition.

RESULTS

Poly(vinylpyrrolidone)

Figure 1 shows the dynamic mechanical loss tangent (tan δ) as a function of temperature for PVP. The curves refer to a first scan up to 140°C of a sample stored in

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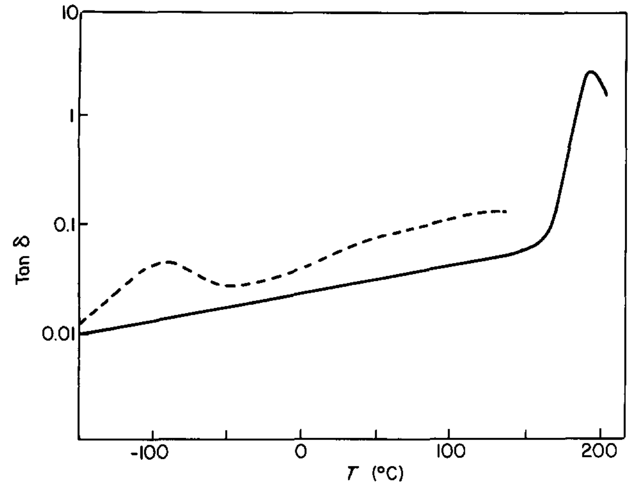

Figure 1 Temperature dependence of the loss tangent of 'room-stored' (---) and 'dry' (——) PVP

normal 'room' humidity conditions and to a second scan on 'dry' PVP (broken and full curves respectively).

Because of the high hygroscopicity of PVP, elimination of absorbed water is extremely difficult: even if the samples are kept in a desiccator under vacuum, humidity is unavoidably absorbed during clamping of the specimen, specially when the polymer is in film form. A treatment that was found to be effective in attaining complete water removal was direct heating in the d.m.t.a. instrument above 140°C. An immediate run, after such a pretreatment under a dry nitrogen purge, is shown in *Figure 1*, the sample being referred to as 'dry' PVP.

The only feature in the spectrum of the 'dry' polymer is the glass-to-rubber transition, whose magnitude ($\tan \delta > 1$) attests the amorphous character of PVP. The peak value ($T = 197°\text{C}$) compares favourably with the calorimetric T_g of dry high-molecular-weight PVP[22]. Room-stored samples, on the other hand, also show a low-temperature secondary relaxation, whose intensity and location depend on the amount of absorbed water, as well as a broad shoulder above room temperature due to water loss. At higher temperature the room-stored samples exhibit a glass transition analogous to that of the 'dry' sample, water being completely eliminated during heating at temperatures well below T_g.

The presence of a secondary relaxation at low temperature in the viscoelastic spectrum of a hygroscopic polymer such as PVP is not surprising. In fact, a number of polymers containing polar groups that may interact with water molecules have been reported to show a dispersion peak below room temperature[23–25], which is commonly attributed to motion of water molecules associated with the polymer chains through polar interactions.

Poly(vinylidene fluoride)

Figure 2 shows the viscoelastic spectrum of PVDF, a highly crystalline, polymorphic polymer. The curves refer to 'as-cast' (full curve) as well as 'melt-crystallized' (broken curve) Foraflon samples. The spectrum of PVDF is rather complex and only three of the four relaxations usually reported[26] are clearly observed in the 'as-cast' film: the broad γ relaxation at about $-100°\text{C}$ and the β and β' relaxations located at about -40 and 35°C, respectively. The high-temperature relaxation of PVDF, commonly denoted as α_c, is observed distinctly only in the 'melt-crystallized' samples, i.e. cast films after heat treatment above the melting temperature.

As regards the assignment of the PVDF relaxations, while it is commonly accepted that the α_c absorption is related to motions in the crystalline phase and that the γ process is associated with local molecular motions in the amorphous phase[26], no general agreement is found in the attribution of the β and β' dispersions, although the relaxation more often associated with the glass transition of the amorphous phase of PVDF is the β process at $-40°\text{C}$ (ref. 26).

Boyer's suggestion of the presence of two T_g values in partially crystalline polymers[27] and the consequent correlation of the β and β' relaxations of PVDF with the 'lower' and 'upper' glass transitions[28–30], related to the 'free' and constrained amorphous regions respectively, is not universally accepted[13,31]. While Hahn *et al.*[13] assign the β relaxation to segmental motions in the crystal–amorphous 'interphase', Loufakis and Wunderlich[31] attribute the β' process to a 'condis' glass transition.

We point out that both spectra in *Figure 2* refer to temperature scans immediately following a run to 140°C, carried out to make the thermal history of the PVDF samples 'uniform'. This procedure has been found to enhance the β' relaxation, whose intensity is strongly affected by storage time at room temperature. In fact, the β' absorption is progressively depressed with increasing storage time, this ageing affect being erased by heating at $T > 100°\text{C}$. Physical ageing has been widely discussed by Struik[32] who ascertained that, in the presence of crystallinity, this phenomenon occurs not only below T_g—as commonly found in amorphous materials—but also above T_g of the 'bulk' amorphous phase.

Figure 3 illustrates the influence of room-temperature storage, as well as of cooling rate, on the viscoelastic spectrum of PVDF. Observation of an ageing effect on the β' relaxation of PVDF suggests that the molecular process involved is a glass transition-like mobilization of chain segments belonging to the amorphous fraction of the polymer.

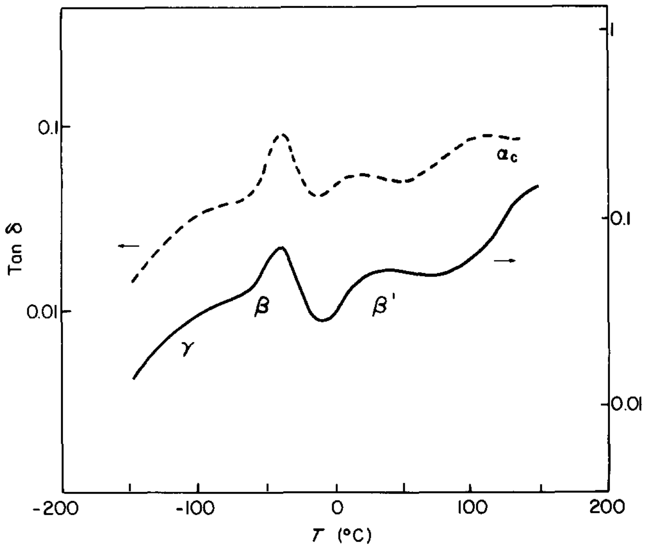

Figure 2 Viscoelastic spectra of PVDF Foraflon: (——) 'as-cast' and (---) 'melt-crystallized'. After heat treatment at 140°C (see text)

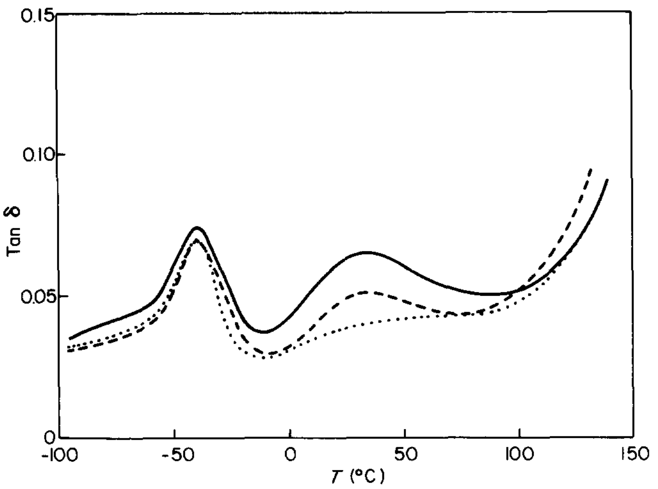

Figure 3 Effect of ageing on the relaxation spectrum of 'as-cast' Foraflon films: (——) quenched from 140°C; (– – –) slowly cooled from 140°C; (· · · ·) stored at room temperature (5 months)

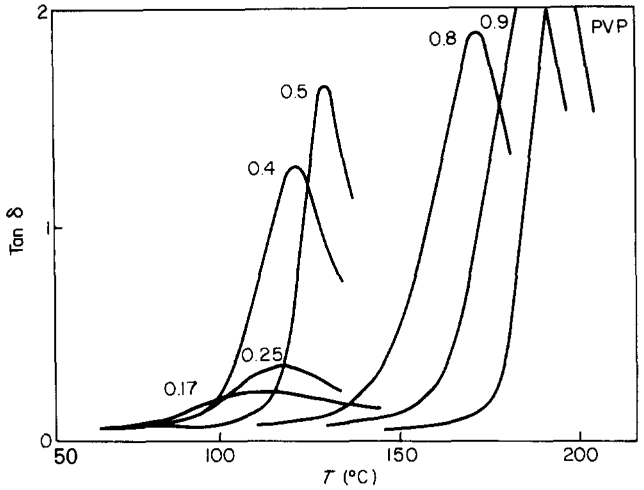

Figure 4 Main relaxation of PVDF–PVP blends at various compositions. The PVP weight fractions, w_1, are indicated

PVDF–PVP blends

Figure 4 shows the viscoelastic spectrum above room temperature of 'as-cast' films of Foraflon–PVP mixtures with various compositions (PVP weight fraction, w_1, from 0.17 to 1). The blends whose PVP concentration is between 0.4 and 1 show an intense glass-to-rubber transition ($\tan\delta_{\max} > 1$) at temperatures that increase with increasing PVP content. When PVP weight fraction is lower than 0.4, a much weaker absorption is found and a new relaxation, whose intensity increases with decreasing PVP concentration, appears in the dynamic mechanical spectrum below room temperature, as illustrated in *Figure 5*. In PVDF-rich mixtures it is clear that this relaxation is located in the temperature range characteristic of the β peak of pure PVDF (about -40°C), while the dispersion centred at about -100°C in the spectra of pure PVP and of PVP-rich blends is related to the presence of some residual humidity: to avoid catastrophic failure of the samples due to drying-induced embrittlement, no drastic thermal treatment was carried out to eliminate absorbed humidity from the blends. The γ peak of PVDF is also located near -100°C; the curves in *Figure 5* therefore result from the combination of three different relaxation phenomena and any quantitative evaluation of the contribution of each process to the complex spectrum is precluded.

Parallel to a weak T_g absorption (*Figure 4*) and an increasingly intense relaxation at -40°C (*Figure 5*), the blends containing less than 40% PVP have been found to show a significant melting endotherm of crystalline PVDF during calorimetric analysis by d.s.c. These results altogether strongly suggest that in the composition range $0 < w_1 < 0.4$ PVDF segregates from the blends and that the T_g relaxations shown in *Figure 4* are related to homogeneous PVDF–PVP mixtures, whose composition is either equal to ($0.4 < w_1 < 1$) or higher than ($w_1 < 0.4$) the overall 'nominal' composition of each blend.

Figure 6 reports the temperature of the absorption maxima (T_g) as a function of the nominal composition for two series of blends containing either Foraflon or Solef PVDF. The behaviour of the two PVDF–PVP systems is identical when $w_1 \geqslant 0.5$, confirming that totally amorphous homogeneous blends are obtained in this composition range. At PVP contents lower than 50%, the T_g values show a plateau, which indicates the existence of a mixed amorphous phase of quasi-constant composition. The plateau values are slightly higher for the blends containing Solef: this result is easily accounted for by the smaller amount of head-to-head defects of this polymer[22], which promotes crystallization and leads to a lower PVDF content in the mixture.

In line with previous results obtained by d.s.c.[22], the above observations indicate that in the composition range corresponding to the plateau of T_g, the PVDF–PVP systems are composed of three phases: a homogeneous blend, whose PVP content does not vary appreciably; pure amorphous PVDF, evidenced by the relaxation at -40°C; and crystalline PVDF, which melts at high temperature.

The films of the partially crystalline blends (PVP < 40%) have been molten in the hot stage of an optical microscope and then cooled to room temperature. Rather independently of the cooling rate, some general features have been found in the blends after melting: they are illustrated for the blend containing 17% PVP in *Figure 7*, where the viscoelastic spectrum of an 'as-cast' film is compared with that obtained after fusion. The

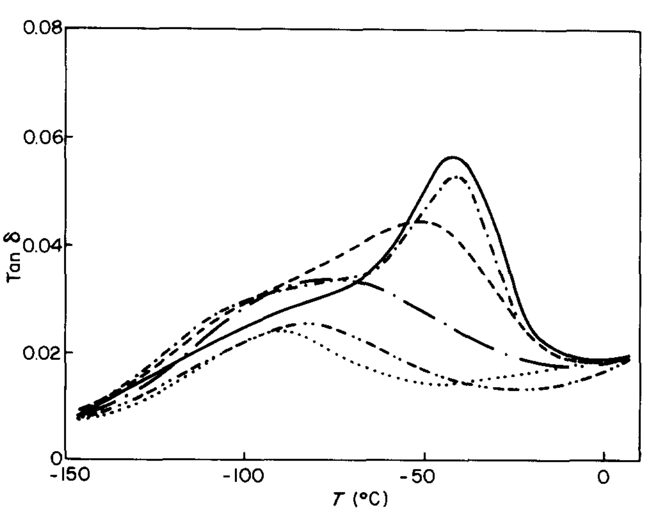

Figure 5 Viscoelastic spectra below room temperature of PVDF–PVP blends with various PVP contents: $w_1 = 0$ (——); 0.06 (–·–·–); 0.25 (– – –); 0.50 (—·—); 0.80 (—— · ——) and 1.0 (· · · ·)

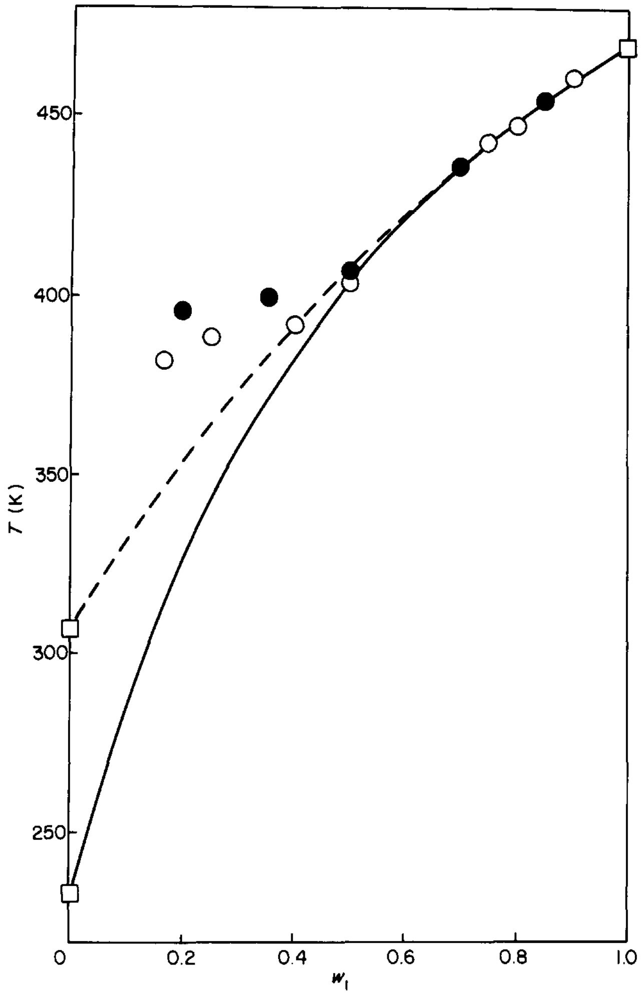

Figure 6 Composition dependence of the peak values of the main dynamic mechanical relaxation of PVDF–PVP mixtures: (○) Foraflon; (●) Solef

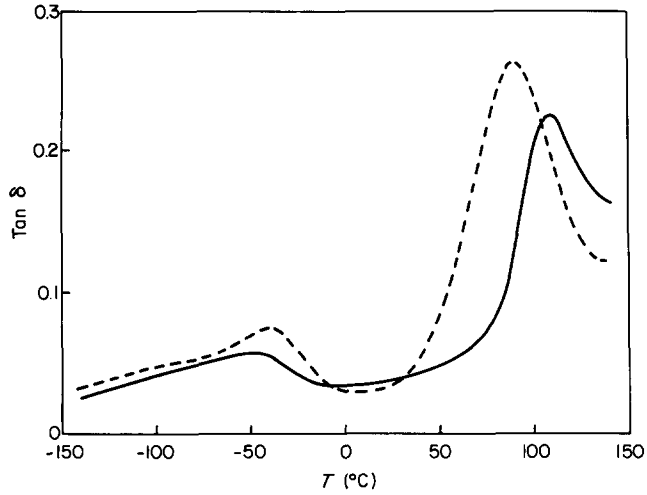

Figure 7 Viscoelastic spectra of Foraflon–PVP blend ($w_1 = 0.17$): (——) 'as-cast'; (– – –) 'melt-crystallized'

temperature of the main peak (T_g) is seen to decrease parallel to an increase in the magnitude of the absorption, suggesting that after melting a higher fraction of PVDF enters the amorphous mixture with PVP. Concomitantly, also the relaxation at about −40°C is enhanced, indicating that the pure non-crystalline PVDF fraction has increased as well. In samples cooled from the melt, there is therefore an overall increase of PVDF in the amorphous state, apportioned between a pure phase and the random mixture with PVP. These findings are corroborated by calorimetric results[33] showing that the enthalpy of fusion of crystalline PVDF is always smaller in melt-crystallized blends than in 'as-cast' films. Effects similar to those shown in *Figure 7*, though of smaller intensity, are caused by heat treatments in the d.m.t.a. instrument at temperatures higher than the glass transition temperature of the mixture but lower than the melting point of PVDF.

DISCUSSION

In partially crystalline polymers, the existence of an 'interphase', located between the crystalline and random amorphous regions, which results from the need to dissipate the order at the crystal surface, has been recently proposed[34,35]. This concept has been extended to semicrystalline blends to account for the presence of two kinds of amorphous regions: one constituted by substantially undiluted chain sequences of the crystallizable component, the other being the randomly mixed true amorphous phase[13,15,17].

A number of blends containing PVDF have been reported in the literature to behave as multiphase systems, much like the mixtures investigated in the present work. In particular, blends of PVDF with poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA) have been found to be partially crystalline and to show, in a specific range of compositions, a low-temperature transition corresponding to the β relaxation of PVDF[7,13,15,17]. Owing to the appearance of a low-temperature peak in the dielectric relaxation spectrum whenever crystalline PVDF was present in the blends, the β relaxation was attributed by Yoon *et al.*[13,17] to motions in the crystal–amorphous interphase. As regards partially crystalline blends of PVDF with PVP, we have recently reported calorimetric data consistent with a three-phase model composed of crystals, mixed amorphous domains and an interphase of undiluted, non-crystalline PVDF chain sequences[22]. Analogous conclusions are suggested by the present dynamic mechanical results which show evidence in PVDF–PVP blends of two ranges of composition: one characterized by a single mixed phase at PVP contents higher than 40%, the other where the system is heterophasic.

As far as blends with PVP contents higher than 40% are concerned, the T_g values plotted in *Figure 6* may be tentatively fitted by means of one of the several empirical equations used to describe the T_g–composition dependence for homogeneous polymer mixtures. A fit has been carried out using the Gordon–Taylor equation:

$$T_g = \frac{w_2 T_{g_2} + K w_1 T_{g_1}}{w_2 + K w_1} \qquad (1)$$

where subscripts 1 and 2 refer to PVP and PVDF, respectively, and K is an adjustable curvature parameter. The full curve in *Figure 6* represents equation (1) with $K = 2.6$ and $T_{g_2} = T_\beta = -40$°C, i.e. the most commonly adopted value for the glass transition temperature of PVDF. A good fit to the experimental T_g values of the homogeneous PVDF–PVP blends is obtained.

As already mentioned, the literature reports many studies on blends containing PVDF and a wealth of T_g data obtained by calorimetry, dynamic mechanical and dielectric spectroscopy are available. In the plots of T_g vs. composition for the different systems, extrapolations that yield a variety of values for T_g of PVDF are found. As an example, for the most widely studied system, PVDF–PMMA, extrapolations to the following temperature are reported: −50 (ref. 6), ~70 (ref. 9), ~40 (ref. 5), −45 (ref. 10), −35 and −50°C (ref. 12). Besides the β absorption at −40°C, the viscoelastic spectrum of PVDF also shows another relaxation—the β' absorption—which has been related to the 'upper' glass transition of the amorphous phase[30]. This relaxation, located near room temperature, has been shown in *Figure 3* to undergo the effects of physical ageing, much like the glass transition of other partially crystalline polymers. Therefore, in line with some of the T_g extrapolations mentioned above, the T_g data of *Figure 6* have been alternatively fitted with equation (1) ($K = 1.6$), taking as T_{g_2} the temperature of the β' relaxation of PVDF (35°C). This is drawn as a broken curve in *Figure 6*, the fit to the experimental results at high PVP content being as good as that of the other calculated curve. In equation (1), K values higher than 1 correspond to T_g values of the mixtures higher than the weighted average of the homopolymers' T_g values and are indicative of strong specific interactions between the components. Analogous convex T_g–composition dependences have been reported for blends containing PVDF[5,6,8,10–12], including PVDF–PVP mixtures[21]. The $K > 1$ values in both fits of *Figure 6* agree with the highly negative value of the thermodynamic interaction parameter χ found for PVDF–PVP blends in the molten state[20,36]. No indication that would help to discriminate between β and β' relaxations has been obtained from the above fit with equation (1).

Another piece of information on this subject is provided by the spectra shown in *Figure 8*. The curves reported are re-runs after a first scan to 140°C of pure PVDF as well as of two blends with PVP (6 and 17%). Two features deserve attention: the β peak at −40°C is present in both PVDF and blends, showing differences in intensity but not in location; on the contrary, the β' relaxation of PVDF is absent in the blends, which show instead a new relaxation—the glass transition of the mixtures—which shifts to higher temperatures with increasing PVP content. On the basis of this experimental evidence, it could be hypothesized that the amorphous PVDF phase that mixes with PVP in the blends is the one responsible for the β' relaxation in pure PVDF.

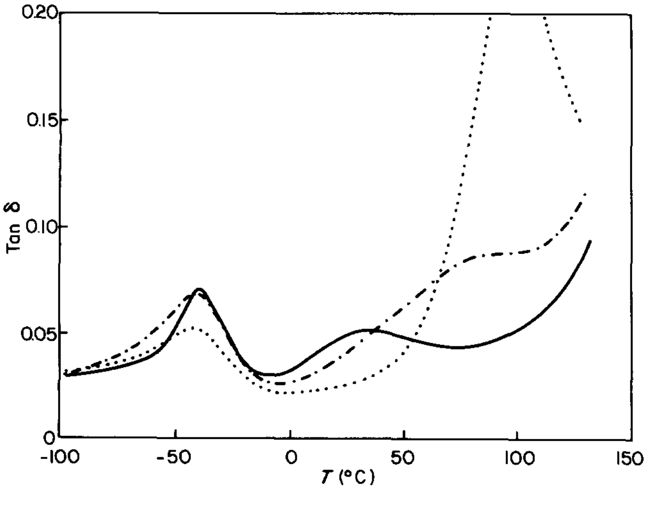

Figure 8 Viscoelastic spectra of: PVDF (——) and blends with 6 (–·–·–) and 17% PVP (····). After heat treatment at 140°C

Recalling that Yoon and Wendorff[13,15,17] assigned the β relaxation at −40°C to the crystal–amorphous interphase, the correlation of the β' relaxation with the 'true' T_g would imply the unreasonable idea of random amorphous regions that acquire mobility at temperatures higher than the interphase. Only if mobilization of the interphase involves much shorter segments than those giving rise to the cooperative motions of a 'classical' glass transition could the above incongruence be justified to some extent. It must be stressed that our PVDF–PVP, as well as the PVDF–PMMA blends studied by Yoon, are heterogeneous systems at high PVDF content and that any extrapolation of the homogeneous blends' T_g values to pure PVDF is highly uncertain. T_g–composition data of homogeneous mixtures in the whole concentration range, up to 90% PVDF, have only been reported in a paper by Nishi and Wang on PVDF–PMMA blends quenched from the melt[6]. Their measurements indicate that the T_g of the blends must be extrapolated to about −50°C, i.e. to the temperature region of the β relaxation of PVDF. This result and Yoon's suggestion can be reconciled only if the T_g of the 'true' amorphous phase and that of the interphase of PVDF are close to each other. In this hypothesis, a problem that has been discussed in the present paper, but still awaits a solution, is the nature of the β' relaxation in PVDF, a process that we have shown to undergo physical ageing and to be present only in pure PVDF, being absent in partially crystalline blends containing as little as 6% PVP.

A last point that deserves attention, and will be investigated to a deeper extent in a forthcoming paper, is the effect of melt crystallization on the viscoelastic spectrum of the blends illustrated in *Figure 7*. Such thermal treatment decreases the amount of crystalline PVDF while it increases both the amorphous fraction randomly mixed with PVP and that of pure PVDF which—according to Yoon—can be associated with the interphase. It appears therefore that the PVDF crystals obtained from the melt carry a higher fraction of interphase than those obtained by solvent casting.

CONCLUSIONS

Dynamic mechanical measurements provide evidence of miscibility of PVDF with PVP. The amorphous component, if present in amounts higher than 40%, inhibits crystallization of PVDF, the blends being formed by a single homogeneous amorphous phase. At lower PVP contents the system is composed of three coexisting phases: a homogeneous blend of quasi-constant composition, crystalline PVDF and a pure amorphous PVDF phase unable to mix with the other component.

The viscoelastic spectrum of the partially crystalline blends depends strongly on the thermal history of the samples, suggesting that the partitioning of PVDF among the different phases varies as a consequence of high-temperature treatments below or above T_m.

The T_g–composition dependence of the homogeneous PVDF–PVP blends reveals strong interactions between the two polymers, in agreement with the highly negative value of the thermodynamic interaction parameter in the molten state[20,36].

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