Miscible polyacetal–poly(vinyl phenol) blends: 2. Thermomechanical properties and morphology

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(Received 11 December 1990; revised 1 February 1991; accepted 7 February 1991)

Blends containing polyacetal and poly(vinyl phenol) were prepared by melt compounding and investigated with respect to dynamic mechanical behaviour, melting behaviour, density and morphology. Evidence of complete miscibility was provided by a single, composition-dependent glass transition temperature intermediate between those of the pure components and a substantial depression of the melting point of the crystalline phase. Analysis of the melting point depression yielded an approximate interaction parameter, which was in excellent agreement with that obtained from the calorimetric mixing of chemical analogs. Also, the observation of a significant negative volume of mixing supported miscibility. The emergence of a banded spherulitic texture upon blending was also noted. The overall thermal behaviour of this miscible system was shown to conform to the theoretical model of Kumar and Yoon.

(Keywords: polyacetal; poly(vinyl phenol); blends; thermomechanical properties; morphology)

INTRODUCTION

In the accompanying paper (Part 1: Predictions based on low molecular weight analogs) we demonstrated favourable enthalpies of mixing between acetal and phenol moieties in low molecular weight compounds, which act as chemical analogs for the title polymers. These results were discussed in terms of hydrogen-bonding interactions and were used to predict miscibility between polyacetal (PAc) and poly(vinyl phenol) (PVP).

Polyacetal, or poly(oxymethylene), is a semi-crystalline engineering thermoplastic of considerable commercial importance. Despite this, blends containing this polymer have received very sparse attention in the literature, especially in comparison to other materials within this class[1–5]. Furthermore, no clear case of miscibility in a polyacetal-containing blend has been reported, although limited degrees of compatibility with poly(vinyl chloride), polyurethanes and ionomers have been described[3–5].

The present contribution concerns melt-compounded blends containing a commercial polyacetal and two poly(vinyl phenol) homopolymers that differ in molecular weight. Evidence of miscibility is provided by the continuous composition dependance of the major thermal transitions.

EXPERIMENTAL

The materials used in this study are described in *Table 1*. The polyacetal is an injection-moulding grade, copolymer-type material, Celcon M-90, obtained from Hoechst-Celanese. N.m.r. reveals that this copolymer contains 2–3% oxyethylene repeat units, the remainder being oxymethylene. The poly(vinyl phenol) materials were also obtained from Hoechst-Celanese and were characterized by g.p.c. in *N*-methyl pyrrolidone.

The blends were prepared by the melt-compounding of pre-dried powder blends in a laboratory-scale Baker-Perkins 15 mm co-rotating twin-screw extruder. The screw design, shown in *Figure 1*, is fully intermeshing and self-wiping and includes a series of mixing paddles, designed for the thorough dispersion of blend components. The extruder was operated at 240°C barrel temperature and 300 rev. min^{-1} screw rotation. The blends were subsequently compression-moulded at 230°C into plaques of 0.75 mm thickness. The moulded plaques were subjected to slow cooling between preheated Teflon sheets.

Dynamic mechanical analysis was performed on specimens derived from moulded samples. A Polymer Laboratories d.m.t.a. operating in the single cantilever beam mode at a frequency of 10 Hz and a heating rate of 3 K min^{-1} was used. Calorimetric analysis was also performed on moulded samples by using a Perkin–Elmer DSC-7 d.s.c. scanning at 20 K min^{-1} between -40°C and $+220$°C. Optical microscopy was performed on thin specimens microtomed from the moulded plaques. Specific volume measurements were made at 25°C in a density gradient column with sodium bromide solution in distilled water.

RESULTS AND DISCUSSION

Dynamic mechanical behaviour

The dynamic mechanical loss tangent of unblended polyacetal prepared according to our protocol is shown in *Figure 2*. Three thermal transitions below the melting point are in evidence. The transition at 125°C, α, has been clearly associated with molecular motion within the

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0032-3861/92/040760-07

Table 1 Materials used in this study

Designation	Description	M_n*	M_w*	T_g (°C)	T_m (°C)	Density (g cm^{-3})
PAc	Polyacetal copolymer	–	–	(−6)	170	1.402
PVP-7k	Poly(vinyl phenol)	8700	17700	153	–	1.163
PVP-50k	Poly(vinyl phenol)	50500	115000	179	–	1.189

*G.p.c. in *N*-methyl pyrrolidone expressed relative to polystyrene standards

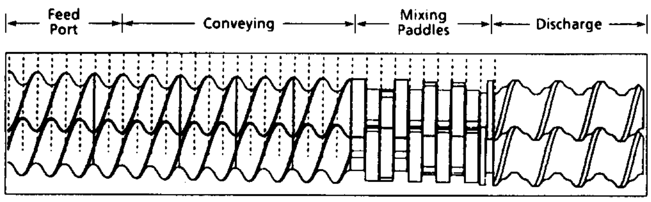

Figure 1 Diagram of the extruder screw design used for melt compounding throughout this study

crystalline phase[6]. The question of whether the transition at −60°C, γ, or the one at −6°C, β, corresponds to the glass transition of the amorphous phase has been a matter of some controversy[6,7]. The transition at −60°C is the dominant one in the dynamic mechanical spectrum. However, the value of −6°C is consistent with the extrapolation of T_gs within the homologous series of poly(alkylene ethers) and with the overall dynamic mechanical behaviour of a series of polyacetal copolymers that vary in oxyethylene content[8]. The assignment of the glass transition temperature associated with the amorphous phase of polymers that possess a high degree of crystallinity is very often an ambiguous and controversial matter. At present, we prefer to associate the β transition that we observe at −6°C with the glass transition of polyacetal.

The dynamic mechanical spectra of the unblended poly(vinyl phenol) homopolymers could not be obtained because these materials were excessively brittle. Nevertheless, the glass transition temperatures of these wholly amorphous materials could be unequivocally identified by d.s.c. and are given in *Table 1*. We expect that the equivalent T_g values, if measured by dynamic mechanical means, would be somewhat higher because of viscoelastic frequency–temperature shifts.

Dynamic mechanical analysis of melt-compounded polyacetal–poly(vinyl phenol) (PAc–PVP-7k) blends provided compelling evidence for miscibility within the amorphous phase. In *Figure 3*, the dynamic mechanical loss tangent is plotted against temperature for blends of each composition. The dominant feature of the mechanical spectra is a relaxation peak, the magnitude and temperature of which increases steadily as the PVP content of the blend increases. The identification of this thermal transition with the glass transition of the blend follows from the observation that the transition temperature steadily approaches the T_g of pure PVP as the blend becomes rich in PVP. *Figure 4* demonstrates the nearly linear T_g–composition relationship, which is both characteristic and diagnostic of a blend system that is miscible[9].

Figure 5 shows loss tangent curves for two blends containing high molecular weight poly(vinyl phenol) (PVP-50k). In these cases the loss tangent exhibits a very broad plateau. Nevertheless, the approximate mid-point of the plateaus appears to follow the expected T_g–composition relationship as given in *Figure 4*, suggesting that perhaps equilibrium miscibility is being approached. The melt processing of these higher molecular weight poly(vinyl phenol) blends was made difficult by high melt viscosities and the rather narrow melt temperature window that these blends will tolerate. The dynamic mechanical results for all of the blends studied are summarized in *Table 2*.

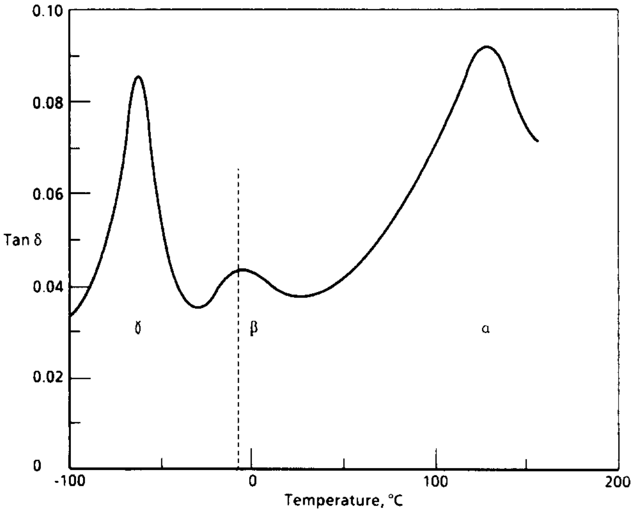

Figure 2 Dynamic mechanical loss tangent of the unblended polyacetal constituent for a frequency of 10 Hz (the three thermal transitions are labelled α, β and γ)

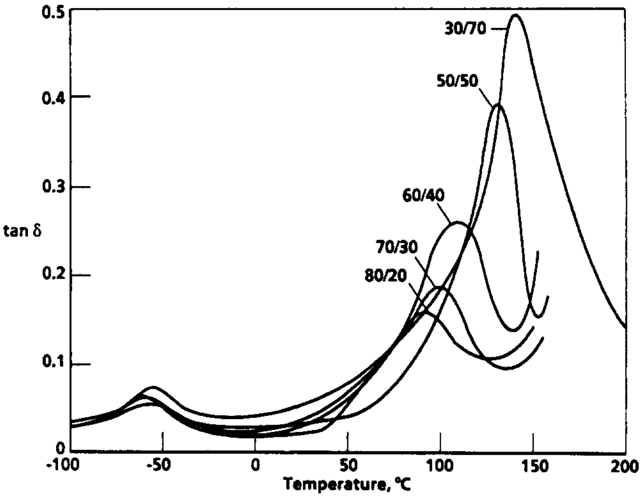

Figure 3 Dynamic mechanical loss tangent as a function of temperature for a series of PAc–PVP-7k blends for a frequency of 10 Hz (the blend compositions are shown as PAc–PVP on a wt/wt basis)

Melting and crystallization behaviour

The present blend system falls within the class of miscible semi-crystalline–amorphous blends. In such

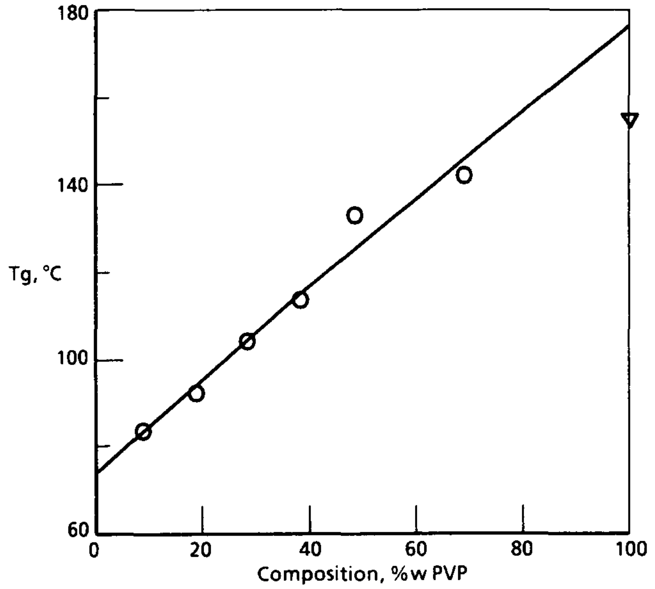

Figure 4 Glass transition temperature as a function of blend composition (blend T_gs were determined from dynamic mechanical measurements, whereas the T_g of neat PVP was determined from d.s.c.)

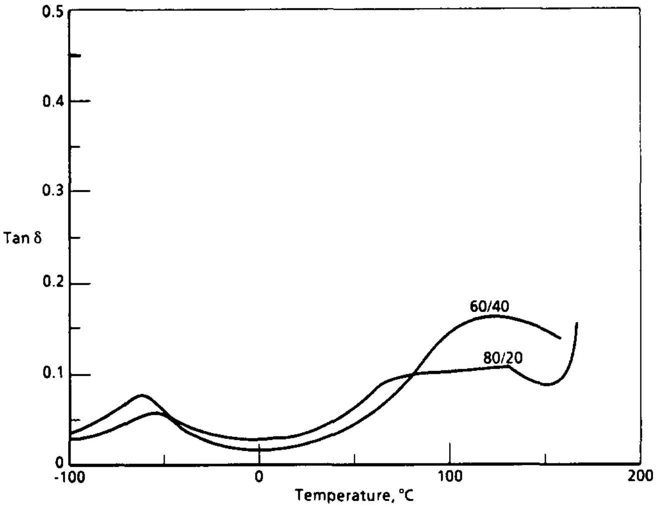

Figure 5 Dynamic mechanical loss tangent as a function of temperature for two PAc–PVP blends containing high molecular weight PVP (PVP-50k) (the blend compositions are shown as PAc–PVP on a wt/wt basis) for a frequency of 10 Hz

systems (e.g. PEO–PMMA, PCL–PVC, PVF_2–PMMA) it is typical for the crystallizable component, if present in an appreciable concentration, to be partitioned between a pure crystalline and a mixed amorphous phase[10–12] (and perhaps a third phase, discussed later). The crystalline phase is affected by changes in the mixed amorphous phase with which it is in (pseudo)equilibrium. This effect is manifested by reductions of the melting point and of the degree of crystallinity. In the present case both phenomena were observed.

D.s.c. thermograms, showing crystalline melting endotherms, are given for blends of various composition in *Figure 6*. The results are summarized in *Table 3*. The enthalpies of melting upon heating and of crystallization upon cooling at constant rate both decrease as PVP is added to the blend. *Figure 7* shows the degree of crystallinity, which has been calculated from the melting enthalpies and normalized for the polyacetal content of the blend, plotted against composition. The degree of crystallinity remains virtually constant up to a PVP content of about 40 wt%. Upon further addition of PVP, the crystallinity of the PAc component is greatly reduced. *Figure 8* gives the peak temperatures of melting and of crystallization as a function of blend composition. Both are significantly reduced as the PVP content increases. Thus crystallization is impeded in the presence of the amorphous component, which implies miscibility in the melt.

It is known that the interaction strength in a polymer blend can be quantified by an analysis of the equilibrium

Table 2 Dynamic mechanical transition temperatures of PVP/PAc blends

Composition (PVP–PAc wt/wt)	PVP M_w	T_α (°C)	T_β (°C)	T_γ (°C)
0/100	–	125	−6	−60
10/90	7k	120	83	−57
20/80	7k	–	92	−57
30/70	7k	–	103	−56
40/60	7k	–	113	−55
50/50	7k	–	132	−53
70/30	7k	–	141	−52
100/0	7k		Too brittle	
20/80	50k	–	100*	−58
40/60	50k	–	120	−51
100/0	50k	–	Too brittle	−52

*Transition was very broad (plateau 70°C to 130°C)

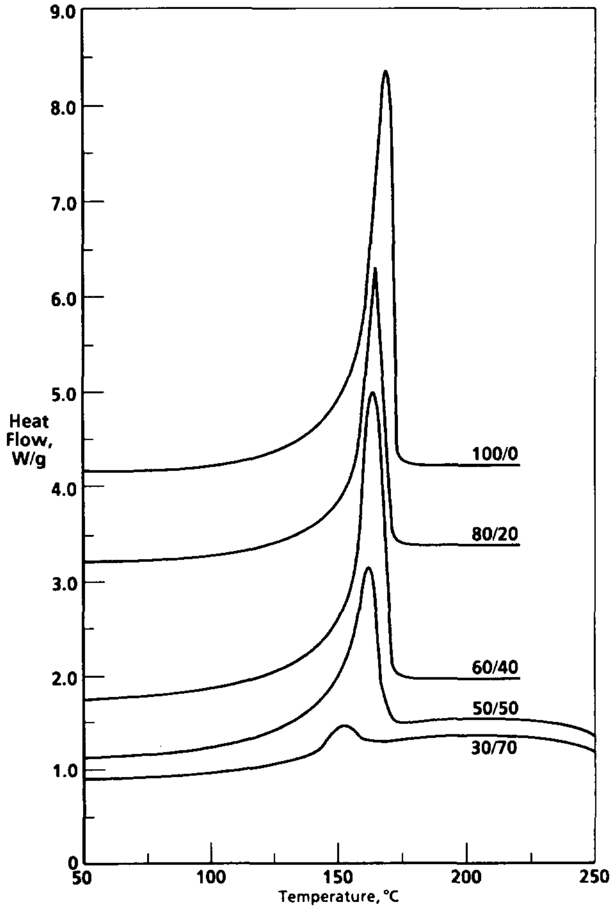

Figure 6 D.s.c. thermograms, upon heating at 20 K min^{-1}, for a series of PAc–PVP-7k blends, showing melting endotherm of PAc crystalline phase (the blend compositions are shown as PAc–PVP on a wt/wt basis)

Table 3 D.s.c. results for PVP/PAc blends

		Heating		Cooling	
Composition (PVP–PAc wt/wt)	PVP M_w	T_m (°C)	ΔH_m (J g^{-1})	T_c (°C)	ΔH_c (J g^{-1})
0/100	–	169.6	171.8	141.3	144.7
20/80	7k	168.0	138.6	141.5	130.2
40/60	7k	162.4	100.3	133.4	91.4
50/50	7k	158.8	71.2	81.4	26.2
30/70	7k	142.9	11.5	–	0.0
20/80	50k	167.2	137.5	138.7	120.8
40/60	50k	166.5	84.6	134.6	70.1

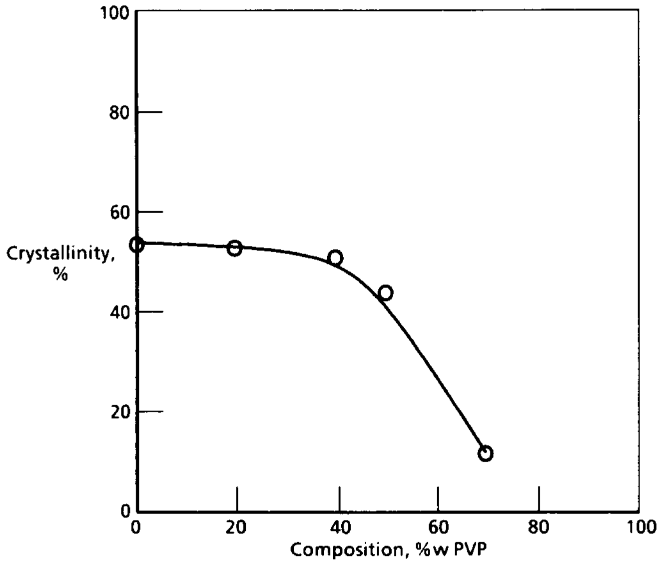

Figure 7 The degree of crystallinity of the polyacetal component as a function of blend composition (the values were calculated from d.s.c. melting endotherms and normalized for polyacetal content)

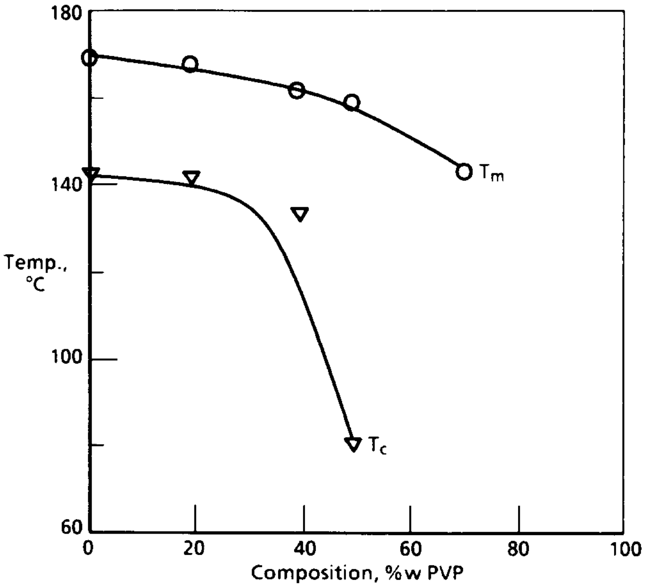

Figure 8 Temperature of melting (upon heating) and of crystallization (upon cooling) from d.s.c. as a function of blend composition

melting point depression in the case where one of the components is crystallizable[13]. A Hoffman–Weeks extrapolation of melting data is most frequently used to obtain equilibrium melting temperatures. In the present case, however, the data from *Table 3* were used without extrapolation and were analysed by using the expression of Nishi and Wang[14], given by:

$$(1/T_m) - (1/T_m)_0 = [(R)(V_c)/(H_f)(V_a)][\chi_{12}][\phi_2]^2 \qquad (1)$$

The parameters are explained in *Table 4*. In *Figure 9*, the left side of the equation is plotted against the square of the volume fraction of the polymeric diluent, which is PVP in this case. The volume of PVP within the amorphous phase was calculated from the blend weight fraction, the degree of crystallinity from d.s.c., and the component densities in *Table 1*. Although the melting data used are not equilibrium values, the resultant plot, shown in *Figure 9*, exhibits remarkable linearity over a broad range of composition. Thus we suggest that this slope reflects a useful estimate of the strength of the physical interaction within the amorphous phase of the blend. The calculated Van Laar interaction parameter, B_{12}, is -10.7 cal cm^{-3} (-44.8 J cm^{-3}), which corresponds to a Flory–Huggins interaction parameter, χ_{12}, of -1.25 at the melting temperature, if we take the reference volume to be the molar volume of one PVP repeat unit (see *Table 4*). These values are in excellent agreement with those determined by the calorimetry of mixtures of low molecular weight chemical analogs, as discussed in Part 1. Thus, we confirm in the polymer mixtures, as in the analog mixtures, that the blend interaction is relatively strong and consistent with the hypothesis of hydrogen bonding.

Table 4 Molecular parameters used for analysis of PAc–PVP blends

Parameter	Quantity	Value
H_f	Heat of fusion of pure PAc crystals	9.79 kJ mol^{-1}* (326 J g^{-1})
V_c	Molar volume of PAc repeat unit in crystalline phase	20.1 cm^3 mol^{-1}*
V_a	Molar volume of PVP repeat unit in amorphous phase	103 cm^3 mol^{-1}*
B_{12}	Van Laar interaction parameter	-10.7 cal cm^{-3} (-44.8 J cm^{-3})
χ_{12}	Flory–Huggins interaction parameter (referred to PVP molar volume)	-1.25

*From or derived from data in references 21 and 22

Blend morphology

The morphology of the blends was investigated by optical microscopy of sections microtomed from the central region of compression-moulded specimens. *Figure 10a* shows a micrograph of unblended polyacetal, which reveals a rather disordered spherulitic structure typical for a non-isothermally melt-crystallized polymer. In *Figure 10b*, an 80/20 PAc–PVP-7k blend also exhibited this morphology. However, as *Figure 10c* demonstrates, a 50/50 PAc–PVP-7k blend exhibited larger spherulites and a very marked ringed texture within the spherulitic superstructure. Such a 'ringed' or 'banded' texture arises from a regular and periodic twisting of crystalline lamellae as they grow in the radial direction[15].

Previous studies of other semi-crystalline–amorphous polymer blends that are known to be miscible (e.g. PCL–PVC and PVF_2–polybutyrolactone) have also shown the emergence of banded textures within spherulites formed from the blends. These textures were not apparent in spherulites formed from the pure semi-crystalline component[16–18]. In these cases the ring spacing (periodicity) of the bands tends to be a function of blend composition. Thus, the morphology seen in *Figure 10c* may be an indicator of miscibility in the melt state. Furthermore, the spherulites observed in the blends are fully impinged and volume-filling, indicating that the amorphous component becomes fully incorporated within the spherulitic superstructure. A detailed SAXS analysis is needed to determine specifically how the amorphous component is arranged with respect to the crystalline lamellae.

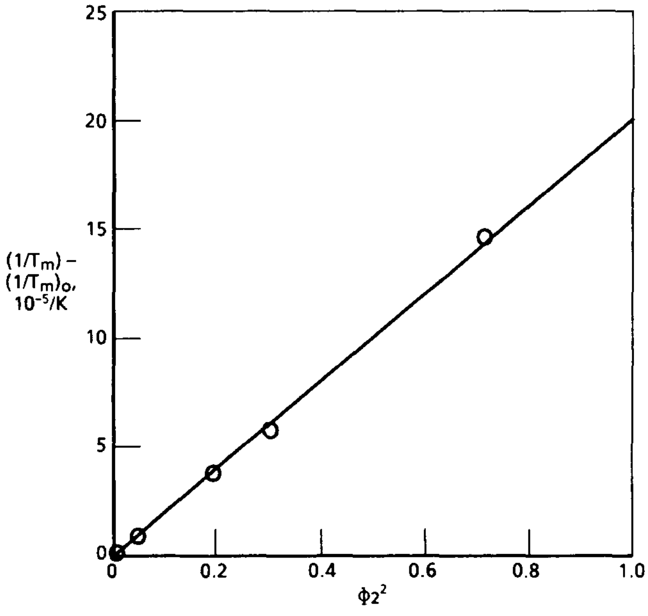

Figure 9 Melting point depression versus the square of the volume fraction of the non-crystallizable component (PVP-7k)

In a 30/70 PAc–PVP-7k blend, no evidence of spherulitic structures or of optical birefringence could be detected. This is attributed to the low level of crystallinity in this blend.

Specific volume

Polymer blends that are miscible as the result of strong specific interactions often exhibit negative volumes of mixing[19,20], i.e. strong interactions promote shorter intermolecular distances at the expense of free volume. Thus, significant negative deviation from additivity of specific volume in a polymer blend system provides an indication of such interactions. In the present case of PAc–PVP blends, it is expected that strong intermolecular hydrogen bonding will give rise to a negative specific volume of mixing.

The specific volume of mixing is defined as

$$\Delta V_m = V_{\text{blend}} - V_{\text{ideal}} \qquad (2)$$

where V_{blend} is the experimental specific volume of the blend and V_{ideal} is the specific volume expected from perfect additivity of the pure components, which is given by

$$V_{\text{ideal}} = (w_1)(V_1) + (w_2)(V_2) \qquad (3)$$

where w_i and V_i correspond to weight fractions and specific volumes, respectively, of pure blend components 1 and 2. In the present case, the semicrystalline nature of polyacetal complicates our analysis because the specific volume of the polyacetal component depends strongly upon its degree of crystallinity, which varies with the composition of the blend. However, this effect can be corrected for by considering the measured degree of crystallinity (from *Figure 7*) and assuming that the corrected specific volume of the polyacetal component

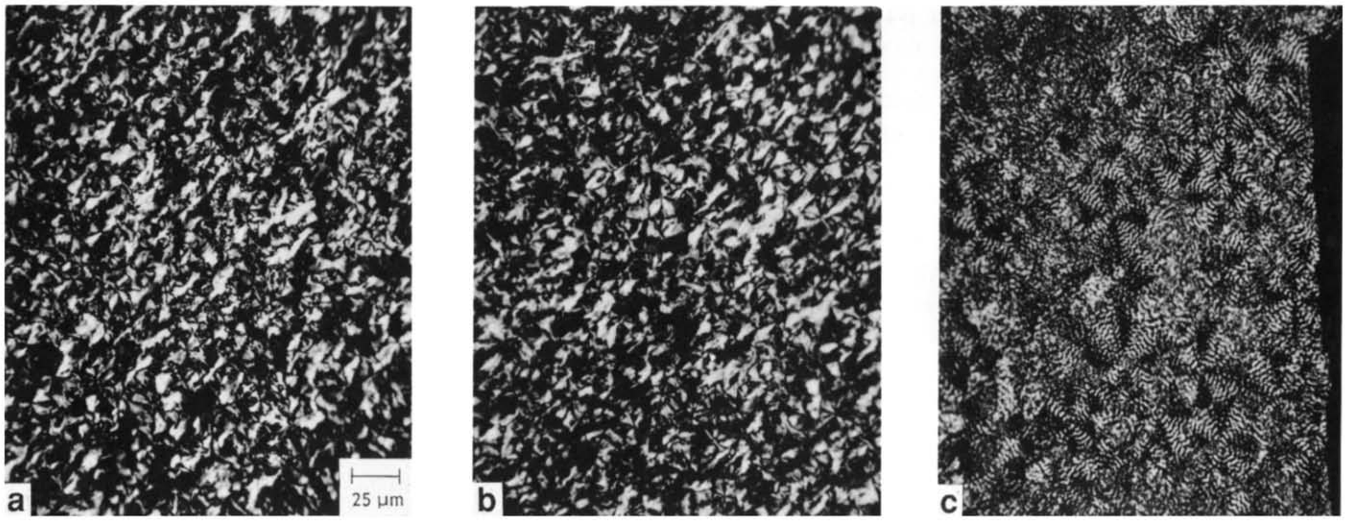

Figure 10 Optical micrographs of microtomed sections obtained from compression-moulded samples and viewed between crossed polars: (a) 100/0 PAc–PVP-7k; (b) 80/20 PAc–PVP-7k; (c) 50/50 PAc–PVP-7k

in the blend is additive:

$$V_{PAc} = (w_c)(V_c) + (w_a)(V_a) \qquad (4)$$

where the subscripts c and a correspond to the pure crystalline and amorphous phases of polyacetal. V_c can be calculated from the crystalline unit cell and is reported to be 0.671 cm^3 g^{-1} (refs 21, 22). For internal consistency V_a was calculated by solving equation (4) for V_a with our measured data for the pure polyacetal control. The resultant V_a, 0.760 cm^3 g^{-1}, is in excellent agreement with published literature values[21]. The resultant experimental and calculated specific volumes are given in *Table 5*.

In *Figure 11*, the corrected specific volume of mixing normalized with respect to the ideal specific volume, $\Delta V_m/V_{ideal}$, is plotted as a function of blend composition for PAc–PVP-7k blends. All the blend compositions exhibited a specific volume of mixing that was reasonably large and negative in sign. The volume of mixing appeared to reach a maximum absolute value in the PVP-rich composition region. These results are consistent with strong hydrogen-bonding interactions and the resultant large, negative value of χ_{12} for the blend.

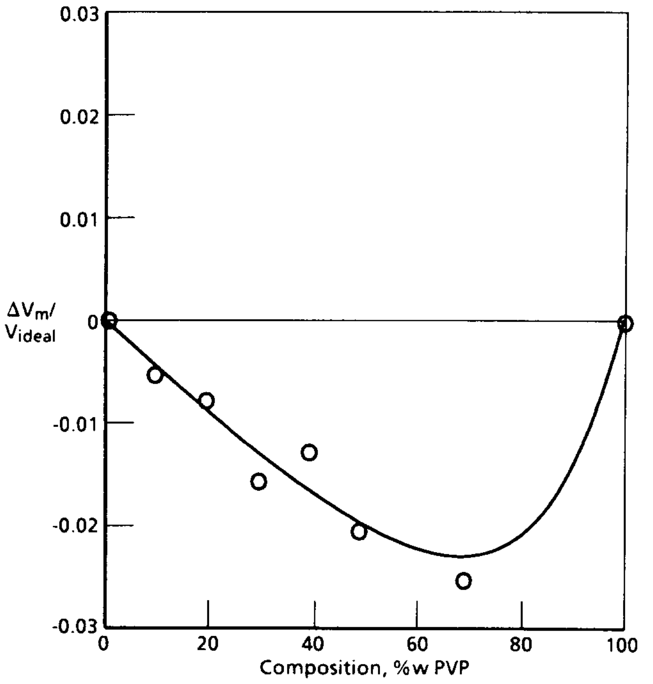

Figure 11 Specific volume of mixing normalized with respect to the ideal specific volume, $\Delta V_m/V_{ideal}$, as a function of blend composition

Phase compositions

Returning briefly to the relationship between the glass transition temperature and the blend composition, given in *Figure 4*, it may be pointed out that the T_gs of the blends do not approach that of pure polyacetal as the PVP content of the blend approaches zero. Such an observation was made previously for PVF$_2$/PMMA blends[23,24], an analogous system known to be both crystallizable and miscible in the amorphous phase. In order to rationalize this T_g–composition relationship, the model of Kumar and Yoon may be invoked, which proposes three phases for semi-crystalline polymers in general and for blends of this type in particular[25,26]. In addition to pure crystalline and mixed, truly amorphous phases, the model includes an interphase. This interphase is a disordered phase immediately adjacent to the crystal in which molecular motion is strongly suppressed as a result of the flux of chains anchored firmly to the crystal surface. The presence of this disordered yet immobile fraction is useful to explain many of the characteristics of semi-crystalline polymers and their miscible blends.

An important characteristic of this interphase, in the case of polymer blends, is that it is unable to accommodate any added amorphous component, even when the component is miscible in the mobile amorphous phase. As a result, the mixed amorphous phase becomes richer in the added miscible component than would be expected from a simple correction based upon the degree of crystallinity.

The present data for PAc–PVP blends can be described within the framework of this theory if it is assumed that the composition of the mixed amorphous phase can be approximated by fitting the measured glass transition temperature to the Fox equation given by

$$1/T_g(\text{blend}) = w_1/T_{g1} + w_2/T_{g2} \qquad (5)$$

where w_is are weight fractions and the subscripts denote the blend components. Pure component T_g values of −6°C and +165°C have been used here for polyacetal and poly(vinyl phenol), respectively. Then, by subtracting the fraction of the crystalline phase derived from d.s.c. measurements, an interphase fraction is left.

Figure 12 shows the calculated weight fraction of each phase as a function of blend composition. The fraction of crystalline material drops off sharply and the fraction of mixed amorphous material rises steeply as the PVP content increases. However, the calculated fraction of interfacial material (approximately 20%) remains

Table 5 Specific volumes of PAc–PVP blends

Composition (PVP–PAc wt/wt)	PVP M_w	PAc crystallinity (%)	V_{blend} (cm^3 g^{-1})	V_{ideal} (cm^3 g^{-1})	ΔV_m (cm^3 g^{-1})
0/100	–	53	0.713	0.713	0
10/90	7k	–	0.724	0.728	−0.004
20/80	7k	53	0.736	0.742	−0.006
30/70	7k	–	0.745	0.757	−0.012
40/60	7k	51	0.762	0.772	−0.010
50/50	7k	44	0.774	0.790	−0.016
70/30	7k	12	0.806	0.827	−0.021
100/0	7k	–	0.860	0.860	0
20/80	50k	53	0.738	0.739	−0.001
40/60	50k	43	0.767	0.770	−0.003
100/0	50k	–	0.841	0.841	0

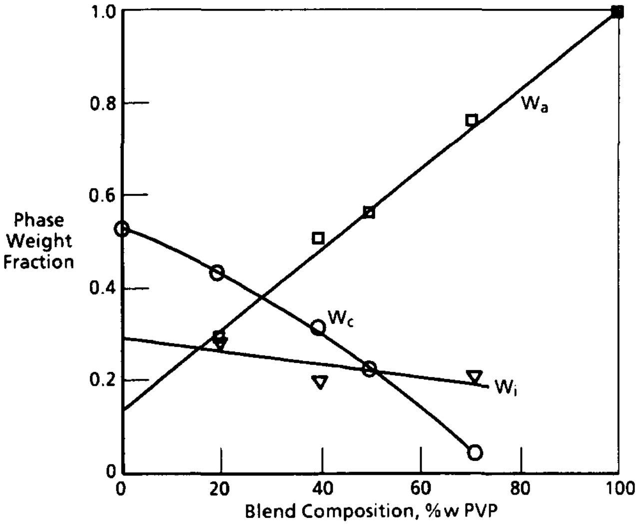

Figure 12 Calculated weight fractions of crystalline PAc phase (w_c), mixed amorphous phase (w_a), and interphase (w_i) as a function of the total blend composition

relatively insensitive to blend composition. This result is similar to that found for PEO–PMMA and other blend systems and is also expected from theoretical considerations[27,28].

CONCLUSIONS

Evidence for the miscibility of the polyacetal–poly(vinyl phenol) blend system is provided by a single glass transition temperature, measured by dynamic mechanical means, which is smoothly and strongly dependent upon blend composition. The specific nature of the observed composition-dependence of the glass transition temperature was interpreted within the framework proposed by Kumar and Yoon.

A significant melting-point depression of the polyacetal crystalline phase was observed, the magnitude of which suggests strong physical interaction in the blend. Further analysis yielded an approximate B_{12} value of -10.7 cal cm^{-3} (-44.8 J cm^{-3}) and χ_{12} interaction parameter of -1.25, which is in good agreement with analog calorimetry experiments made on model compounds.

A substantial negative volume of mixing was measured for blends across the full composition range, suggesting strong physical interactions.

Spherulites found in blends in the intermediate composition range were volume-filling and larger than those found in pure polyacetal that had been subject to the same thermal history. Furthermore, a well developed 'banded' texture was observed in blend spherulites which was not found in those of pure polyacetal.

ACKNOWLEDGEMENTS

We are pleased to acknowledge D. L. Handlin, D. R. Paul and D. Y. Yoon for helpful discussions and L. J. Sikirica, R. P. Gingrich and G. J. Koplos for experimental assistance.

REFERENCES

1 Pabst, A. and Wendorff, J. H. *Die Angew. Makromol. Chem.* 1990, **178**, 153
2 Chang, F. C. and Yang, M. Y. *Polym. Eng. Sci.* 1990, **30**, 543
3 Margaritis, A. G. and Kalfoglou, N. K. *J. Polym. Sci., Polym. Phys. Edn.* 1988, **26**, 1595
4 Chiang, W. Y. and Lo, M. S. *J. Appl. Polym. Sci.* 1988, **36**, 1685
5 Horrion, J. and Cartasegna, S. 'Abstracts 33rd IUPAC Int. Symp. Macromolecules', Montreal, Canada, 1990, session 1.1.3
6 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids', John Wiley and Sons, London, UK, 1967
7 Suzuki, H., Grebowicz, J. and Wunderlich, B. *Br. Polym. J.* 1985, **17**, 1
8 Bohn, V. L. *Kolloid Z. Z.* 1965, **201**, 20
9 MacKnight, W. J., Karasz, F. E. and Fried, J. R. 'Polymer Blends', Vol. I (Ed. D. R. Paul and S. Newman), Academic Press, Orlando, FL, USA, 1978
10 Rostami, S. *Polymer* 1990, **31**, 899
11 Ellis, T. S. *Polymer* 1988, **29**, 2015
12 Leonard, C., Halary, J. L. and Monnerie, L. *Macromolecules* 1988, **21**, 2988
13 Olabisi, O., Robeson, L. and Shaw, M. T. 'Polymer–Polymer Miscibility', Academic Press, New York, 1979
14 Nishi, T. and Wang, T. T. *Macromolecules* 1976, **8**, 909
15 Bassett, D. C. 'Principles of Polymer Morphology', Cambridge University Press, Cambridge, UK, 1981
16 Nojima, S., Watanabe, K., Zheng, Z. and Ashida, T. *Polym. J.* 1988, **20**, 823
17 Keith, H. D., Padden, F. S. and Russel, T. P. *Macromolecules* 1989, **22**, 666
18 Marand, H., Collins, M. B., Prasad, A. and Edie, S. L. 'Abstracts 33rd IUPAC Int. Symp. Macromolecules', Montreal, Canada, 1990, session 2.1.7
19 Fried, J. R., Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1978, **11**, 150
20 Chiou, J. S. and Paul, D. R. *J. Appl. Polym. Sci.* 1987, **34**, 1503
21 Wunderlich, B. 'Macromolecular Physics Vol. 3: Crystal Melting', Academic Press, New York, USA, 1980
22 Brandrup, J. and Immergut, E. H. 'Polymer Handbook' 3rd Edn., John Wiley and Sons, New York, USA, 1989
23 Paul, D. R. and Altamirano, J. O. *Adv. Chem. Ser.* 1975, **142**, 371
24 Paul, D. R., Barlow, J. W., Bernstein, R. E. and Wahrmund, D. C. *Polym. Eng. Sci.* 1978, **18**, 1225
25 Kumar, S. K. and Yoon, D. Y. *Macromolecules* 1989, **22**, 4098
26 Hahn, B., Wendorff, J. and Yoon, D. Y. *Macromolecules* 1985, **18**, 718
27 Alfonso, G. C., Turturro, A., Scandola, M., Pizzoli, M. and Ceccorulli, G. *J. Polym. Sci., Polym. Phys. Edn.* 1989, **27**, 1195
28 Runt, J. P., Barron, C. A., Zhang, X. F. and Kumar, S. K. *Macromolecules* 1991, **24**, 3466