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Blends of rigid and flexible macromolecules: poly(benzimidazole) mixed with poly(vinyl acetate-*stat*-vinyl alcohol) copolymers

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Abstract

Miscibility in a series of blends, derived from poly(benzimidazole) (PBI) and a range of poly(vinyl acetate-*stat*-vinyl alcohol) [PV(Ac/OH)] copolymers with vinyl alcohol contents between 20 and 73 mol%, has been studied by differential scanning calorimetry, dynamic mechanical thermal analysis, Fourier transform infra-red spectroscopy (FTi.r.), scanning electron microscopy and optical haze measurements. The results show that as the vinyl alcohol content of the copolymer component increases, the level of dispersion of the two components of the blend improves. While no one-phase blends, miscible at the molecular level, were obtained, the levels of dispersion in blends with PV(Ac/OH) compositions of 56.0 and 73.0 mol% vinyl alcohol were good enough to allow the formation of optically clear films. An enhanced storage modulus (E') for blend 5, which was larger than that for PBI alone, was also obtained. Evidence for significant hydrogen bonding between the blend components was found from FTi.r. measurements, but none of the blends exhibited a single glass transition temperature. Consequently it is estimated that the phase-domain sizes for the well-dispersed blends lie in the range: 20 nm $<$ domain size $<$ 500 nm, which are larger than one would expect from single-phase miscible blends. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Blend miscibility; Poly(benzimidazole); Poly(vinyl acetate-*stat*-vinyl alcohol)

1. Introduction

The study of polymer blends is still a subject that attracts interest in spite of the large body of work that now exists in both the open and patent literature [1]. Both single- and multi-phase blends have their uses, particularly if the latter group can be modified to give materials with desirable properties. One of the major problems encountered in the production of single-phase blends has been the inherent tendency for most polymer combinations to demix because of the very small contribution from the entropy of mixing, resulting from the high molecular weight of the components. Several strategies have evolved to overcome this drawback that can be used to enhance mixing and lead to single-phase, binary and ternary polymer blends, and these are well documented [2].

Attention has been turning gradually towards what was described originally by Helminiak et al. [3] as a molecular composite. This is defined as an isotropic material consisting of a rigid, rod-like polymer dispersed molecularly in a more flexible polymer matrix. While most polymer blends will differ to some extent in the flexibility of the component polymer chains, the idea of the molecular composite is that the reinforcing component is fairly rigid and the flexibility of the other chains in the matrix is significantly greater.

This principle has its limitations, not the least of which has been pointed out by Flory and Abe [4,5], who have evaluated the thermodynamic implications of mixing a rigid rod polymer with a flexible coil polymer in a solvent. They demonstrated that there are substantial thermodynamic barriers to obtaining a one-phase system with mixing of the components at a molecular level, because of the tendency for rigid polymers to form self-aligned phases with exclusion of the flexible component from that phase.

If such difficulties can be overcome, then the resulting materials could have a range of desirable features such as possession of a modulus that is greater than that expected from simple additivity rules, the absence of defects, and elimination of the interfacial weaknesses normally associated with multi-phase composites and blends. As the theoretical predictions are based on the assumption that the mixtures are athermal, then miscibility in such blends may be promoted by having strong secondary forces, such as hydrogen-bonding, dipole–dipole and charge–transfer interactions, operating between the two components that

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will overcome the demixing tendency. This has been used successfully in many blends where the chain flexibilities of the components are not as extreme as required for a molecular composite, but the same principles can be exploited and have been used already.

Poly(benzimidazole) (PBI) is a macromolecule that is considered to be relatively rigid and also possesses both donor and acceptor hydrogen-bonding sites. It has been found to form homogeneous, one-phase blends with aromatic polyimides [6], promoted by hydrogen bonding. However, these poly(ether imide)s are also fairly rigid molecules with glass transition temperatures (T_gs) above 490 K, even though these T_gs are about 100–200 K lower than that for PBI. Consequently they are regarded as blends rather than molecular composites. PBI has also been blended [7] with a more flexible second component, poly(4-vinyl pyridine) (PVP), where again miscibility was reported which was attributed to the strong hydrogen bonding between the components.

In the present study, PBI has again been used as the rigid component but now the aim was to use a much more flexible second component with an even lower T_g than PVP. Thus copolymers of poly(vinyl acetate-*CO*-vinyl alcohol) [PV(Ac/OH)] have been selected because of the presence of potential hydrogen-bonding sites, and the relatively high flexibility of the component chains. The structures are shown in Fig. 1.

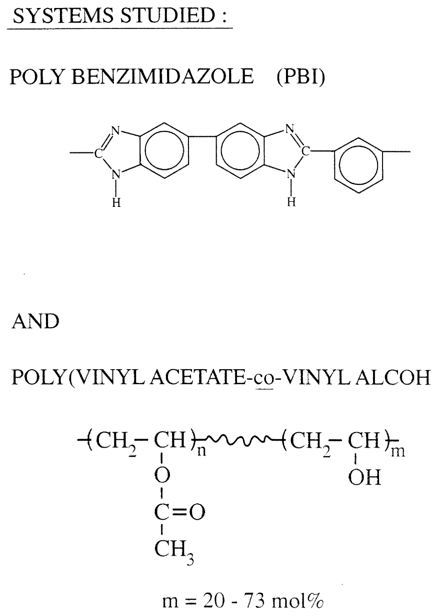


Fig. 1. Structures of the blend components.

2. Experimental

2.1. Materials

2.1.1. Polymer samples

PV(Ac/OH) samples with varying degrees of hydroxyl content were supplied by Harlow Chemicals. The PBI sample was obtained from Aldrich. Details of the sample compositions are given in Table 1.

2.1.2. Blend preparation

The common solvent used to prepare blends of PV(Ac/OH) and PBI was *N,N′*-dimethylacetamide (DMAc). PBI is difficult to dissolve, but 2% (w/v) solutions in DMAc were prepared by using a steel autoclave fitted with a stirrer. The reactor was connected to a nitrogen cylinder and heated to 498 K for 1.5 h with stirring to effect dissolution of the PBI. After cooling over a 2 h period, the PBI solution was mixed with the appropriate PV(Ac/OH) sample, which was also dissolved in DMAc, in a 1:1 (w/w) ratio. Coprecipitation was found to be an unsatisfactory way to prepare the blends, so films were cast from solutions and then dried in a vacuum oven at 353 K and 10 mbar pressure, for at least 72 h or until constant weight was achieved. Films were examined by Fourier transform infra-red spectroscopy (FTi.r.) to ensure that there was no residual solvent present. These methods resulted in solvent-free films that could be characterized for optical clarity.

2.2. Characterization

2.2.1. Glass transition temperatures

The T_g values of the blend components were measured by differential scanning calorimetry (d.s.c.) with a Perkin–Elmer DSC 7 at a heating rate of 20 K min^{-1}. Several heating and cooling cycles were used to ensure the removal of DMAc from the blends and to obtain reproducible results.

Table 1
Characteristic parameters for the blend components poly(benzimidazole) and poly(vinyl acetate-*co*-vinyl alcohol)

Sample	Vinyl alcohol (mol%)	δ [(MPa)$^{1/2}$]	Refractive index, n_D	T_g (K)
PVAc	0	19.6	1.47	311
PV(Ac/OH)20	20.0	22.7	1.48	313
PV(Ac/OH)36	36.0	25.1	1.49	322
PV(Ac/OH)47	47.0	26.9	1.50	310
PV(Ac/OH)56	56.0	28.2	1.50	320
PV(Ac/OH)73	73.0	30.8	1.51	314
PVOH	100	34.9	1.52	—
PBI	0	26.8	1.80	683

The T_g was estimated from the onset of the baseline shift that occurs during the transition.

Transition temperatures were also estimated from dynamic mechanical thermal analysis (d.m.t.a.), on a Polymer Labs DMTA at a frequency of 1 Hz. Samples were prepared by casting films of approximately 10 μm thickness in preformed aluminium boats and drying these as described previously.

2.2.2. Infra-red analysis

A Perkin–Elmer 16 PC FTi.r. spectrometer was used to obtain spectra with a resolution of 2 cm^{-1}. Samples were cast on sodium chloride discs and annealed in an oven at 398 K for 1.5 h, then cooled at 1 K min^{-1} prior to measurement.

2.3. Optical haze

Measurements of the optical clarity were made with an EEL spherical haze meter, which measures the percentage of light deviating by more than 2.5° from a perpendicular source. Samples were prepared as for the FTi.r. measurements.

2.4. Scanning electron microscopy (SEM)

A Hitachi FP82 scanning electron microscope was used to examine specimens of the various blends. Samples were examined either after cryopolishing under liquid nitrogen using a microtome or after freeze-fracture.

2.5. Measurement of modulus

Because of difficulties experienced in trying to prepare samples for tensile test measurements, it was decided to estimate the modulus of the blends and components from low-strain measurements in the d.m.t.a. instrument at a frequency of 1 Hz and heating rate of 2 K min^{-1}. Solution-cast films were cut by scalpel to 5 cm × 0.1 cm test samples, after degrassing in an ultrasonic bath to avoid bubble or void formation in the test specimens. The storage modulus was measured in the conventional manner.

3. Results

Six blends with PBI as the common component were prepared by using each of the PV(Ac/OH) samples with varying mol% of the vinyl alcohol component. These are numbered, for convenience, as shown in Table 2.

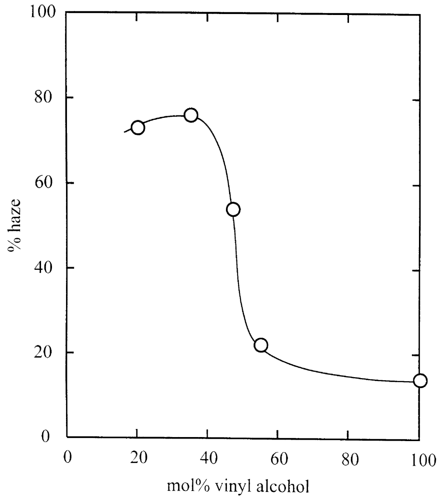


Fig. 2. % Haze in the blends plotted as a function of the vinyl alcohol content in the PV(Ac/OH) copolymers.

3.1. Optical clarity

One of the criteria that can be used to judge whether blends are single- or multi-phase is the optical clarity of the films produced. Both visual estimations and haze measurements were used and the results are shown in Table 2. There is a sharp drop in the % haze measured for each sample between blends 3 and 4, as can be seen more clearly in Fig. 2, corresponding to a change from opaque films for samples 0 to 3 to clear films for samples 4 and 5. Optical clarity measurements can give misleading results if the refractive indices of the two components of a blend are similar, which will often result in the observation of a transparent film produced from an immiscible blend. The refractive indices for the components were calculated from group contributions to the molar refraction at $\lambda = 589$ nm as suggested by van Krevelen [8], and all of the values are listed in Table 1 for each blend component. In no case is there a sufficiently close match between PBI and the other component to assume that the optical transparency of blends

Table 2
Some characteristics of (1:1) blends of PBI with various PV(Ac/OH) samples

Blend	Mol% vinyl alcohol in PV(Ac/OH)	% Haze	Visual optical clarity	$\Delta\delta$ ($\delta_{PBI} - \delta_{PV(Ac/OH)}$)
0	0.0	75.0	Opaque	+7.2
1	20.0	73.0	Opaque	+4.1
2	36.0	76.6	Opaque	+1.7
3	48.0	53.5	Opaque	−0.1
4	56.0	22.1	Clear	−1.4
5	73.0	14.0	Clear	−2.0

4 and 5 is due to similar refractive indices. Thus the initial assumption is that, when the hydroxyl content exceeds ~50 mol%, there is distinct improvement in the miscibility of the blends.

3.2. Solubility parameters

The solubility parameters of the blend components were calculated from the group contribution tables published by Askadskii [9]. A simple approach to polymer blending is to assume that if the solubility parameters of the components are closely matched, then a one-phase system will be obtained. This has been quantified by Wakker and van Dijk [10], who have calculated that if a one-phase miscible blend is to be obtained then the difference in solubility parameters, $\Delta\delta$, between the components of the blend should be no greater than $0.82\,(\mathrm{MPa})^{1/2}$. This would normally refer only to dispersive forces acting in the blend of the two relatively high-molecular-weight components. The presence of strong secondary interactions, such as hydrogen bonding, could increase the tolerance limits of $\Delta\delta$. This may pertain to the present system: optically clear films have been observed for blends 4 and 5, yet $\Delta\delta$ is 1.4 and 2.0, respectively; whereas the solubility parameters for PBI and PV(Ac/OH)47 are essentially the same, yet the films cast from blend 3 are opaque. It is worth commenting here that while the solubility parameters, quoted in Table 1, were estimated from the group contribution scheme proposed by Askadskii, δ was also estimated for each component by using the alternative schemes presented by van Krevelen [8] and Fedors [11]. While there are small numerical differences in the values calculated by each method, the relative values for the blends are the same, irrespective of the method used to calculate δ. Thus each method suggests that δ for PBI matches that for blend 3 most closely.

3.3. Scanning electron microscopy

Micrographs for blends 3 and 4 at × 2000 magnification and for blend 5 at × 9900 magnification are shown in Figs 3(a), (b) and (c), respectively. Blend 3 shows clearly a two-phase system with oval-shaped domains approximately 3 μm × 1.5 μm in size. Blends 4 and 5 show none of these features and, even when moving to ×9900 magnification for blend 5, there is little evidence for a grossly phase-separated system as the irregularities observed are casting imperfections, and no features greater than 0.1 μm are obvious. The blends 4 and 5 gave clear films when cast from solvents, whereas the film for blend 3 was opaque. Thus if blends 4 and 5 are two-phase, then the microphase-separated domains must be quite small.

In order to gain further information on the nature of the blends, 2 and 5 were freeze-fractured in liquid nitrogen and micrographs of the two fracture surfaces are shown in Figs 4(a), (b) and (c) at magnifications of ×10 000 and ×20 000. The micrographs of the blends are radically different. Blend 2, at ×10 000 magnification, shows the distinct oval-shaped phases embedded in a more uniform matrix. These appear to have a rod-like shape with cross-sectional dimensions of 2–3 μm × 1 μm, and are points of fracture within the blend. Further magnification to ×20 000 Fig. 4(b) shows distinctly one of these symmetrical oval-shaped phase domains, again with dimensions of ~3 μm × 1.5 μm. The micrograph for blend 5 shows a markedly different structure (see Fig. 4(c)). Now there are no discrete symmetrical features in the blend as these have been replaced by a plate-like structure, which suggests that a greater uniformity of mixing is present in blend 5. This is shown clearly on comparison of the micrographs and, while it is not conclusive proof of a one-phase system in blend 5, it indicates that the mixing of the two components in this blend is much more intimate than in blends 2 and 3. This

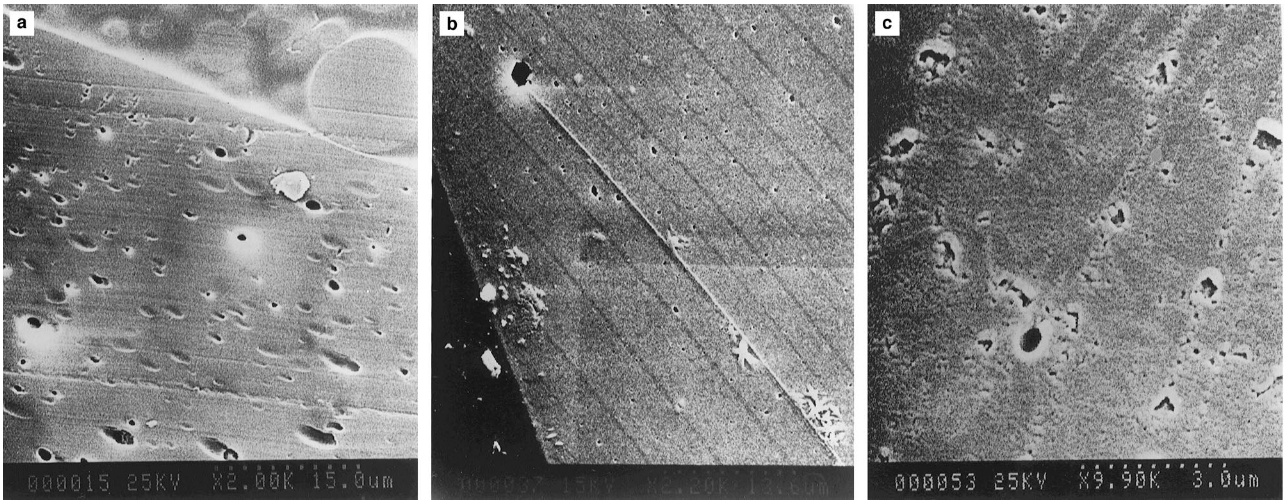


Fig. 3. SEM micrographs of: (a) blend 3 (magnification: ×2000); (b) blend 4 (magnification: ×2000); (c) blend 5 (magnification: ×9900).

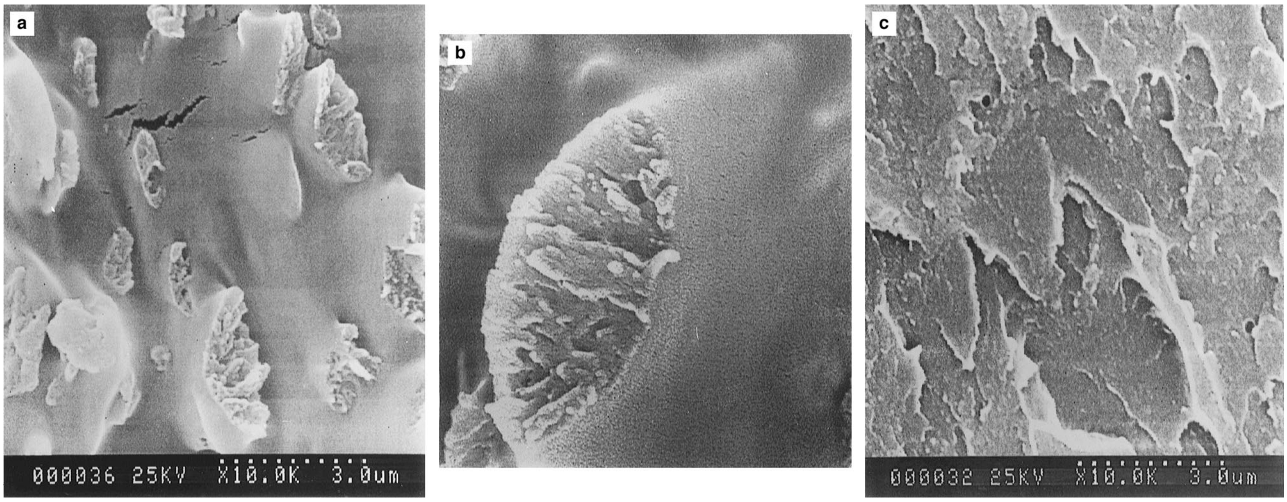


Fig. 4. SEM micrographs of: (a) blend 2 (magnification: ×10 000); (b) blend 2 (magnification: ×20 000); (c) blend 5 (magnification: ×10 000).

would be consistent with the optical clarity of the film for blend 5.

3.4. Infra-red spectroscopy

Miscibility in polymer blends is often enhanced by contributions to the free energy of mixing from favourable secondary specific interactions between the components. Both PBI and the PV(Ac/OH) copolymers possess hydrogen-bonding donor and acceptor sites along their chains which makes interpretation of the infra-red spectra of the blends more complicated. As shown in Fig. 5, there are three types of intermolecular hydrogen bond which should enhance miscibility, but there are also intramolecular hydrogen-bonding possibilities in both components that will

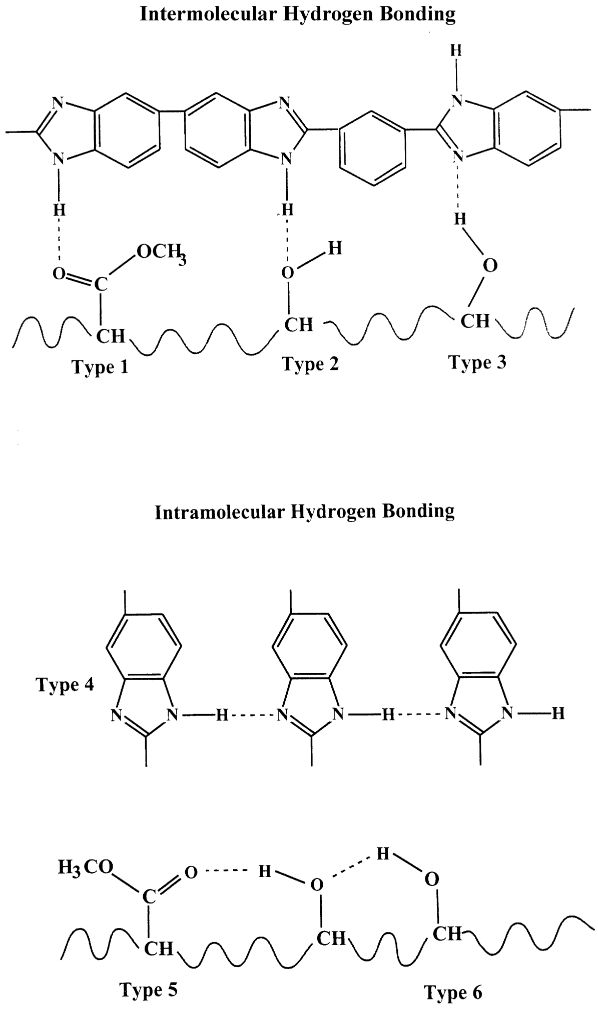


Fig. 5. Various possible forms of hydrogen bonding likely to be present in the blends.

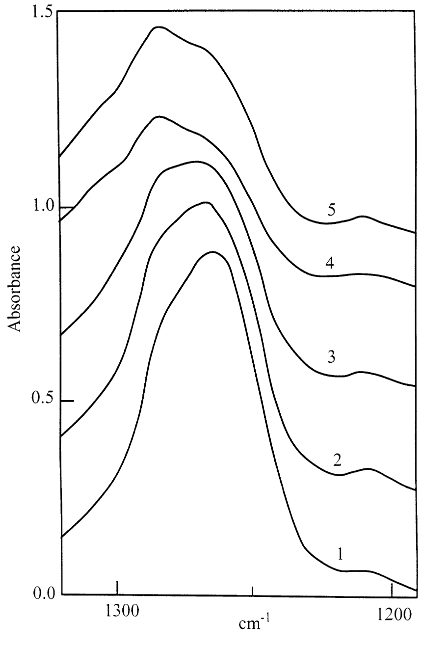
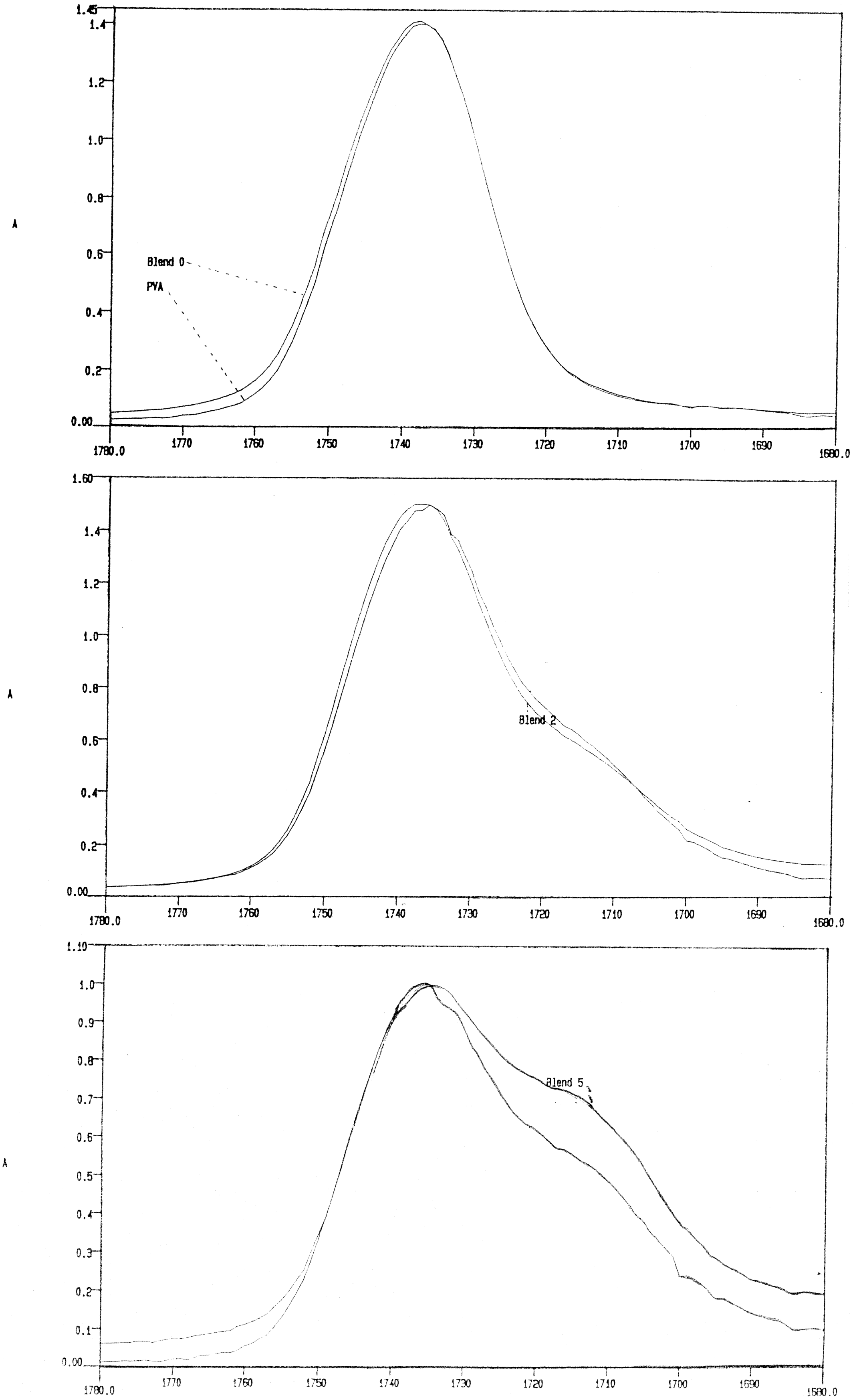


Fig. 6. FTi.r. spectra for blends 1–5 in the region 1180–1320 cm^{-1}. The spectra are displaced vertically for clarity.


A
1.45
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.00
Blend 0
PVA
1780.0
1770
1760
1750
1740
1730
1720
1710
1700
1690
1680.0
A
1.60
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.00
Blend 2
1780.0
1770
1760
1750
1740
1730
1720
1710
1700
1690
1680.0
A
1.10
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.00
Blend 5
1780.0
1770
1760
1750
1740
1730
1720
1710
1700
1690
1680.0
CM-1

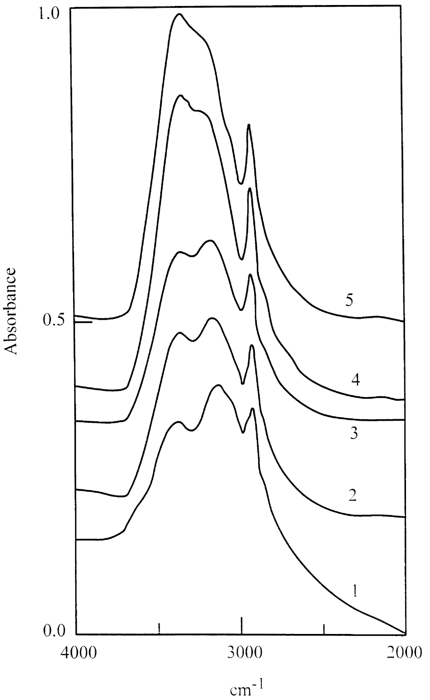


Fig. 8. FTi.r. spectra for blends 1 to 5 in the region 2000–4000 cm^{-1}. The spectra are displaced vertically for clarity.

compete with the intermolecular interactions and will hinder the formation of one-phase blends. The relative ratio of the intermolecular to intramolecular hydrogen-bonding sites will also alter with changing copolymer composition.

Four areas in the FTi.r. spectra are relevant to an examination for the presence of hydrogen bonding in the blend. These are: 1320–1180 cm^{-1}, 1680–1565 cm^{-1}, 1780–1700 cm^{-1} and 3700–2650 cm^{-1}, which correspond to the C–O stretch, an N–H deformation, the carbonyl stretch, and both N–H and O–H stretching frequencies, respectively.

3.4.1. Region 1: 1320–1180 cm^{-1}

In this region, absorptions caused by C–O stretching can be observed at 1000–1200 cm^{-1} but this can be affected by hydrogen bonding. All of the copolymer samples have a strong absorption at 1244 cm^{-1} which remains unchanged with an increase in the vinyl alcohol content, although the intensity also increases. It is likely that this is due to self-association of the hydroxyls through hydrogen bonding and with the carbonyl unit of the vinyl acetate moieties. The peaks are quite broad and there is slight suggestion of a shoulder around 1260 cm^{-1} which may be due to the non-bonded units. There is no significant absorption by PBI in this region.

The blends exhibit these absorptions more strongly. In blend 1 the major absorption peak is at 1244 cm^{-1} with a distinct shoulder at 1264 cm^{-1}. As we move through to blend 5 the absorption band broadens, but the balance of the two absorptions also changes, so that in blends 4 and 5 the peak at 1264 cm^{-1} is quite pronounced and the 1244 cm^{-1} absorption is now the lesser shoulder, see Fig. 6. This is attributed to hydrogen bonding of type 2 and type 3 (shown in the schematic diagram of Fig. 5) with the PBI. While one would normally expect the hydrogen-bonded species to show absorptions at a lower frequency than the non-associating groups, the resultant shift will depend on the relative magnitudes of the self-associating components and the interaction with the second component in the blend. It might be expected that the self-association in the copolymers would increase as the hydroxyl content is raised, but this is not the case in the blends, where there is a progressive decrease. This tends to support the suggestion that in blends 4 and 5, the hydrogen bonding (types 2 and 3) with PBI is sufficiently strong to compete with self-association in both blend components.

Table 3
The storage modulus, E', measured by d.m.t.a. for PBI and three blend samples

Material	Storage modulus, E' (GPa) at 290 K
PBI	2.00
Blend 1	1.80
Blend 2	2.80
Blend 5	6.08

3.4.2. Region 2: 1560–1680 cm^{-1}

There is no absorption in this region for the copolymer samples but PBI exhibits a peak at 1625 cm^{-1} that can be assigned to the N–H bonding deformation in an amine. The blended samples also show this absorption but a weak shoulder develops at 1610 cm^{-1} in blends 4 and 5 that can be attributed to hydrogen bonding between the components.

3.4.3. Region 3: 1700–1780 cm^{-1}

PBI shows virtually no absorption in the 2000–1650 cm^{-1} range, so the strong peak observed in the blends at 1735 cm^{-1} is the C=O stretch and represents the non-associated species, see Figs 7(a), (b) and (c). Prominant shoulders develop on these peaks at 1710 cm^{-1} for blends 4 and 5, which are missing in blends 1 to 3. This represents hydrogen bonding with the N–H group in PBI, although there could be some contribution from the self-associating $\rangle$C=O···H–O– interactions. The latter contribution should be small as this should reach a maximum in copolymer PV(Ac/OH)47 (blend 3) and there is no evidence of the 1710 cm^{-1} absorption shoulder in blend 3.

Fig. 7. FTi.r. spectra for blends 0, 2 and 5, in the region 1700–1780 cm^{-1}, with the spectra for the corresponding copolymer component in the blend for comparison.

3.4.4. Region 4: 2650–3700 cm^{-1}

Musto et al. [12,13] have reported that the region most sensitive to hydrogen bonding in the i.r. spectrum of PBI is 2500–3500 cm^{-1}. They have assigned the self-associating N–H interactions to the absorption peak at 3145 cm^{-1} and the non-interacting N–H groups to the 3415 cm^{-1} peak. Examination of the spectra in Fig. 8 illustrates the pronounced changes exhibited as we move through blends 1 to 5. Both absorption peaks are present but the relative ratio of A_{3145}/A_{3415} changes progressively through the blend series. The self-association peak (3145 cm^{-1}) decreases and shifts to 3220 cm^{-1} as the hydroxyl content of the PV(Ac/OH) samples increases, indicating a weakening of the self-association, to be replaced by hydrogen bonding of types 2 and 3. There is also a shift of the 3415 cm^{-1} non-bonded peak down to 3350 cm^{-1} in blends 4 and 5, with a concomitant increase in the intensity of the absorption peak. This again supports the idea of increased hydrogen bonding in the blends as the hydroxyl content increases from blend 1 to blend 5. This interpretation could be complicated by the presence of self-associating –OH groups, often seen around 3370 cm^{-1} in the spectrum [14], which would reinforce the peak at 3350 cm^{-1}.

3.5. Other criteria for miscibility

It is usually assumed that, in a binary blend, the presence of a single glass transition temperature is indicative of a miscible, one-phase blend. The T_g values for the two components in each blend are widely separated and the PV(Ac/OH) copolymers begin to degrade between 520 and 620 K, which is lower than the T_g for PBI of 683 K. Measurements of T_g for each blend with d.s.c. and d.m.t.a. showed no evidence of a single T_g that could be attributed to the blends. Glass transitions were observed by d.m.t.a. in blends 1 to 5 that were on average 10–30 K higher than those corresponding to the relevant PV(Ac/OH) component. This indicated that there was an element of mixing but not at the level one would expect for a one-phase system. The upper T_g in the blend could not be located, because the onset of degradation tended to mask the contribution from the PBI phase.

3.6. Blend moduli

The storage modulus, E', for PBI and blends 1, 2 and 5 was measured and compared at 290 K. The data are summarized in Table 3. It was observed that the modulus for blend 5 was significantly higher than that for PBI and blends 1 and 2. This would suggest that in blend 5, where the mixing of the two components was closest to a one-phase miscible system, there was a substantial reinforcing effect of the PV(Ac/OH) matrix, contributed by the presence of the PBI component. This produced a modulus in the blend that was greater than in PBI alone. These data can only be taken as a comparative guide to the behaviour. Because difficulty was experienced in attempting to measure the tensile modulus with an Instron machine, these are the best results that can be offered at present, and will not be analysed in greater detail.

4. Discussion

The experimental results obtained in this study suggest that, while miscible one-phase blends with mixing of the components at the molecular level are not achieved, some dispersion of the components in the blends does occur as the hydroxyl content of the PV(Ac/OH) increases beyond 50 mol%. Optically clear films were obtained from blends 4 and 5, implying a high level of dispersion of the components, as this cannot be due to a matching of the refractive indices for each component which are well separated by about 0.3 refractive index units.

Similarly, there is also evidence of increasing hydrogen bonding between the components as one moves through blends 1 to 5, which helps to promote greater dispersion of the components in blends 4 and 5. However, none of the blends exhibits a single T_g, either from d.s.c. or d.m.t.a. measurements, and so one must conclude that the dispersion in blends 4 and 5 cannot be at the molecular level and one cannot classify these systems as molecular composites. From these data and the SEM observations, it is reasonable to estimate that the domain sizes in blends 4 and 5 probably lie in the range $20\ nm < \text{domain size} < 500\ nm$. The lower limit is defined by the lack of a single T_g for the blends, whereas the upper limit is estimated from SEM measurements and the accepted premise that phase domains of approximately 500 nm and larger give the blend a white appearance [15].

It is interesting to note that while the solubility parameters of PBI and PV(Ac/OH) match when the vinyl alcohol content is around 47 mol%, this blend film is opaque, and optically clear films are only obtained when the vinyl alcohol content of the copolymer is higher. This is likely to be a consequence of the intermolecular hydrogen-bonding contribution increasing as the OH content rises. The absence of better mixing when the solubility parameters match is probably caused by the large difference in chain flexibility between the two components. This can only be overcome, in this case only partially, by an increase in secondary interactions such as hydrogen bonding in the blends, which assists and promotes mixing.

Finally, it is clear that while trying to mix rigid and flexible macromolecules to form homogeneous blends is an attractive prospect, the different thermal stabilities of the components can be problematic. The PV(Ac/OH) copolymers degrade at temperatures that are lower than the T_g of PBI, and so processing of these blends is restricted to solution- rather than melt-blending.

Nevertheless, the PBI does appear to have a reinforcing effect in blends 4 and 5. While miscible, one-phase blends are not obtained, the system studied does give some guidance as to how much of a difference in chain flexibility could be tolerated and overcome by the introduction of strong secondary bonding interactions, to produce either well-dispersed or one-phase blends.

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