

Miscibility and characterization of the ternary crystalline system: poly(vinyl butyral)/poly(vinyl alcohol)/nylon6

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Abstract

This contribution extends the study of the interaction of poly(vinyl butyral) (PVB), containing systematically varying hydroxyl levels, in a ternary crystalline blend system of poly(vinyl butyral)/poly(vinyl alcohol)(PVA)/nylon6(N6). Thermodynamic miscibility of the amorphous phases is indicated for blends of PVB/PVA/N6 in the range of approximately 0.4–0.6 volume fraction of vinyl alcohol (VA) in the blends in which two co-continuous crystalline phases are also present. The miscibility parameter model proved useful in examining potential regions of compatibility/miscibility and indicates that mainly dispersive–polar interactions are responsible for miscibility of the amorphous phases. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Miscibility; Polymer blends; Nylon

1. Introduction

Poly(vinyl butyral) (PVB) is commonly used to describe random copolymers that contain both hydrophilic (polar and hydrogen bonding) unreacted hydroxyl groups and hydrophobic or dispersive butyral groups. In our investigation of the interactions of PVB with itself and other polymers [1,2], the goal has been to obtain a broader understanding of general polymer miscibility, the factors that influence miscibility, and the assessment of models which can guide the estimation of polymer–polymer miscibility.

In a previous paper [1], we have studied the interactions and miscibility of the nylon6 (N6)/poly(vinyl butyral) (N6/PVB) system. PVB synthesized by controlled acetalization of a poly(vinyl alcohol) (PVA) backbone results in a random copolymer of vinyl butyral and unreacted vinyl alcohol (VA) units. The composition of the copolymer can be varied over a wide range and these copolymers can exhibit miscibility and/or compatibility with a variety of other systems.

Our previous work [1] showed that blends of N6 (crystalline) and PVB (amorphous) were miscible between $\cong 55$ wt% VA and $\cong 69$ wt% VA content in PVB. In the present work we consider a blend where the VA content of the PVB is less than that necessary to form a miscible blend. The question arises as to the effect of adding a third

component, PVA to the N6/PVB blend that then results in a ternary blend containing a total concentration of VA equivalent to that which yields miscibility in a binary blend. The additional VA is a component that is crystalline and has not been incorporated into the amorphous PVB copolymer.

This approach allows us to investigate regions of miscibility and to separate the influence of group interactions when the respective groups are contained in a separate polymer component in contrast to being integral to the chain of one of the blending components. We also note that the (N6)/PVB system [1] showed excellent physical properties in miscible blend preparations.

2. Experimental

2.1. Materials

Nylon 6 was purchased from Sp² Scientific Products, Inc. The relative viscosity of the N6 was 30 and the glass transition temperature and the melting point were 62 and 221°C, respectively. Poly(vinyl butyrals) of systematically varying VA contents were synthesized as described in our previous papers [1,2]. The analytical results for PVBs of different VA content are shown in Table 1. The analyses were performed by titration of liberated acid following acetylation. By acetic

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Table 1
Analytical results for PVBs

PVB sample no	Vinyl alcohol content of PVB			PVB T_g (°C)
	Wt%	Mol%	Volume fraction	
PVB14	14.2	34.8	0.12	71
PVB23	22.9	48.9	0.19	76
PVB28	28.0	55.7	0.24	–
PVB31	31.0	59.1	0.27	79
PVB36	36.4	64.8	0.32	–
PVB45	45.1	72.6	0.40	83
PVB55	55.0	79.8	0.50	85
PVB63	63.3	84.8	0.59	–
PVB70	69.5	88.0	0.65	88
PVB89	89.0	96.3	0.87	90

anhydride according to ASTM D-1396 for the determination of VA content of PVBs [3].

2.2. Preparation of PVB/N6 blends

Nylon6 and PVB components were dried at 50°C under reduced pressure for 24 h before blending. PVB/PVA/N6 blends were prepared by freeze milling the powder mixtures in liquid nitrogen with a Freezer Mill (SPEX Industries, INC.) These blends were then dried for 24 h under reduced pressure at 50°C. The PVBs used to prepare the melt blends with N6 had previously been shown to be immiscible with N6 at the VA content present.

The PVB/PVA/N6 melt blends were prepared by molding after melt mixing for 15 min at 220°C with a Mini-Max Molder (Atlas Electric Devices Co., CS-183 MMX). The rotation speed was 15 rpm. The nomenclature identifying the samples is such that the weight concentration of residual VA immediately follows “PVB.” Thus the sample PVB31 has a VA content of 31 wt%, the remainder being vinyl butyral.

2.3. Thermal analysis

The phase behavior of the melt blends was studied using differential scanning calorimetry (DSC: Perkin–Elmer 7) and dynamic mechanical thermal analysis (DMTA: Rheometric Scientific IV). The scanning rate of DSC is 20 or 5°C/min. and the measurement of DMTA was conducted at a scanning rate of 2°C/min and a frequency of 10 Hz. The PVB/PVA/N6 weight ratio samples used for measurement by DSC were annealed at 240°C for 10 min or 30 min and quenched in liquid nitrogen. All DMTA specimens were annealed at 200°C for 1 h, quenched in liquid nitrogen, and dried under reduced pressure for 24 h at 50°C.

2.4. Scanning electron microscopy

The phase structure for PVB/PVA/N6 and PVB14, 23, 45 and 55 blends was investigated by means of a scanning electron microscope (SEM: JEOL LTD., JSM-35CF). For

the SEM observation, the PVB/PVA/N6 blends were immersed in liquid nitrogen, fractured at room temperature, and etched with methanol for 20 h, methanol being a non-solvent for N6 and PVA. The fracture surfaces of the PVB/PVA/N6 blends, after etching was coated with gold for the SEM observation.

2.5. Physical property measurement

All PVB/PVA/N6 specimens were prepared for tensile property measurements by molding at 240°C for 10 min using a Mini-Max Molder. The blends were cooled to room temperature and dried under reduced pressure for 48 h at 50°C. The testing was done using flat dumbbell-shaped samples on an Instron 4468 machine at room temperature following the procedure described in ASTM D-638. The static load cell was 50 kN and the cross-head speed was 3.0 mm/min. Five test specimens were used for each blend and the values averaged.

2.6. Estimation of miscibility/compatibility window from the miscibility parameter model

A model used to estimate potential areas of compatibility/miscibility is based on solubility parameters (δ) but utilizes the individual components that make up the total solubility parameter assess possible windows of compatibility/miscibility. For each repeat unit of a polymer in a blend of two or more polymers, we have:

$$(\delta_x^{\text{poly}})^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (1)$$

where $\delta_x = \text{SP}$ for each polymer repeat unit. Weight fractions of repeat units (w_s) are multiplied by their respective individual SP contributions. Then for component A:

$$\delta_A^{\text{poly}} = \delta_1^{\text{poly}} w_1 + \delta_2^{\text{poly}} w_2 \quad (2)$$

and for the second polymer blend component:

$$\delta_B^{\text{poly}} = \delta_3^{\text{poly}} w_3 + \delta_4^{\text{poly}} w_4 \quad (3)$$

and in general:

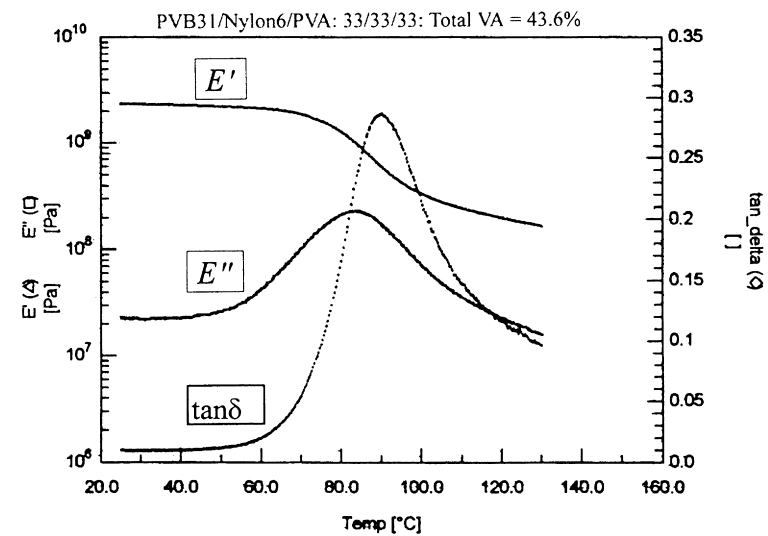
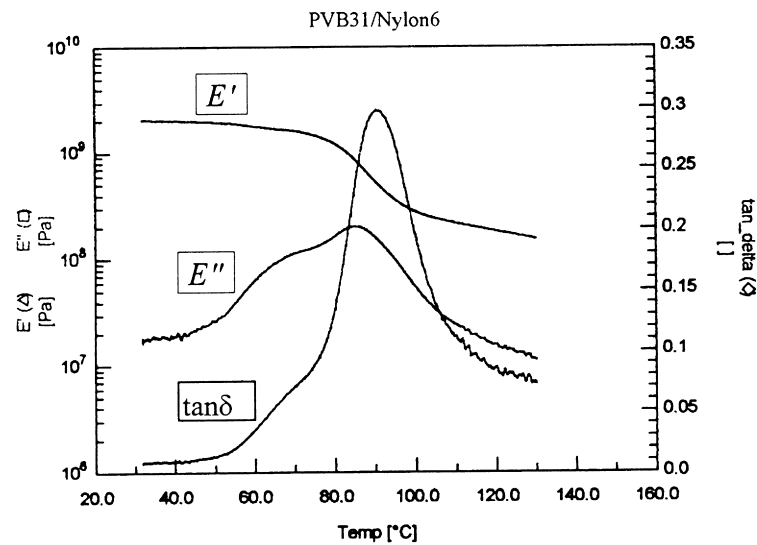
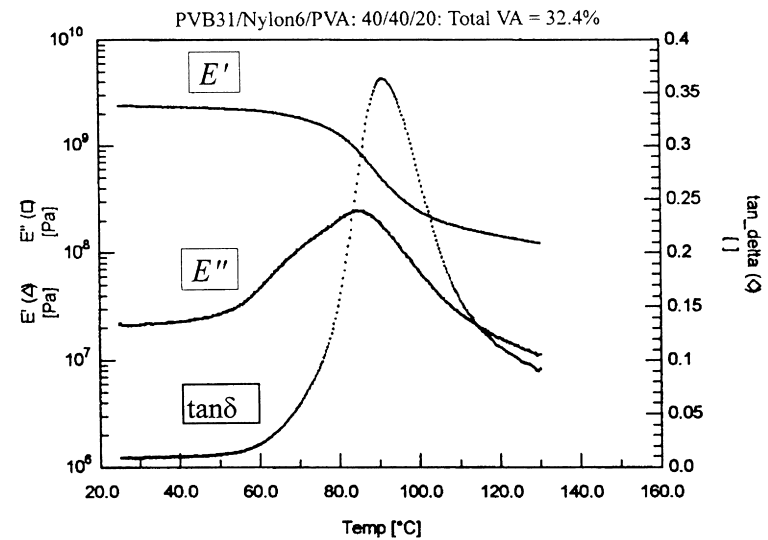
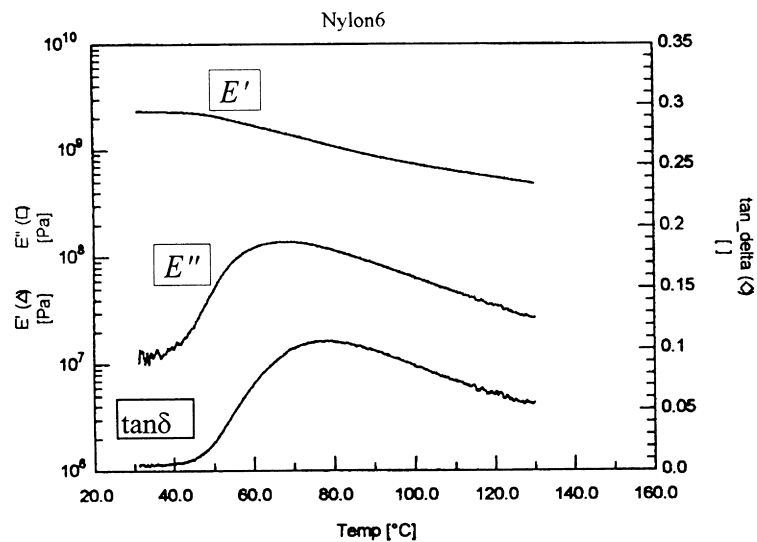
$$\delta_i^{\text{poly}} = \delta_1^{\text{poly}} w_1 + \delta_2^{\text{poly}} w_2 + \delta_3^{\text{poly}} w_3 + \dots + \delta_i^{\text{poly}} w_i \quad (4)$$

The miscibility parameter is given by:

$$\text{MP} = (\delta_A^{\text{poly}} - \delta_B^{\text{poly}})^2 \quad (5)$$

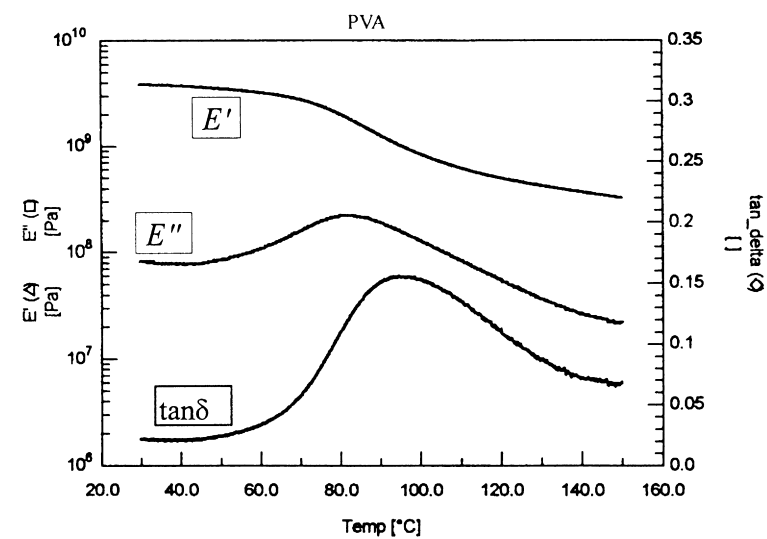
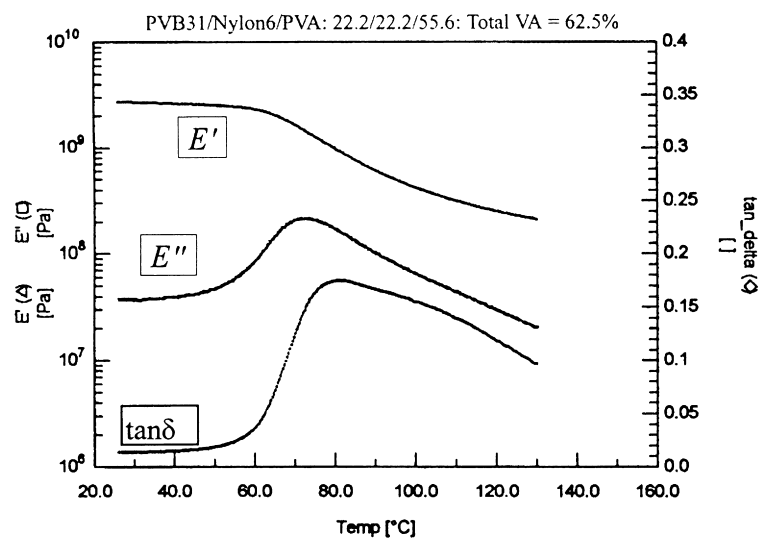
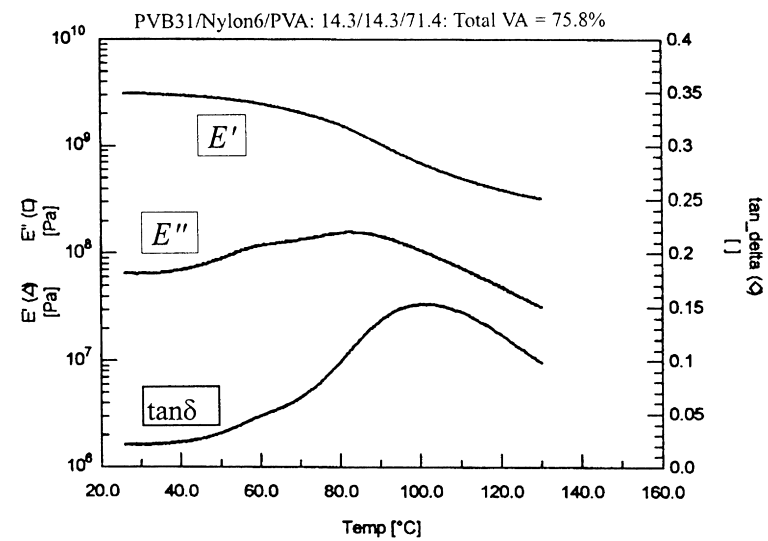
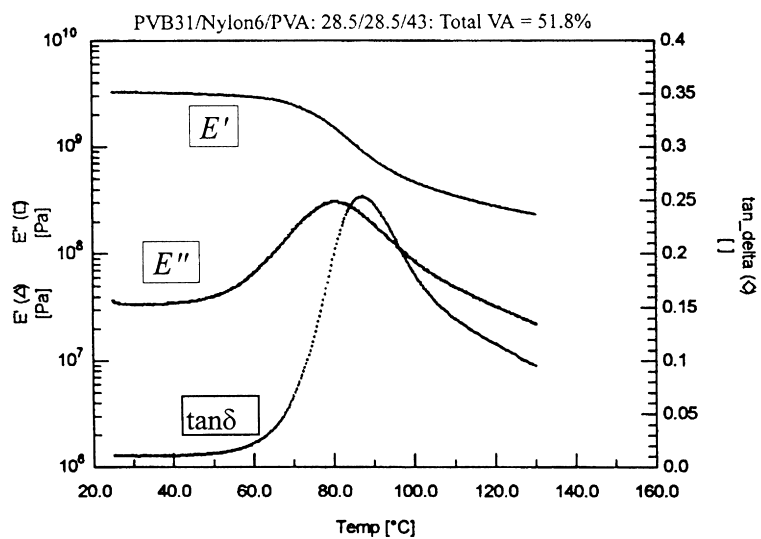
where MP represents appropriate combinations of the dispersive (d), polar (p), and hydrogen bonding (h), components of the solubility parameter [4,5] such that for any polymer blend system the four possible MPs are: MP_{dph} , MP_{dp} , MP_{ph} , and MP_{dh} .

It can be seen from the above equations, that this approach is not limited to a two component polymer blend system since one of the components constituting polymer A or polymer B may consist of multiple components, although this is not the usual case.



Series (a)

Fig. 1. Representative dynamic mechanical analysis (DMTA) curves illustrating the effects of composition on blend miscibility as indicated by moduli and $\tan \delta$ responses: (a) Nylon6 = polyamide; PVB31/nylon6 = 50:50 blend of 31 wt% VA in PVB with nylon6; PVB31/nylon6/PVA = 40:40:20 blend of 31 wt% VA in PVB with 40 wt% nylon6, 20 wt% PVA: total VA = 32.4%; PVB31/nylon6/PVA = 33:33:33 blend of 31 wt% VA in PVB with 33 wt% nylon6, 33 wt% PVA: total VA = 43.6%; (b) PVB31/nylon6/PVA = 28.5:28.5:43 blend of 31 wt% VA in PVB with 28.5 wt% nylon6, 43 wt% PVA: total VA = 51.8%; PVB31/nylon6/PVA = 22.2:22.2:55.6 blend of 31 wt% VA in PVB with 22.2 wt% nylon6, 55.6 wt% PVA: total VA = 62.5%; PVB31/nylon6/PVA = 14.3:14.3:71.4 blend of 31 wt% VA in PVB with 14.3 wt% nylon6, 71.4 wt% PVA: total VA = 75.85%; PVA = vinyl alcohol.



Series (b)

Fig. 1. (continued)

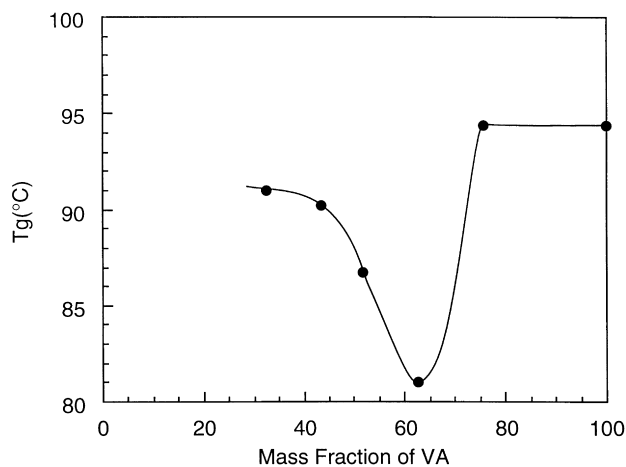


Fig. 2. T_g of PVA in the PVB31/PVA/nylon6 blends measured by DMTA.

3. Results and discussion

3.1. PVB/PVA/N6 blend systems

Miscibility in a ternary blend consisting of a random copolymer and two homogeneous crystalline polymers would not be expected to show the properties of a binary blend of the random copolymer and the crystalline homopolymer (e.g. PVB and N6; see Ref. [1]). In the previous study, DMTA results for PVB/N6 blends showed that blends containing PVB with $\cong 45$ wt% VA is immiscible, blends with $\cong 55$ –70 wt% VA in PVB are miscible, while a blend containing $\cong 89$ wt% VA is immiscible. These results were reinforced from DSC, SEM, melting and crystallization behavior, and physical properties, and yield the estimated blend lower limit of miscibility to be about 55 wt% VA in PVB while the upper limit of miscibility is about 70 wt% VA in PVB. Thus blends of PVB/N6 exhibit thermodynamic miscibility in the ranges of approximately 0.5–0.65 volume fraction of VA in PVB. The polymer

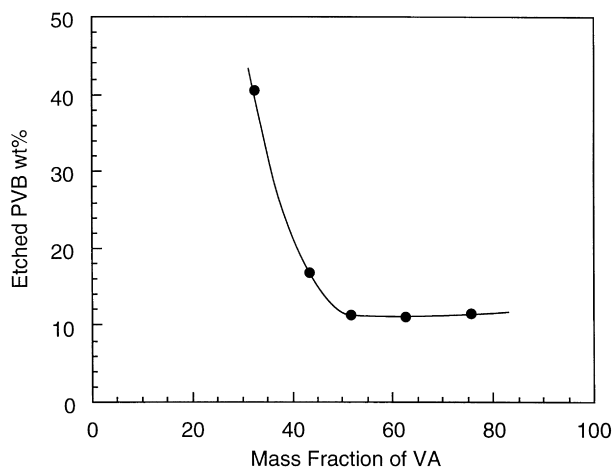


Fig. 3. Weight loss of PVB31/nylon6 blend films ~ 100 μm thick after etching with methanol.

interaction parameters, $\chi_{N6/VA}$ and $\chi_{N6/VB}$ were estimated using the PVB/N6 lower and upper miscibility limits and found to be ~ -0.04 and 0.04 , respectively. These values are consistent with a previous report on compatibility of N6 and PVA [6] in which a favorable interaction between the nylon and PVA was demonstrated but miscibility was absent. This was ascribed to energetic interactions between the VA and polyamide groups indicated by the almost neutral interaction parameter, $\chi_{N6/VA}$.

In the ternary blend studied here, the third component is added at a concentration that matches the structural group composition of the random copolymer in the binary blend of the crystalline/amorphous species. Important aspects of the effects of crystal structure and crystallite size impose severe restrictions on the third component since it has to be miscible with the other two as well as the latter with each other for the ternary blend components to be thermodynamically miscible. This would seem to place large enthalpic, entropic, volume and crystallite restrictions on such a system.

In these studies the storage and loss moduli are represented in their usual form by E' and E'' respectively, and $\tan \delta$ is the ratio of E''/E' . Fig. 1 shows the temperature dependence of E' and E'' , and $\tan \delta$ at 10 Hz for several ternary blend compositions. The relaxation corresponding to the glass transition consists of a single peak in both $\tan \delta$ and E'' is seen only for blends with overall VA contents of 44 and 52 wt%. All other blend compositions exhibit two relaxation peaks in the glass transition region. The temperature of the relaxation peak corresponding to the T_g of the PVA phase decreases rather rapidly in the composition range from about 40 to 60 wt% VA content (Fig. 2). While these results by themselves do not prove the existence of a single miscible amorphous phase in this composition region, they at least indicate considerable interaction between blend constituents. Below 40 wt% and above 60 wt% VA content, there is very little composition dependence observable for the PVA T_g . Above 60–65 wt% VA content, the PVA phase has a T_g indistinguishable from pure PVA.

Weight loss studies of 100 μm thick films of the blends showed a gradually decreasing weight loss by extraction with methanol to a constant lower VA concentration range of miscibility was reached, after which there was a slight increase in the PVB extracted as the limit of the upper VA concentration range of miscibility was reached as shown in Fig. 3. The effects on T_g and the weight loss results are consistent with the DMTA results. When the blends were etched with methanol, it was not possible to extract the PVB constituents to any significant degree above a VA content of 40 wt%.

Taken together, these results suggest a miscibility window for the amorphous phase of the ternary blends in the composition range of 40–60 wt% VA. This window therefore occurs at somewhat lower VA contents than is the case for the binary blends of PVB/N6.

Even if a single amorphous phase exists for some blend

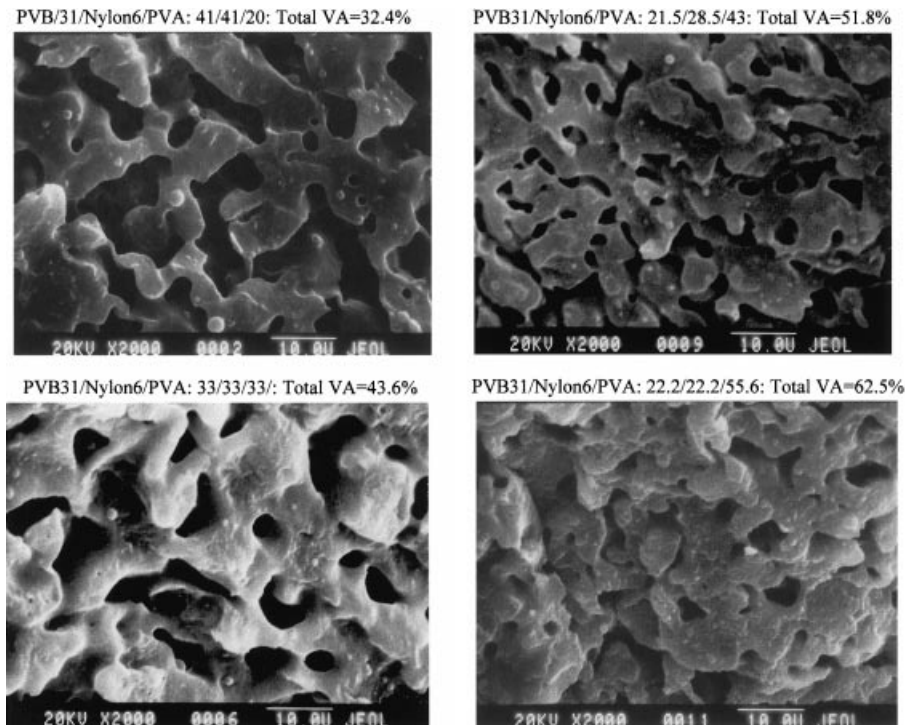


Fig. 4. SEM micrographs illustrating the morphology of poly(vinyl butyral)/poly(vinyl alcohol)/nylon6 blends at compositions from immiscibility to miscibility of the amorphous phases. All specimens were fractured after cooling in liquid nitrogen using DMTA samples. Fractured surfaces were etched with methanol.

compositions, we would expect that co-crystallization of N6 and PVA would be unlikely in as much as the crystal structure of PVA and N6 are different [7,8]. Fig. 4 shows methanol-etched SEM results for ternary blends of overall VA content between 32 and 63 wt%. The morphologies all appear to be quite similar and appear to consist of two co-continuous phases. The lighter phase contains raised nodules and is believed to be crystalline N6 [1]. These SEM observations do not show a separate PVA crystalline phase.

Studies of the melting behavior as a function of annealing time reinforce the above results and show a strong interaction between components in the VA concentration range found to exhibit miscibility of the amorphous phases. A plateau region is observed through the VA concentration range of amorphous phase miscibility and crystalline

phase compatibility (See Fig. 5c) after sufficient annealing. Further lowering of the T_m of N6 occurs at the higher concentrations of PVA (71%) in N6/PVB, which is consistent with previous reports of PVA and N6 compatibility [7]. Although the trends are clear, these interpretations are somewhat compromised by the broadness of the melting peaks.

Crystallization behavior parallels what would be expected based upon the melting results in Fig. 5. Fig. 6 shows that for the mass fraction of total VA where the amorphous phases of the blend exhibit miscibility, i.e. ~ 40 wt% VA to ~ 62 wt% VA the crystallization temperatures of the two crystalline phases (PVA and N6) are the same. Outside this VA concentration range separate curves are followed.

Table 2

Results of physical property measurement of blends of PVB/N6, PVB/PVA/N6, and PVA/N6

	Nylon6	PVB31/N6 50:50	PVB31/PVA/N6 28.5:28.5:43: Total VA = 51.8%	PVA/N6 50:50	PVA
TS, maximum (MPa)	80.6 \pm 5.2	86.4 \pm 3.7	101.4 \pm 4.7	85.1 \pm 5.1	109.1 \pm 5.5
TS, yield (MPa)	62.2 \pm 5.2	74.2 \pm 3.7	–	–	95.7 \pm 5.5
TS, break (MPa)	63.2 \pm 5.2	74.2 \pm 3.7	101.4 \pm 4.7	85.1 \pm 5.1	95.7 \pm 5.5
Elongation, yield (%)	14.7 \pm 2.2	13.2 \pm 1.5	–	–	4.2 \pm 2.3
Elongation, break (%)	33.7 \pm 2.2	80.2 \pm 1.5	6.7 \pm 2.2	3.9 \pm 1.5	7.5 \pm 2.3
Modulus (MPa)	2633 \pm 25	2633 \pm 20	3473 \pm 20	2545 \pm 25	5261 \pm 25

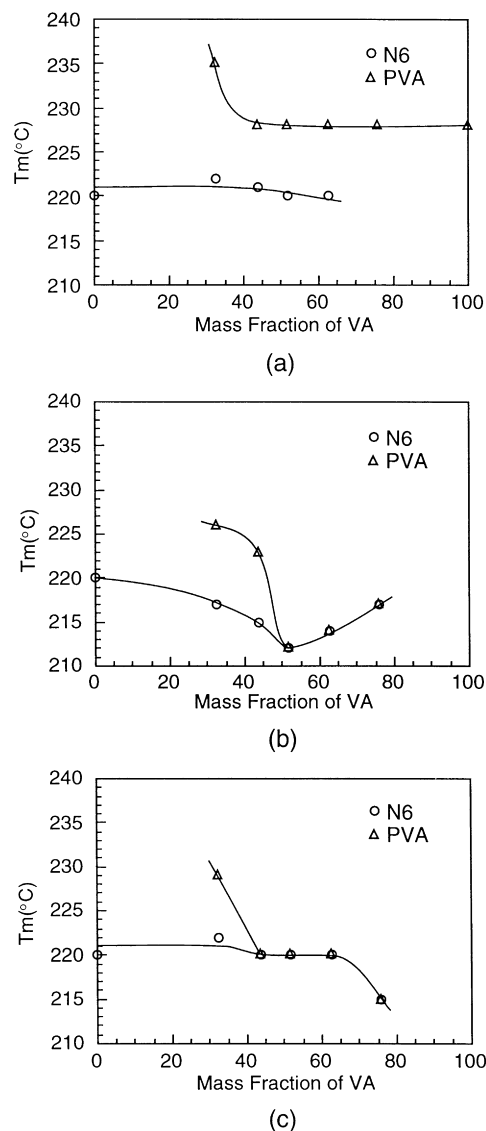


Fig. 5. Melting point of N6 and PVA in the PVB31/PVA/nylon6 blends: (a) non-annealing; (b) annealing at 240°C for 10 min; and (c) annealing at 240°C for 30 min.

The results of the physical property measurements are shown in Table 2. N6 and PVA are also included for completion and to allow valid comparisons at each end of the property map.

The maximum tensile strength physical property results show that in the immiscible PVB/N6 blend (PVB31/N6), N6 dominates the physical properties while in the PVB/N6/PVA blend, PVA dominates the physical properties. At roughly the same total VA content in a PVB blend of PVB/N6, the tensile strength and % elongation at break of the PVB/N6/PVA blend are comparable to that of PVA while the modulus is closer to a weighted average of the components. These results are consistent with the morphologies observed and show that the addition of PVA as a separate component yields a brittle polymer blend, probably

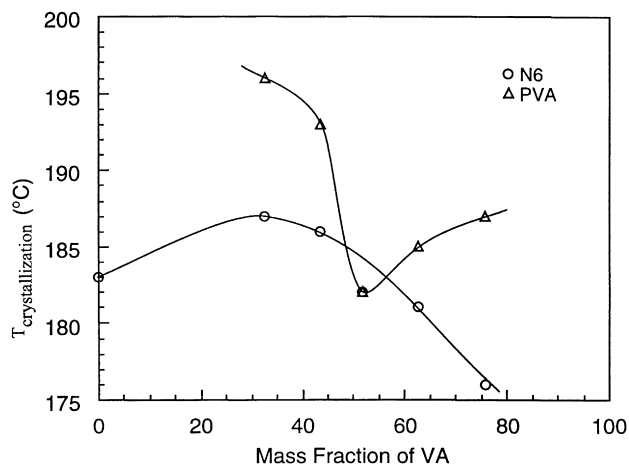


Fig. 6. Crystallization point of nylon6 and PVA in the PVB31/PVA/nylon6 blends annealed at 240°C for 10 min.

due to immiscibility of the crystalline phases, even though the amorphous phases are miscible.

In the previous work [1], we observed strong dispersive–polar interactions as indicated by the miscibility parameter (MP) model [5,6]. In the present work, we also used the dispersive–polar MP (MP_{dp}) to estimate potential regions of compatibility and/or miscibility. The range of total VA in the PVB31/PVA/N6 blend at the level of VA in PVB31 that showed compatibility/miscibility was approximately in the range of 43–62 wt% VA.

The regions of compatibility/miscibility estimated closely match those found—especially for the dispersive–polar component (upper limit ~57% total PVA) as Fig. 7 illustrates. Thus the MP model is a useful guide in selecting composition regions that may prove fruitful to examine but does not allow estimation of the effects of various blend ratios and the types of molecular interactions largely responsible for favorable reactions leading to compatibility/miscibility.

4. Summary

Blends of PVB/PVA/N6 exhibit thermodynamic miscibility in the amorphous phases in the ranges of approximately 0.4–0.6 volume fraction of VA in PVB/PVA/N6 as evidenced from DMTA. The SEM results show the existence of two phases consistent with the physical property data. The MP model results also compared favorably with the miscibility window determined. The MP model proved useful in examining regions where compatibility/miscibility might be expected and the estimated region of compatibility/miscibility agrees with the experimental results.

Acknowledgements

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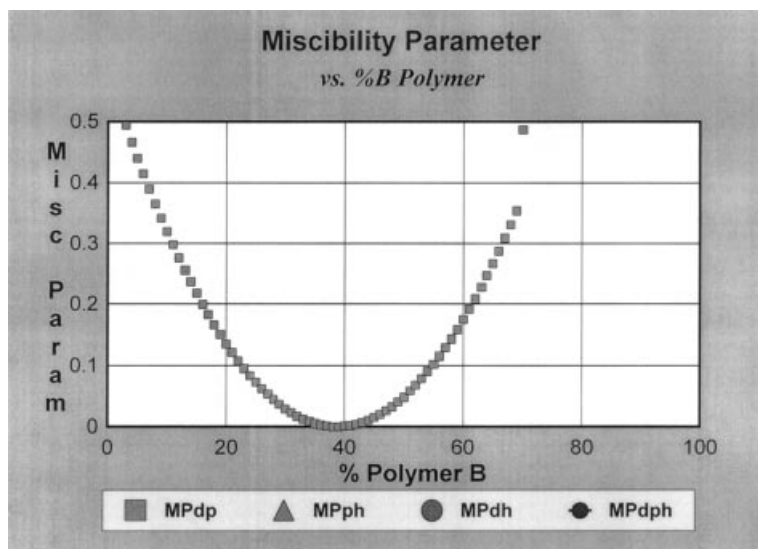


Fig. 7. Results of the miscibility parameter model showing potential windows of computability/miscibility. % Polymer B = wt% poly(vinyl alcohol) in poly(vinyl butyral) + added poly(vinyl alcohol).

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