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Miscibility and morphology of blends of poly(3-hydroxybutyrate) and poly(vinyl butyral)

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Abstract

The miscibility and morphology of blends of biodegradable poly(3-hydroxybutyrate) (PHB) and poly(vinyl butyral) (PVB) were studied by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). PHB is a semi-crystalline polymer while PVB can be regarded as a random copolymer containing vinyl butyral (VB) and vinyl alcohol (VA) units whose composition ratio can be systematically changed over a wide range. DSC measurements show two T_gs in the amorphous phase for all PVB and PHB blends, indicating phase immiscibility. However, partial miscibility was observed in 50/50 w/w blends containing PVBs with 25–36 wt% VA content, demonstrated by the inward shift of the T_gs of the two phases relative to those of the neat components. This shift exhibits a maximum value around 31 wt% of VA in PVB. The segmental interaction parameters $\chi_{\mathrm{VA,HB}}$, $\chi_{\mathrm{VB,HB}}$ and $\chi_{\mathrm{VA,VB}}$ were determined and the copolymer composition dependence of the overall interaction parameter between PVB and PHB, χ_{12}, was then calculated. This parameter shows a minimum around 31 wt% VA content, consistent with the experimental data. The presence of a minimum can be interpreted in terms of a copolymer effect in which the unfavorable interaction between PVB and PHB is minimized at a certain copolymer compositions due to the repulsive intramacromolecular interaction between VA and VB units within the PVB chains. The composition manifesting minimum immiscibility was also consistent with the melting temperature (T_m) depression and a minimum in the fractional crystallinity of the PHB phase in the blends around this VA content. A co-continuous morphology was observed in the blends containing 25–33 wt% VA content PVBs, which might well result from more favorable interactions between the two component polymers at this copolymer composition. © 2001 Published by Elsevier Science Ltd.

Keywords: Poly(3-hydroxybutyrate); Poly(vinyl butyral); Polymer blends

1. Introduction

Poly(3-hydroxybutyrate) (PHB) is a crystalline biodegradable thermoplastic polymer [1], Fig. 1. PHB can in principle be used in many applications, however, since PHB is highly crystalline and forms large spherulites and also has a relatively high glass transition temperature in comparison with polypropylene, polyethylene, etc., the material itself is regarded as unacceptably brittle. Furthermore, PHB suffers from an economic disadvantage and limited processing temperatures. These drawbacks have restricted the widespread application of PHB. Efforts to upgrade the properties by blending with other polymers [2–15], or by copolymerizing [16] have been reported.

Poly(vinyl butyral) (PVB) has been used extensively in laminated safety glass and surface treatments. The polymer is synthesized by reacting poly(vinyl alcohol) (PVA) with butyraldehyde in an acid medium [17]. Although the product of this reaction is generally termed 'poly(vinyl butyral)', this name is ambiguous since substantial amounts of unreacted vinyl alcohol (VA) groups are permitted to remain in the macromolecular chain. Hence it is more useful to consider PVB as a random copolymer of vinyl butyral and unreacted VA units, Fig. 1. The ratio of these two widely different types of units, i.e. VA (polar and hydrophilic) and vinyl butyral (hydrophobic) can be controlled over a wide range. Modifying PHB by blending with PVB can be expected to improve the economics and enhance the mechanical properties of the former.

The thermodynamic effect of using random copolymer as one or both constituents in polymer blends has been investigated extensively [18–23]. A major result is that a copolymer may form a miscible blend with a given homopolymer (or second copolymer) within a certain copolymer composition and temperature range, provided that there is a strong unfavorable intra-chain interaction between the comonomer units in the copolymer, notwithstanding the

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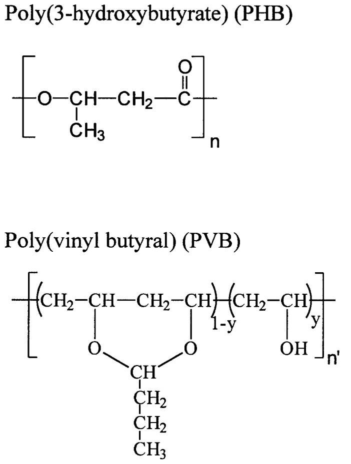

Poly(3-hydroxybutyrate) (PHB)

Poly(vinyl butyral) (PVB)

Fig. 1. Structures of PHB and PVB.

fact that all three segmental interactions in such a system may be positive (unfavorable). This behavior gives rise to the so-called miscibility window [18,19], which appears when the phase state is plotted, for a given blend composition, as a function of copolymer composition and temperature. The qualitative explanation for this phenomenon is that mixing the copolymer with a second homopolymer reduces the number of unfavorable non-bonded contacts between the two types of segments in the copolymer. This concept has been widely used to explore miscible copolymer/homopolymer or copolymer/copolymer blends in which there are no attractive interactions. Miscibility windows have been reported for many such blends, e.g. poly(styrene-*co*-acrylonitrile) (SAN) with poly(methyl methacrylate) (PMMA) [24–26]. There is also the implication that in a nominally immiscible, phase separated blend, unfavorable interaction between the two constituents one or both of which is a copolymer can be minimized by tailoring the copolymer composition(s); an example is the case of the blend of bisphenol A polycarbonate (PC) and SAN [27]. In this system, thermodynamic miscibility is not achieved; however, the optimum performance of such a blend is attained at the random copolymer composition providing the least unfavorable interaction. This therefore provides a general method of compatibilization by finding the appropriate copolymer composition at which this minimization occurs. Here compatibility is defined as the state of aggregation at which the synergistic improvement of properties resulting from the blending of polymers is optimized. This concept of compatibilization, without the aid of a third compatibilizing component, has been widely applied in polymer blends [28].

In the present study, blends of PVB and PHB using PVBs having a systematic variation in VA content were prepared by melt-blending; the miscibility and the morphology of the resulting blends were investigated by using differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). It was found that the blends of PHB with all the PVBs studied are always phase-separated. However, as predicted above, interactions within the PVB/PHB blends depend on the VA content of PVB component, and some indication of a tendency towards miscibility were observed in certain blends; for example, the optimum blend of PVB and PHB in terms of T_g displacement from the pure components was seen in blends containing PVBs having 25–36 wt% VA content. A co-continuous morphology was also observed in 50/50 w/w blends at this optimum copolymer composition.

2. Experimental

2.1. Materials

PVBs with several VA contents were synthesized from the acetalization reaction of a 'mother' PVA with butyraldehyde as described previously [29]. PVA (Aldrich Chemical) had weight average degree of polymerization (DP) of 2×10^3 and contained 1 wt% of residual vinyl acetate. PHB with weight average molecular weight (M_w) of 3.0×10^5 (Aldrich) was used as received. Codes and the relevant characterization data for samples used in this study

Table 1
Characterization of samples used in this study

Samples	VA content (wt%)	VA content (volume fraction)	DP[a] ($\times 10^3$)	T_g (°C)
PVB16	16.5	0.138	2.0	64.4
PVB18	18.2	0.152	2.0	67.0
PVB22	21.6	0.182	2.0	68.2
PVB25	24.8	0.211	2.0	68.6
PVB31	30.9	0.266	2.0	71.6
PVB33	32.9	0.284	2.0	72.8
PVB36	36.4	0.316	2.0	75.7
PVB46	45.6	0.404	2.0	77.7
PVB55	55.0	0.497	2.0	82.1
PHB	–	–	3.5	0.6

[a] Weight averages DP for PVBs were obtained from its mother PVA.

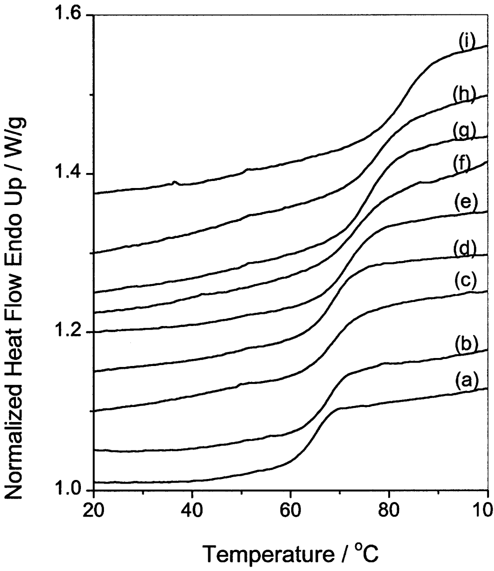

Fig. 2. DSC curves for nine PVBs with systematic variation of VA content: (a) PVB16; (b) PVB18; (c) PVB22; (d) PVB25; (e) PVB31; (f) PVB33; (g) PVB36; (h) PVB46; (i) PVB55.

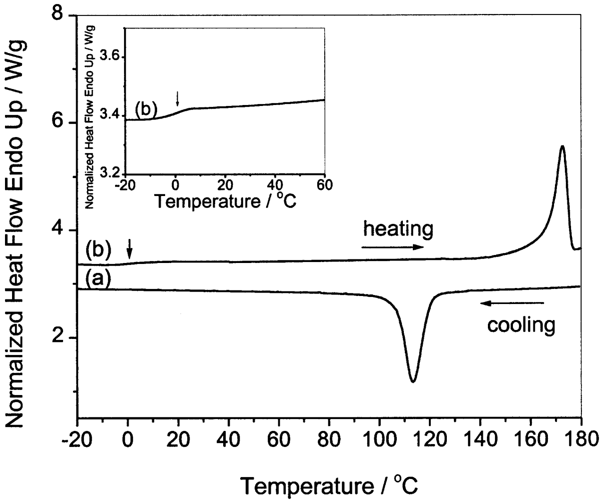

Fig. 3. DSC curves for pure PHB as function of thermal treatment. Curve (a): cooling from 180°C at −10°C/min; Curve (b): heating at 10°C/min. The inset plot is an enlargement of the heating curve in the range −20 to 60°C displaying the PHB glass transition.

are presented in Table 1. The numbers immediately followed 'PVB' denote the weight percent of VA content in the sample.

2.2. Blend preparation

The 50/50 w/w PVB/PHB blend samples were prepared by molding after melt-blending at 190°C for 6 min with a Mini-Max Molder (Atlas Electric Devices, CS-183 MMX). The rotation speed was 80 rpm. The samples prepared from melt blending were cooled to room temperature by retaining the sample in the mold, and the samples were then dried in vacuo for 24 h.

2.3. Characterization

DSC analysis was conducted using a Perkin–Elmer DSC-7 calibrated with indium and mercury. Samples were first heated to 180°C rapidly under a nitrogen atmosphere and annealed for 5 min to remove any previous thermal history of the material. Samples were then rapidly cooled down to −50°C and scanned to 180°C at a heating rate of 10°C/min (first scan). Samples were then held again for 5 min at 180°C and cooled down to −50°C at a rate of −10°C/min (second scan) to study nonisothermal crystallization. Finally, the samples were rescanned to 180°C at a heating rate of 10°C/min (third scan) to characterize melting behavior. Glass transition temperatures (T_gs) were taken as the mid-point transition of the heat capacity step change during the first scan; the crystallization temperature T_c on cooling and melting temperature T_m were taken as those of the main exo- and endo-thermal peaks in the second and third scan, respectively.

A JEOL JSM-35CF scanning electron microscope (SEM) was used to study the morphology of blend samples. Samples for SEM observation were prepared by fracturing immediately after they had been immersed in liquid nitrogen for 5 min followed by surface etching with 60°C chloroform for 1 min, causing the removal of the PHB phase. Surface images were recorded at a voltage of 10 keV.

3. Results and discussion

3.1. DSC studies of the component polymers

Fig. 2 shows the DSC curves of the PVB polymers having a range of VA contents from 16 to 55 wt%. The T_g of PVBs is shifted monotonically to higher temperature with increase of VA content (Table 1). No evidence of melting was observed up to 240°C; all the PVBs used in this study are amorphous.

Fig. 3 shows DSC scans of PHB during cooling and heating. The cooling crystalline exotherm appears at 113.5°C; melting is at 173°C. The inset shows an enlarged DSC curve in the temperature range of −20 to 60°C during heating, in which the glass transition of the PHB amorphous phase can be seen at 0.6°C. The T_g and melting temperature T_m observed here are similar to the values reported in the literature [14,15]. The crystallinity of PHB sample crystallized during nonisothermal cooling crystallization is 55%, obtained according to the usual equation:

$$X_c = \frac{\Delta H}{\Delta H^0} \tag{1}$$

where ΔH is the observed enthalpy of melting of the sample and ΔH^0 (151 J/g; Ref. [7]) is the enthalpy of melting for the 100% crystallized component.

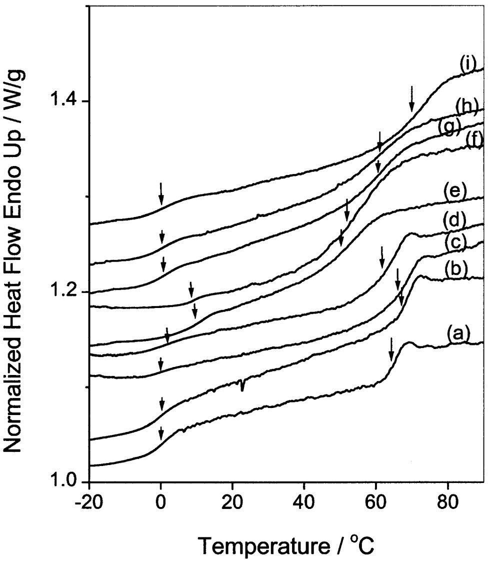

Fig. 4. T_gs of 50/50 w/w PVB/PHB blends for: (a) PVB16; (b) PVB18; (c) PVB22; (d) PVB25; (e) PVB31; (f) PVB33; (g) PVB36; (h) PVB46; (i) PVB55.

3.2. The glass transition of the blends

Fig. 4 shows the DSC curves near the glass transitions during the first scan for 50/50 w/w blends of PHB with nine PVBs of systematically varying VA content. For all blends, two glass transitions were observed, indicating that these mixtures of PVB/PHB are phase separated in the amorphous phase. Nevertheless, the T_gs of the PVB-rich and the PHB-rich amorphous phases in the blends are dependent on the VA content of the PVB used. The T_gs for the PVB-rich and PHB-rich phases are shown (Fig. 5) as a function of VA content of PVB, together with the T_gs of the pure PVBs for comparison. The T_gs of the pure PVBs are dependent on VA content and increase linearly. In contrast, the T_gs of PVBs in blends do not increase linearly with VA content, and moreover, deviate negatively from those of the neat PVBs except for the blends containing PVBs containing between 16 and 22 wt% VA. The minimum of the T_gs of the PVBs in the blends occurs in the 25–36 wt% range of VA content. In parallel, the T_gs of the PHB-rich phases in the blends were shifted upwards relative to that of the neat component for the blends of PVBs containing 25–36 wt% VA. This is typical behavior of what is often referred to as a partially miscible system. For blends containing PVBs with VA contents larger than 36 wt%, the T_gs of the PHB-rich phase are virtually identical to that of the neat component, while the T_gs of the PVB-rich phase remain somewhat lower than that of neat PVB. This asymmetric behavior indicates that the PHB-rich phase is nearly pure while PHB is solubilized to some extent in the PVB phase in systems employing PVB containing more than 36 wt% VA.

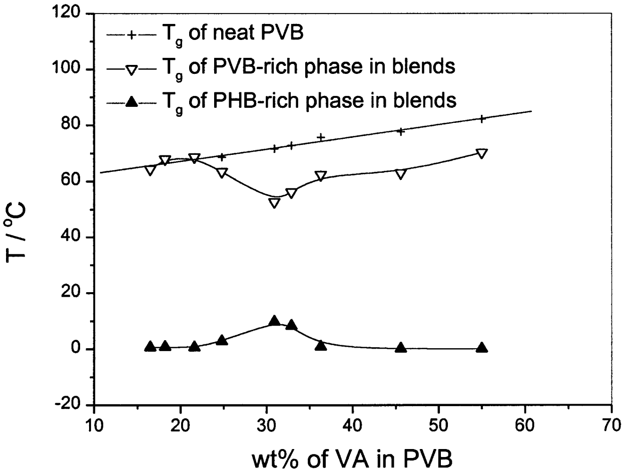

Fig. 5. T_gs of 50/50 w/w PVB/PHB blends as function of VA content of PVB. The T_gs for the neat PVBs are shown for comparison.

The compositions of the two coexisting phases in the blends can be estimated from the Fox equation, i.e.

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \tag{2}$$

where T_{g1} and T_{g2} represent the glass transition temperatures of the neat component polymers PHB and PVB, and W_1 and W_2 are the weight fractions of the PHB and PVB components in the coexisting phases, respectively, T_g is the glass transition temperature of the coexisting phase. Table 2 shows the calculated compositions for blends of 50/50 w/w PVB31/PHB and PVB33/PHB.

These results permit us to estimate the interaction parameter χ_{12} from the usual expression of the type

$$\Delta\mu_1 = RT\left(\ln\phi_1 + \left(1 - \frac{V_1}{V_2}\right)\phi_2 + \frac{V_1}{V_r}\chi_{12}\phi_2^2\right) \tag{3}$$

and equating chemical potentials in the two coexisting phases [30,31], where R is the universal gas constant, T the absolute temperature, V_r the molar volume of each interacting segment, $\Delta\mu_i$, ϕ_i and V_i the chemical potential, volume fraction and molar volume of component i, respectively, and χ_{12} the overall Flory–Huggins interaction parameter between component polymer 1 and polymer 2.

From the calculated overall interaction parameter χ_{12} for two blends containing two different VA content PVB copolymers (Table 2), the three binary segmental interaction parameters describing interactions between all the segments present in the blends were calculated, using [18,19]:

$$\chi_{12} = y\chi_{\mathrm{VA,HB}} + (1-y)\chi_{\mathrm{VB,HB}} - y(1-y)\chi_{\mathrm{VA,VB}} \tag{4}$$

where y denotes the volume fraction of VA monomer in the copolymer, $\chi_{\mathrm{VA,HB}}$, $\chi_{\mathrm{VB,HB}}$ and $\chi_{\mathrm{VA,VB}}$ are the respective segmental interaction parameters between VA and VB units of PVB copolymer and HB, the repeating unit of PHB. The values $\chi_{\mathrm{VA,HB}} = 0.039$ and $\chi_{\mathrm{VB,HB}} = 0.0058$ were then obtained by using $\chi_{\mathrm{VA,VB}} = 0.07$ at 180°C obtained from a previous study [32]. It is noted that

Table 2
T_gs and compositions of PHB-rich and PVB-rich phases and the interaction parameters χ_{12}s for 50/50 w/w PVB31/PHB and PVB33/PHB blends

Blends	T_g of PHB-rich phase (°C)	T_g of PVB-rich phase (°C)	Composition of PHB-rich phase		Composition of PVB-rich phase		χ_{12} ($\times 10^{-4}$)
			W_1	W_2	W_1	W_2	
PVB31/PHB	9.7	52.7	0.844	0.156	0.224	0.776	9.54
PVB33/PHB	8.3	56.2	0.869	0.131	0.191	0.809	9.92

$\chi_{\mathrm{VA,HB}}$ is larger than $\chi_{\mathrm{VB,HB}}$, which suggests that favorable interactions such as hydrogen bonding between the VA and HB groups cannot play an important role in the present system. This can well be attributed to the fact that self-association between VA groups in PVB itself is much stronger than the interaction between the VA and HB groups.

By using the calculated values for the three segmental interaction parameters, χ_{12} at 180°C as a function of VA content of PVB was calculated from Eq. (4) (Fig. 6). The critical interaction parameter χ_{cri} for the PVB/PHB blends given by [30,31]

$$\chi_{\mathrm{cri}} = \frac{1}{2}\left(\frac{1}{\sqrt{n}} + \frac{1}{\sqrt{n'}}\right)^2 \tag{5}$$

where n and n' are the weight average degrees of polymerization (DP) of the two polymers is also shown in Fig. 6. The parameter χ_{12} displays a minimum at about 27 vol% (equivalent to 31 wt%) VA content in PVBs, indicating the point of minimum immiscibility. Clearly the fact that the χ_{12} is minimized at this copolymer composition is a result primarily of a relatively large repulsive interaction between VA and VB units in the PVB chain and it may also be noted that this cannot occur if a solubility parameter approach is used. Fig. 6 also shows that χ_{12} is positive for all compositions and substantially exceeds χ_{cri} for the PVB/PHB blends, confirming that complete miscibility cannot be attained for blends of any PVB with PHB without substantially reducing the molecular weight in one or both components.

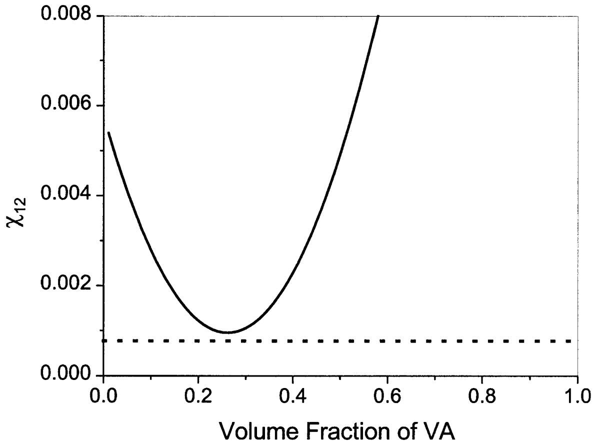

Fig. 6. Overall interaction parameter χ_{12} for PVB and PHB (180°C) as a function of VA content of PVB. Dotted line indicates χ_{cri} for PVB/PHB blends used.

3.3. Melting in the blends

Fig. 7 shows DSC curves (third scan) in the melting temperature range for the 50/50 w/w PVB/PHB blends. The endotherms represent the melting of the PHB crystalline phase in the blends formed during the cooling process. The presence of a second PVB phase did not have obvious influence on the melting behavior for blends of PVB16/PHB and PVB18/PHB. However, both the temperature and area of the melting peak are dependent on the VA content of PVB for blends having higher VA contents. The melting peak temperature, T_m, and the crystallinity of PHB in the blends, X_c, Eq. (1), are shown in Fig. 8 as a function of the VA content of the PVB. The T_m of the PHB in the blends decreases with increase of VA content of PVB up to 33 wt% and remained at a lower level, compared to the neat component value, for blends having PVBs of VA content greater than 33 wt%. The crystallinity of PHB in the blends exhibits a minimum for blends containing PVBs around 33 wt% VA content.

A depression of the melting temperature has been usually observed in miscible polymer blends, arising from the

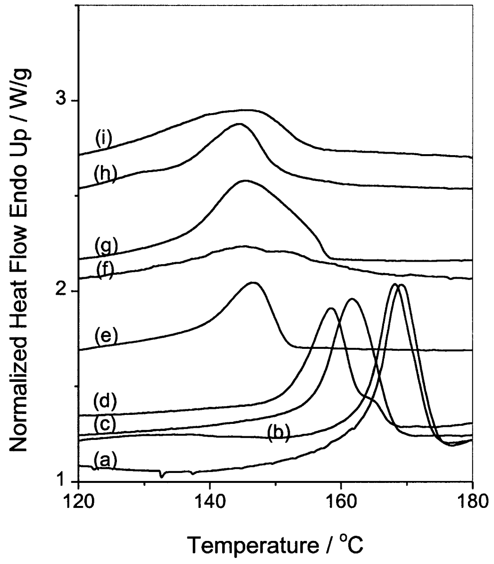

Fig. 7. Melting behavior of 50/50 w/w PVB/PHB blends for nine PVBs: (a) PVB16; (b) PVB18; (c) PVB22; (d) PVB25; (e) PVB31; (f) PVB33; (g) PVB36; (h) PVB46; (i) PVB55.

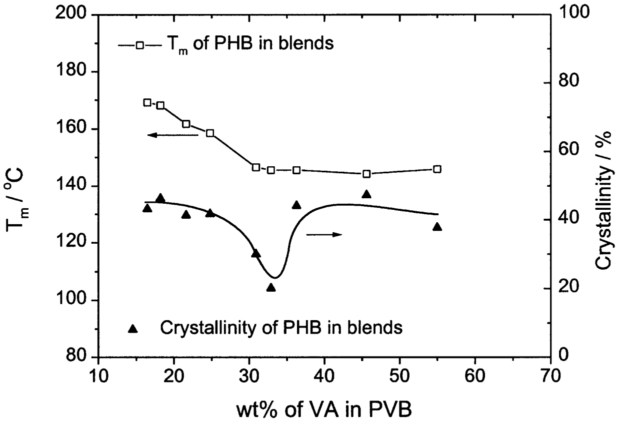

Fig. 8. Melting temperatures (T_ms) and fractional crystallinities (X_cs) of PHB in 50/50 w/w PVB/PHB blends as a function of VA content of PVB.

reduction in chemical potential in the presence of the second polymer [30,33]. For an immiscible blend exhibiting some phase mixing, the presence of a second partially solubilized polymer will also depress the melting temperature. The melting temperature of PHB decreases with the VA content up to 33 wt%, indicating the increase of solvating effect of PVB on PHB, which in turn reflects the lower immiscibility of PVB and PHB in this VA content regime in comparison with the lower VA content PVB blends. It is noted that the melting temperature of PHB in blends containing PVBs with VA contents larger than 36 wt% is also depressed, which reflects a decrease of crystallite size and imperfection in the crystallites, as the higher VA content PVBs having higher T_gs may restrict the growth of PHB crystals and result in less perfect crystallites.

The PHB crystallinity in the blends exhibits a minimum for blends containing PVBs around 33 wt% VA content and is accounted for by assuming that the PHB solubilized in the PVB amorphous regions does not crystallize. The result that the minimum crystallinity of PHB in the blends appears in the range of 25–36 wt% VA content is thus consistent with all the evidence cited above regarding the minimum PVB and PHB immiscibility in the blends of PVB with this range of VA content.

3.4. Blend morphology

Fig. 9 shows SEM micrographs for several 50/50 w/w PVB/PHB blends containing PVBs with a range of VA contents. It was found that the characteristic morphology depends on the VA content of the PVB component, even for constant 50/50 w/w blend compositions and identical thermal histories. The SEM micrographs illustrate that the PHB phase was dispersed (before etching) in discrete domains within the PVB matrix in the PVB/PHB blends containing PVBs of 16–22 wt% VA content; that a co-continuous morphology was formed for blends containing PVBs of 25–33 wt% VA content, while the PHB phase forms the continuous phase for those blends containing PVBs with VA content larger than 33 wt%.

It is important in practice to establish the range of copolymer composition where the co-continuous morphologies can be formed, and where either one of the component is dispersed as discrete particles and which component forms the continuous phase, since the mechanical properties and biodegradability of the blends depend on the morphologies. In principle, which component in a binary blend assumes the continuous or the dispersed phase can generally be predicted from the knowledge of viscosity and volume fraction of the components in the blend. The larger fractional volume phase and component with the lower viscosity tend to be more continuous in space. This concept was formulated quantitatively (Paul and Barlow [34] and Jordhamo et al. [35]):

$$\frac{\phi_1}{\phi_2} \times \frac{\eta_2}{\eta_1} = C \tag{6}$$

where if

$C > 1$, phase 1 continuous;
$C \approx 1$, co-continuous of two phases;
$C < 1$, phase 2 continuous.

In Eq. (6), ϕ represents the volume fraction and η is the melt viscosity of phase 1 or phase 2, according to subscript. In this study, the viscosity ratio can be approximated by the torque ratio when using a twin-screw microcompounder (DACA). The data show that the torque of neat PVB changes from 5.8 to 7.6 N m with increase of VA content, and the torque of PHB is around 1.2 N m under standardized condition. Hence, it is to be expected that the PVB phase will tend to form the dispersed phase in 50/50 w/w blends, which was in fact observed in the blends containing PVBs with the higher VA contents. A co-continuous morphology is expected to be formed when the melt viscosities of the two phases are close to each other in blends with 50/50 composition. The formation of a co-continuous morphology for the blends of PVB25/PHB, PVB31/PHB and PVB33/PHB implies that the viscosity ratios of two phases for these blends are close to each other, which results from the partial miscibility between the two components as was demonstrated above. The reason that the PHB phase appears to be the dispersed phase for blends containing PVBs having lower VA content is not clear, but is likely to be related to the segregation of a crystalline PHB phase from the mixture that is formed during the cooling process.

4. Conclusion

The miscibility and morphology for blends of PVB with varying VA content and PHB have been studied. The PVB and PHB blends are immiscible regardless of the VA content of the PVB. However, an inward shift of the T_gs

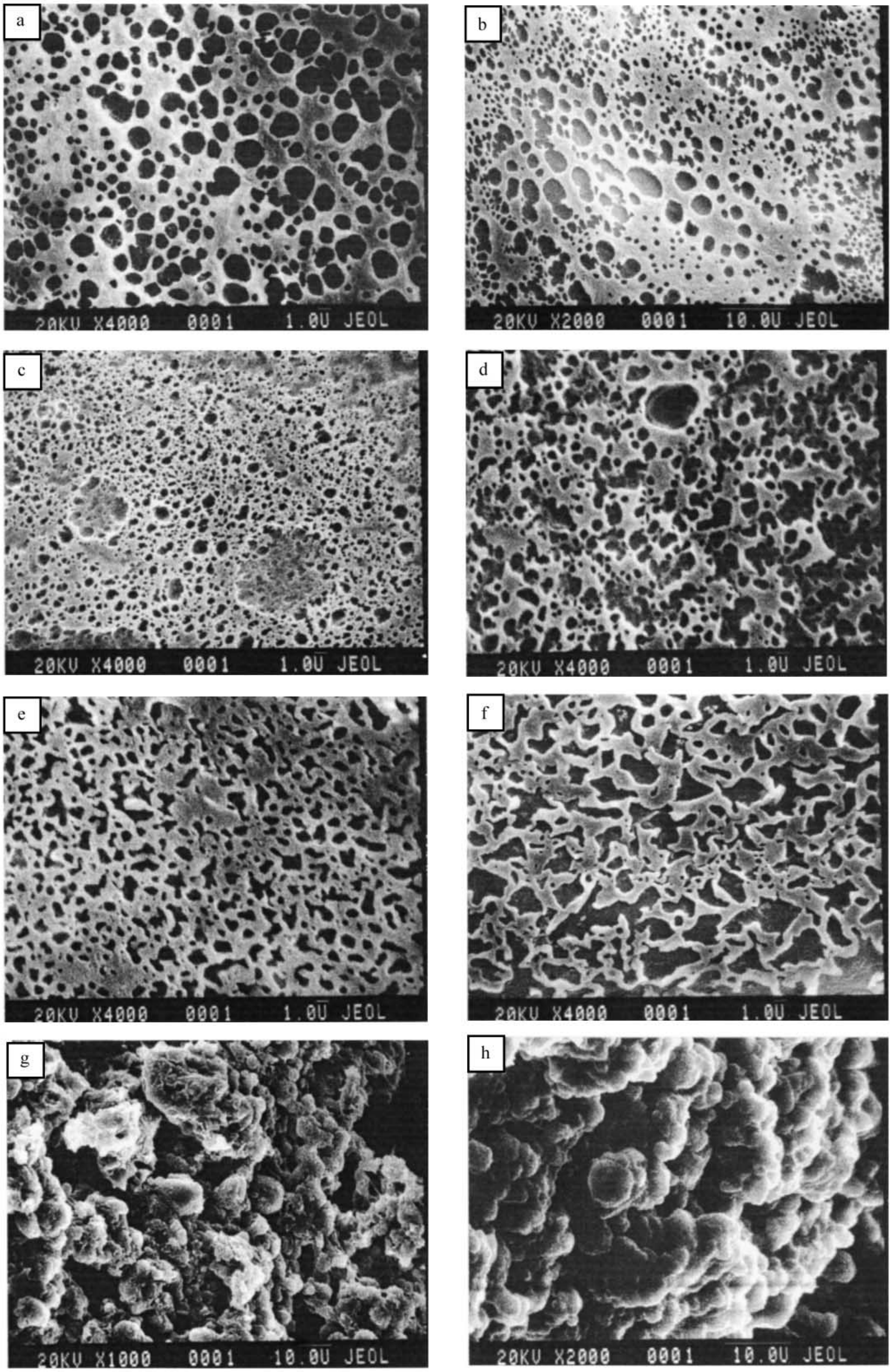

Fig. 9. SEM micrographs for 50/50 w/w PVB/PHB blends for PVBs with a range of VA contents: (a) PVB16; (b) PVB18; (c) PVB22; (d) PVB25; (e) PVB31; (f) PVB33; (g) PVB36; (h) PVB46.

of the two phases was seen for blends containing PVBs with 25–33 wt% VA contents, implying partial miscibility. The actual solubilities within the coexisting phases were estimated from the measured T_gs, and the overall interaction parameters between PVB and PHB, χ_{12}s, were calculated for blends of PVB31/PHB and PVB33/PHB in which some mutual miscibility occurs. From the χ_{12} values, binary segmental interaction parameters between the three units, i.e. $\chi_{\mathrm{VA,HB}}$, $\chi_{\mathrm{VB,HB}}$ and $\chi_{\mathrm{VA,VB}}$, were determined. The copolymer composition dependence of χ_{12} was then calculated for the range of PVB copolymer composition, and shows a concavity with a minimum around 31 wt% VA content. This result indicates that the minimum unfavorable interaction between PVB and PHB, which produces the maximum mutual solubilization is achieved in this range of VA content, and primarily arises from the relatively large repulsive interaction between the VA and VB units in the PVB copolymers. The same optimum miscibility was also observed in the melting behavior of the blends, demonstrated by a minimum crystallinity of the PHB phase in the blends having PVBs in this range of VA content and a depression of T_m. A co-continuous morphology was observed for the blends containing PVBs having 25–33 wt% VA content, which also results from the optimum miscibility between the component polymers.

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