Miscibility of Ternary Amorphous Nylon/Poly(methyl methacrylate)/Poly(4-vinylphenol) Blends

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ABSTRACT: The miscibility of ternary blends consisting of amorphous nylon (Am-Nylon)/poly(methyl methacrylate) (PMMA)/poly(4-vinylphenol) (PVPh) at 190°C was investigated by differential scanning calorimetry (DSC), thermo-photometry, Fourier transform infrared spectroscopy (FT-IR), and scanning electron microscopy (SEM). In the ternary blends, more than 70–90 wt% PVPh was required to cause miscibility between Am-Nylon and PMMA, and the experimental ternary diagram indicating symmetrically miscible regions was obtained. FT-IR results showed this miscibility was attributed to intermolecular hydrogen bonding interactions. Using stoichiometric equations, the equilibrium constant ($K_c = 3.2$) describing hydrogen bonding between the OH group of PVPh and amide group of Am-Nylon was determined from quantitative FT-IR analysis. The miscible region was affected by individual equilibrium constants (K_i), since individual binary interaction parameters (χ_{ij}) were significantly larger than the critical value of χ_{ij} . The miscibility of Am-Nylon/PMMA blends was enhanced by adding 20 wt% PVPh to binary immiscible polymer. The size of the dispersed PMMA phase was thus smaller than in the absence of PVPh. This suggests that PVPh acts as a compatibilizer for immiscible Am-Nylon / PMMA blends.

KEY WORDS Miscibility / Ternary Blends / Phase Diagram / Hydrogen Bonds / Compatibilizer /

Recently, due to the industrial importance of multi-component blends, the miscibility and morphology of ternary blends have been investigated.^{1–7} By ternary blends one could obtain more polymer composites than binary blends, having high ability and faculty. However, it is clear that the complexity of calculating phase diagrams, problems of experimental accuracy and interpretation of results of ternary blends increase dramatically over that of analogous binary blends.

The phase behavior of ternary polymer blends involving strong specific interactions (hydrogen bonding), has only been studied by Coleman, Pomposo, and others.^{8–11} A binary association model which was suggested by Coleman *et al.*, and has been extended to ternary hydrogen bonding polymer mixtures. This model was based on the suggestion to separate favorite ‘chemical’ specific interactions from unfavorable ‘physical’ ones.^{12–17} The free energy of mixing ΔG_m of ternary systems can be expressed in eq 1 by adding free energy (ΔG_m^{FH}) of mixing based on the Flory–Huggins theory (2) and free energy (ΔG_m^H) of association formation as eq 3:

$$\frac{\Delta G_m}{RT} = \frac{\Delta G_m^H}{RT} + \frac{\Delta G_m^{FH}}{RT} \quad (1)$$

$$\frac{\Delta G_m^{FH}}{RT} = \frac{\phi_A}{rN_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B + \frac{\phi_C}{qN_C} \ln \phi_C + \phi_A \phi_B \chi_{AB} + \phi_B \phi_C \chi_{BC} + \phi_A \phi_C \chi_{AC} \quad (2)$$

where ϕ_A , ϕ_B , and ϕ_C are the volume fractions of Polymer A, Polymer B, and Polymer C in the blend, respectively, which have polymerization, N_i .

The parameters $r = V_A/V_B$ and $q = V_C/V_B$ are the ratios

of the segment molar volumes of Polymer A to Polymer B and Polymer C to Polymer B, respectively.

$$\begin{aligned} \frac{\Delta G_m^H}{RT} = & \left[\phi_B \ln \left(\frac{\phi_{B1}}{\phi_{B1}^0} \right) + \frac{\phi_A}{r} \ln \phi_{A1} + \frac{\phi_C}{q} \ln \phi_{C1} \right. \\ & + \phi_B \left[\left(\frac{\Gamma_1^0}{\Gamma_2^0} \right) - \left(\frac{\Gamma_1}{\Gamma_2} \right) \right] + \phi_B \left(\frac{\Gamma_1}{\Gamma_2} \right) \left(\frac{X+Y}{1+X+Y} \right) \\ & \left. - \left[\frac{\phi_B}{n_H^0} \ln \phi_B + \frac{\phi_A}{r} \ln \phi_A + \frac{\phi_C}{q} \ln \phi_C \right] \right] \quad (3) \\ \Gamma_1 = & \left(1 - \frac{K_2}{K_B} \right) + \left(\frac{K_2}{K_B} \right) \left[\frac{1}{1 - K_B \phi_{B1}} \right] \\ \Gamma_2 = & \left(1 - \frac{K_2}{K_B} \right) + \left(\frac{K_2}{K_B} \right) \left[\frac{1}{(1 - K_B \phi_{B1})^2} \right] \\ n_H^0 = & \Gamma_2^0 / \Gamma_1^0 \end{aligned}$$

where ϕ_{A1} , ϕ_{B1} , and ϕ_{C1} are the corresponding volume fractions of isolated (non-hydrogen-bonded) Polymer A, Polymer B, and Polymer C segments, K_2 and K_B are self-association equilibrium constants of formation of Polymer B dimers and multimers, K_A and K_C are inter-association equilibrium constants describing specific interactions of Polymer A/Polymer B and Polymer B/Polymer C, $X = K_A \phi_{A1}/r$ and $Y = K_C \phi_{C1}/q$ and the superscript 0 denotes the pure material.

In this case, the phase behavior of polymer blends that involves strong specific interactions is a sensitive function of the magnitude of the individual χ_{ij} and K_i . This phase behavior is greatly influenced by K_i .^{9–10}

In this work, the miscibility of ternary amorphous nylon (Am-Nylon)/poly(methyl methacrylate) (PMMA)/poly(4-vinyl phenol)(PVPh) blends predicted the existence of strong specific interaction, investigated by DSC, thermo-photometry, FT-IR, and SEM. The factor that

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Table I. Polymers in this work

Polymer	$10^{-4} \times M_w$	$10^{-4} \times M_n$	$\bar{M}_w/\bar{M}_n$	$T_g/^\circ\text{C}$
PMMA	7.00	3.90	1.80	100
PVPh	2.22	0.41	5.41	164
Am-Nylon ^a	4.70	1.20	3.92	124

^a

1,3-/1,4-Phenyl substitution is approximately 2/1
(provided by Du pont).

dominates this ternary phase behavior was studied. PVPh was miscible with PMMA, and PMMA was immiscible with Nylon. If PVPh is miscible with Am-Nylon, PVPh should act as 'compatibilizer' for immiscible Am-Nylon/PMMA blends. It seemed interesting to find a new compatibilizer, because of the industrial importance of overcoming property deficiencies of immiscible blends.

EXPERIMENTAL

The polymers used in this study and some characteristics are summarized in Table I.

Am-Nylon/PMMA/PVPh blends were prepared by solution mixing. PVPh and Am-Nylon were dissolved in dimethyl sulfoxide (DMSO) at 2 wt% polymer concentration. PMMA was dissolved in tetrahydrofuran (THF) at 2 wt% polymer concentration. After reprecipitation in refined water, the polymer mixture was filtrated and collected. The polymer mixture was dried for 6 days at room temperature, and then for 6 days at 110°C and finally for 1 day at $T_g + 20^\circ\text{C}$ in vacuum oven.

The glass transition temperature (T_g) data were obtained by Du Pont 910-Differential scanning calorimeter (DSC) or Seiko I&E DSC10 equipped with SSC/580 thermal controller. Blend samples were annealed for 1 h at desired temperatures in vacuum oven and then quenched in liquid N_2 before measurement. All samples were measured at $10^\circ\text{C min}^{-1}$ under N_2 purging.

Transmittance data were obtained by a hand-made thermophotometer equipped with He-Ne laser. The heating rate was at 2°C min^{-1} .

The samples for infrared analysis were included in KBr, and of sufficient concentration to be within the absorbance range where the Beer-Lambert law is valid. Infrared spectra were obtained by JASCO FT-IR 550 and FT-IR-8000 equipped with Mettler heat controller. All samples were held at 190°C for 1 h under N_2 purging. Representative infrared spectra were recorded by averaging 124 scans at a resolution of 4 cm^{-1} .

Samples for scanning electron microscopy were prepared with pressing blend mixtures in melt, and then parted and coated with gold on fracture surfaces. Morphology was observed using a JOEL JSM-5200 scanning microscope operated at 10 kV.

RESULTS AND DISCUSSION

First, we estimated the miscibility of three binary blends of this ternary systems.

Figure 1. Composition dependence of T_g for PVPh/PMMA blends at 190°C : Continuous line is the Fox prediction and broken line is the Gordon-Taylor prediction ($k=0.834$).

Am-Nylon/PMMA Blends

Nylon is immiscible with PMMA, but miscibility of polymer blends is often affected by differences in chemical structures and molecular weight. We estimated the miscibility of Am-Nylon/PMMA blends used in this work.

DSC analysis of Am-Nylon/PMMA blends showed the presence of two glass transitions (T_g) nearly independent of blend composition. By thermo-photometry, we determined the miscibility of Am-Nylon/PMMA blends. At all compositional ranges, transmittance of blend films was very low. Thus, Am-Nylon/PMMA blends may be immiscible.

PVPh/PMMA Blends

The miscibility of PVPh/PMMA blends was previously studied by Coleman, Pomposo, and others. They observed the miscibility in all compositional ranges, and showed this system was miscible as a result of intermolecular hydrogen-bonding interactions.¹⁸⁻²⁰

T_g of PVPh/PMMA blends as a function of composition are shown in Figure 1. This system gave a single T_g in all compositional ranges and had T_g between T_g of PVPh and that of PMMA. Experimental T_g were in good agreement with a curve calculated from the Gordon-Taylor equation. In all compositional ranges, transmittance of blend films was very clear. These results suggest complete miscibility of PVPh/PMMA blends, in agreement with Coleman *et al.*¹⁸⁻²⁰

Representative infrared spectra recorded at 190°C in the carbonyl stretching region for PVPh/PMMA blends are shown in Figure 2. As PMMA did not self-associate, only "free" carbonyl groups attributed to 1734 cm^{-1} were seen. The addition of PVPh fraction shifted the absorption of "free" carbonyl group to hydrogen bonded carbonyl group attributed to 1716 cm^{-1} . We confirmed this was a hydrogen bond between PVPh and PMMA.

PVPh/Am-Nylon Blends

Representative thermograms for a series of PVPh/Am-Nylon blends are shown in Figure 3. In all blends, single T_g s were observed as evidence for the presence of a single phase. The endothermic peak attributed to the melting point, was observed at 200°C in PVPh/Am-Nylon (10/90) blends and Am-Nylon, even though the nylon used in this work was amorphous. It seemed that crystals of nylon were formed by annealing at 190°C . In the blend ratio of PVPh/Am-Nylon (90/10),

Figure 2. FT-IR spectra of PMMA and 70/30, 90/10 wt% PVPh/PMMA blends recorded at 190°C in the carbonyl stretching region.

Figure 3. DSC thermograms for PVPh/Am-Nylon blends annealed at 190°C.

70/30, 50/50, and 30/70), peaks attributed to crystal were not observed. The reason for crystallization of nylon was prevented by intermolecular specific interactions (hydrogen bond) between PVPh and Am-Nylon. T_g of PVPh/Am-Nylon blends as a function of composition are shown in Figure 4. Specific interactions between PVPh and Am-Nylon were predicted by this system, because experimental T_g s were larger than T_g s calculated from

Figure 4. Composition dependence of T_g for PVPh/Am-Nylon blends at 190°C: Continuous line is Fox prediction and broken line, Gordon-Taylor prediction ($k=0.533$).

Figure 5. FT-IR spectra of Am-Nylon and 50/50, 70/30 wt% PVPh/Am-Nylon blends recorded at 190°C in the carbonyl stretching region.

the additivity rule. Using FT-IR, we observed intermolecular specific interactions. Representative infrared spectra recorded at 190°C in the carbonyl stretching region of amide for Am-Nylon are shown in Figure 5. Since Am-Nylon was self-associated, “free” carbonyl groups and hydrogen bonded carbonyl groups attributed to approximately 1666.2 cm^{-1} and 1646 cm^{-1} , were observed. The addition of PVPh fraction shifted the “free” carbonyl group to hydrogen bonded carbonyl group. This confirmed hydrogen bonds between PVPh and Am-Nylon.

DSC and FT-IR measurements showed PVPh/Am-Nylon blends to be miscible. This miscibility was attributed to intermolecular hydrogen bonding interactions.

Figure 6. T_g of ternary PVPh/Am-Nylon/PMMA blends as a function of PVPh composition for mixture having Am-Nylon/PMMA ratio 9/1, 7/3, 5/5, 3/7, and 1/9.

Figure 7. Determination of optical clarity of ternary blend samples.

Ternary Am-Nylon/PMMA/PVPh Blends

T_g s were measured for a variety of compositions of ternary Am-Nylon/PMMA/PVPh blends containing Am-Nylon/PMMA blends of 9/1, 7/3, 5/5, 3/7, and 1/9 ratio. The effects of PVPh addition on T_g behavior of ternary blends are shown in Figure 6. When more than 70–90 wt% PVPh was added to immiscible Am-Nylon/PMMA blends, ternary blends showed single T_g . However, judging from only one T_g , one could not assume that the blend was miscible. T_g s for two co-existed phases containing more than 70–90 wt% PVPh (*i.e.*, Am-Nylon/PVPh and PMMA/PVPh) are very close. By thermo-photometry, we reexamined the miscibility of some blend samples for which single T_g were observed. The results are shown in Figure 7. Horizontal and vertical

Table II. Blend compositions in this work

Sample No.	PVPh	PMMA	Am-Nylon
1	0.1	0.09	0.81
2	0.1	0.27	0.63
3	0.1	0.45	0.45
4	0.1	0.63	0.27
5	0.1	0.81	0.09
6	0.3	0.07	0.63
7	0.3	0.21	0.49
8	0.3	0.35	0.35
9	0.3	0.49	0.21
10	0.3	0.63	0.07
11	0.5	0.05	0.45
12	0.5	0.15	0.35
13	0.5	0.25	0.25
14	0.5	0.35	0.15
15	0.5	0.45	0.05
16	0.7	0.03	0.27
17	0.7	0.09	0.21
18	0.7	0.15	0.15
19	0.7	0.21	0.09
20	0.7	0.27	0.03
21	0.9	0.01	0.09
22	0.9	0.03	0.07
23	0.9	0.05	0.05
24	0.9	0.07	0.03
25	0.9	0.09	0.01

Figure 8. Phase diagram of Ternary PVPh/Am-Nylon/PMMA blends through results from T_g and transparency. Open circles represent compositions where single T_g and optical clear are observed and full circles represent compositions where two T_g s are observed.

axis indicate sample numbers which corresponded to Table II and transmittance of blend films, respectively. DSC and thermo-photometry showed sample numbers 16, 20, 21, 22, 23, 24, and 25 to be miscible.

The ternary diagram denoting composition where miscibility or phase separation was observed is shown in Figure 8. The phase diagram showed a large symmetric heterogeneous area. When more than 70 wt% PVPh was

Figure 9. SEM photomicrographs of ternary blends containing an Am-Nylon/PMMA ratio of 3/7 varying amounts of PVPh: (a) 0 wt% PVPh; (b) 30 wt% PVPh; (c) 70 wt% PVPh; (d) 90 wt% PVPh; annealed at 190°C.

added to immiscible Am-Nylon/PMMA blends (9/1 and 1/9) or more than 90 wt% PVPh was added to immiscible blends (7/3, 5/5, and 3/7), the ternary blends changed from a heterogeneous to homogeneous region. This suggests that PVPh acts as a compatibilizer in immiscible Am-Nylon/PMMA.

Additional information was obtained by SEM. Photomicrographs observed for the Am-Nylon/PMMA (3/7) blends with the addition of 0, 30, 70, and 90 wt% PVPh are shown in Figure 9. Am-Nylon/PMMA (3/7) blends clearly expressed phase separation as shown in Figure 9(a). The Am-Nylon/PMMA (3/7) blends with 30 wt% PVPh also exhibited phase separation, with a matrix-dispersed phase morphology and a wide size distribution of the dispersed phase as shown in Figure 9(b). However it could be seen that the compatibility of Am-Nylon/PMMA was better than in the absence of PVPh. The Am-Nylon/PMMA (3/7) blends with 90 wt% PVPh showed monophasic nature as shown in Figure 9(d). These experimental results well agree with the ternary phase diagram shown in Figure 8.

Determination of PVPh–Am-Nylon Inter-Association Equilibrium Constant K_c

The phase behavior of ternary Am-Nylon/PMMA/PVPh blends having strong specific interactions, was dominated by individual binary interaction parameters (χ_{ij}) and equilibrium constants (K_i).¹⁰ This behavior was affected by K_i . The magnitude of inter-association

equilibrium constant (K_A) of PVPh/PMMA is thus nearly equal to K_c of PVPh/Am-Nylon. K_A was previously determined by Coleman *et al.* In the same way, we determined K_c quantitatively using FT-IR.^{9,11}

Calculation of Stoichiometric Equations¹³

The formation of PVPh(B) hydroxyl-hydroxyl dimers and hydroxyl-hydroxyl “chain-like” multimers was confirmed by FT-IR method.¹² The formation of Am-Nylon(C) amide–amide dimers and amide–amide multimers has been confirmed.¹² We used four self-association equilibrium constants, K_2 , K_B , K'_2 , and K'_B to describe the dimers and multimers of PVPh and dimers and multimers of Am-Nylon, respectively, *i.e.*,

Inter-association equilibrium constants describing specific interactions between PVPh and PMMA(A), and specific interactions between PVPh and Am-Nylon, are represented by,

The inter-association equilibrium constants describing specific interactions between PMMA and Am-Nylon are not shown, because there were no interactions between them. The total volume fraction of PVPh in the blend is the sum of the volume fractions of isolated PVPh, self-associated PVPh, PVPh-PMMA interaction and PVPh-Am-Nylon interactions, show that

$$\phi_B = \phi_{B1} + \sum_{n=2}^{\infty} \phi_{Bn} + \sum_{i=1}^{\infty} \phi_{B_i A} (i/(i+r_A)) + \sum_{j=1}^{\infty} \phi_{B_j C} (j/(j+r_C)) \quad (4)$$

where ϕ_B , ϕ_{B1} , ϕ_{BA} , and ϕ_{BC} are the volume fraction of PVPh, isolated (non-hydrogen-bonded) PVPh, PVPh associated with PMMA and PVPh associated with Am-Nylon in the blend. The parameters $r_A = V_A/V_B$ and $r_C = V_C/V_B$ are the ratios of the segment molar volumes of PMMA to PVPh and Am-Nylon to PVPh, respectively.

Using above equilibrium constants to eq 4, we obtained

$$\phi_B = \phi_{B1} \left(1 - \frac{K_2}{K_B} + \frac{K_2}{K_B} \left(\frac{1}{(1 - K_B \phi_{B1})^2} \right) \right) \times \left(1 + \frac{K_A \phi_{A1}}{r_A} + \frac{K_C \phi_{C1}}{r_C} \right) \quad (5)$$

The total volume fraction of PMMA in the blend is the sum of the volume fractions of isolated PMMA and PVPh-PMMA interactions, and the total volume fraction of Am-Nylon in the blend is the sum of the volume fractions of isolated Am-Nylon, self-associated Am-Nylon, and PVPh-Am-Nylon interaction, as shown by,

$$\phi_A = \phi_{A1} + \sum_{i=1}^{\infty} \phi_{B_i A} (r_A/(i+r_A)) \quad (6)$$

$$\phi_C = \phi_{C1} + \sum_{n=2}^{\infty} \phi_{Cn} + \sum_{j=1}^{\infty} \phi_{B_j C} (r_C/(j+r_C)) \quad (7)$$

where ϕ_A , ϕ_{A1} , ϕ_C , and ϕ_{C1} are the volume fractions of PMMA, isolated PMMA, Am-Nylon, and isolated Am-Nylon, respectively.

Similarly, using above equilibrium constants to eq 6 and 7, we obtained

$$\phi_A = \phi_{A1} + K_A \phi_{A1} \phi_{B1} \left(1 - \frac{K_2}{K_B} + \frac{K_2}{K_B} \left(\frac{1}{(1 - K_B \phi_{B1})^2} \right) \right) \quad (8)$$

$$\phi_C = \phi_{C1} \left(1 - \frac{K'_2}{K'_B} + \frac{K'_2}{K'_B} \left(\frac{1}{(1 - K'_B \phi_{C1})^2} \right) \right) + K_C \phi_{C1} \phi_{B1} \left(1 - \frac{K_2}{K_B} + \frac{K_2}{K_B} \left(\frac{1}{(1 - K_B \phi_{B1})^2} \right) \right) \quad (9)$$

Determination of PVPh-Am-Nylon inter-association equilibrium constant K_C .

More than 70–90 wt% PVPh was added to immiscible

Figure 10. FT-IR spectra of PVPh/Am-Nylon/PMMA blends in the carbonyl stretching region recorded at 190°C: (A) 90/1/9; (B) 90/3/7; (C) 90/5/5; (D) 90/7/3 wt%.

ble Am-Nylon / PMMA blends, and thus ternary blends indicated miscible regions (Figure 8). The volume fraction of Am-Nylon was less in this region. Even if the self-association constant (K'_B) of Am-Nylon is considered, the relationship of $1 \gg K'_B \phi_{C1}$ is established. Hence, eq 9 could approximate as eq 10.

$$\phi_C = \phi_{C1} + K_C \phi_{C1} \phi_{B1} \left(1 - \frac{K_2}{K_B} + \frac{K_2}{K_B} \left(\frac{1}{(1 - K_B \phi_{B1})^2} \right) \right) \quad (10)$$

If the equilibrium constants (K_2 , K_B , and K_A) and segment molar volume (V_A , V_B , and V_C) are known, K_C may be determined from the experimental infrared f_{HB} (the fraction of hydrogen bonded carbonyl groups of PMMA) and eq 5, 8, 10, and 11, for a given blend composition (ϕ_A , ϕ_B , ϕ_C).

$$f_{HB} = 1 - \frac{\phi_{A1}}{\phi_A} = \frac{A_H}{(aA_f + A_H)} \quad (11)$$

A_H and A_f are areas corresponding to the hydrogen-bonded and the free C=O groups, respectively, and a is the absorptivity ratio of 1.5.

K_2 (=21.0 at 25°C), K_B (=66.8 at 25°C), and K_A (=3.66 at 165°C) were previously determined from binary blend systems, as having corresponding enthalpies of hydrogen bond formation (−5.6, −5.2, and −4.58 kcal mol^{−1}, respectively, for h_2 , h_B , and h_A). Assuming a van't Hoff relationship, K_2 (=0.722), K_B (=2.92), and K_A (=2.75) were determined at 190°C.

Representative infrared spectra at 190°C in the carbonyl stretching region for a series of blend containing a constant concentration (90 wt%) of PVPh are shown in Figure 10. In Figure 10, free and hydrogen bonded carbonyl groups are given at approximately 1733 cm^{−1} and 1711 cm^{−1}, respectively. For these spectra, f_{HB} could be determined by the separation of the carbonyl band into two components using the Lorenz function, and are summarized in Table III. Using the above constants, we determined K_C by solving simul-

Table III. Curve fitting for PVPh/Am-Nylon/PMMA blends

PVPh : Am-Nylon : PMMA blend comp. (wt%)	Free C=O bond		H bonded C=O		$f_{\text{HB}}^{\text{C=O}}$
	ν/cm^{-1}	Area	ν/cm^{-1}	Area	
90 : 01 : 09	1733	2.95	1711	4.42	0.500
90 : 03 : 07	1733	6.53	1709	9.8	0.500
90 : 05 : 05	1730	10	1705	15.1	0.502
90 : 07 : 03	1736	5.07	1705	7.65	0.501

Table IV. PVPh/Am-Nylon/PMMA blends, parameter list

Polymer	V^a	δ^b	χ^c	K^d
PVPh	100.0	10.6		
Am-Nylon	196.2	11.5	0.123	3.20
PMMA	85	9.10	0.225	2.75
Am-Nylon/PMMA			0.256	

^a V is molar volume. ^b δ is solubility parameter. ^c χ is interaction parameter at 190°C. ^d K is inter-association equilibrium constant at 190°C.

taneous equations (eq 5, 8, 10, and 11). We obtained $K_C=3.2$ at 190°C. Parameter values for ternary Am-Nylon/PMMA/PVPh blends are summarized in Table IV. The solubility parameters were calculated from the molar attraction constants of Hoy. The interaction parameters were calculated from eq 12.¹²

$$\chi_{ij} = \frac{V_B}{RT} (\delta_i - \delta_j)^2 \quad (12)$$

In general, ternary phase behavior of polymer blend systems in which there are strong specific interactions is governed by binary interaction parameters (χ_{ij}) and equilibrium constants describing self- and inter-associations (K_i). Factors affecting the miscibility of ternary Am-Nylon/PMMA/PVPh blends described above are not applicable, because these values were significantly larger than the critical χ_{ij} . The miscibility of ternary Am-Nylon/PMMA/PVPh blends involving strong specific interaction may thus be due to equilibrium constants (K_i).

Effects of Compatibilizer for PVPh

Finally, we observed the morphology of Am-Nylon/PMMA (=7/3) blends with 10 and 20 wt% PVPh by using SEM. Figure 11 shows SEM photomicrographs of the blends. The Am-Nylon/PMMA (=7/3) with 20 wt% PVPh exhibited that the particle size of PMMA was smaller than in the absence of PVPh. PVPh thus may act as a common solvent and improve the compatibility of binary immiscible blends. PVPh may thus act as a compatibilizer for immiscible Am-Nylon/PMMA blends.

CONCLUSION

The miscibility of ternary blends consisting of Am-Nylon/PMMA/PVPh was investigated by DSC, thermo-photometry, FT-IR, and SEM. Binary Am-Nylon/PMMA blends revealed phase separation by DSC analysis. Binary PVPh/Am-Nylon and PVPh/PMMA blends ex-

(a) 0 wt%

(b) 10 wt%

(c) 20 wt%

Figure 11. SEM photomicrographs of ternary blends containing a Am-Nylon/PMMA ratio of 7/3 varying amounts of PVPh: (a) 0 wt% PVPh; (b) 10 wt% PVPh; (c) 20 wt% PVPh; annealed at 190°C.

hibited miscibility by DSC and thermo-photometry analysis. FT-IR showed that these miscibility were attributed to intermolecular hydrogen bonding interactions.

In ternary blends at 190°C, more than 70–90 wt% PVPh was required to attain miscibility between Am-Nylon and PMMA. The experimental ternary diagrams indicated symmetrically miscible regions. Using stoichiometric equations, the equilibrium constant ($K_C=3.2$) describing hydrogen bonding of PVPh/Am-Nylon blends was determined from quantitative FT-IR analyses. As the individual binary interaction parameters (χ_{ij}) were significantly larger than the critical χ_{ij} , con-

firming that the miscible region is affected by the equilibrium constant (K_i).

The miscibility of Am-Nylon/PMMA blend was improved by adding 20 wt% PVPh to binary immiscible polymer. Thus, PVPh may act as a compatibilizer for immiscible Am-Nylon/PMMA blends.

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