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Miscibility of nylon 6 with poly(maleic anhydride-*co*-vinyl acetate) and hydroxylated poly(maleic anhydride-*co*-vinyl acetate) blends

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The miscibility of blends of nylon 6 with poly(maleic anhydride-*co*-vinyl acetate) (poly(MAH-*co*-VAc)), or hydroxylated poly(maleic anhydride-*co*-vinyl acetate) (poly(MAH-*co*-VAc)H) was investigated by means of Fourier transform infra-red (*FT*i.r.) spectroscopy, differential scanning calorimetry (d.s.c.), and X-ray diffraction. Poly(MAH-*co*-VAc) was prepared by radical copolymerization and the copolymers were hydrolysed to form poly(MAH-*co*-VAc)H at reflux temperature in H_2O. Poly(MAH-*co*-VAc) and poly(MAH-*co*-VAc)H were characterized by *FT*i.r. and ^{1}H-n.m.r. spectroscopy. On the basis of optical clarity, glass transition temperature (T_g), *FT*i.r. spectra, and X-ray diffraction, it was found that the nylon 6/poly(MAH-*co*-VAc) blends showed immiscible behaviour over the entire blend concentration but the poly(MAH-*co*-VAc)H showed miscibility with nylon 6 over blend concentrations above 75 wt% of poly(MAH-*co*-VAc)H. The *FT*i.r. results showed that strong specific interactions between the carboxylic acid group of poly(MAH-*co*-VAc)H and the amide group of nylon 6 are responsible for the miscibility. Copyright © 1996 Elsevier Science Ltd.

(Keywords: miscibility; nylon 6; poly(maleic anhydride-*co*-vinyl acetate))

INTRODUCTION

Over the last two decades, polymer miscibility has been one of the main themes in the study of polymer blends[1–9]. Most polymers exhibit immiscible behaviour with other polymers because of the small entropy gain on mixing from their long chain characteristics. The compatibilization of immiscible blends, therefore, has attracted much interest. Several attempts have been made to compatibilize immiscible blends by introducing specific interactions between the component polymers or adding a compatibilizer or interfacial agent to the blends[10–19].

The enhancement of poor miscibility of nylon 6 with other polymers has attracted our interest for several years, since it has been expected that nylon 6 containing blends may find applications in plastic, fibre, or biological industries[20–23]. It is known that the strong hydrogen bonding character of nylon 6 limits its use as a blend material, even though nylon 6 itself is used as one of the important engineering plastics because of the strong hydrogen bonding character. Recently, we prepared a graft copolymer of poly(ethylene glycol) (PEG) onto nylon 6 and used it as a compatibilizer for nylon 6 and PEG blends[24]. We found out that nylon 6 and poly(vinyl acetate) (PVAc) were immiscible but the graft copolymer itself showed a miscibility window over the blend concentrations above 50% of the copolymer in the graft copolymer/PVAc blends. We reported that the partial miscibility is attributed, in part, to the specific interaction between PEG in the graft copolymer and PVAc[25].

Meanwhile, the chemical modification of the other component has been also attempted to explicitly achieve the compatibilization of nylon 6 containing blends. A typical example is the grafting of maleic anhydride onto polypropylene (PP) for the blend of nylon 6 and PP[26,27].

In the present work, we prepared a copolymer of vinyl acetate with maleic anhydride (poly(MAH-*co*-VAc)) and blended it with nylon 6, expecting the miscibility of nylon 6 with PVAc could be improved due to the introduction of the polar maleic anhydride group which could provide an intermolecular interaction site with the amide groups of nylon 6. We also prepared hydroxylated poly(MAH-*co*-VAc) to blend it with nylon 6. The objective of this work is to investigate the miscibility of nylon 6 with poly(MAH-*co*-VAc) or poly(MAH-*co*-VAc)H and to clarify the nature of the specific interactions in the blends, if any, by Fourier transform infra-red (*FT*i.r.) spectroscopy.

EXPERIMENTAL

Materials

Maleic anhydride (Junsei Chemical) was dissolved in chloroform and then was recrystallized from methanol. Azobisisobutyronitrile (AIBN) (Yakuri Pure Chemical) was purified by recrystallization from ethanol. Vinyl

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acetate (Junsei Chemical) was washed with 10% aqueous solution of NaOH to remove inhibitor, followed by washing with distilled water until it became neutral, and dried with $CaCl_2$ for 2 days. Nylon 6 with $M_w = 3.4 \times 10^4$ and $M_w/M_n = 1.99$ was obtained from the Research Institute of Kolon Co. Ltd and reprecipitated in diethyl ether after being dissolved in formic acid and then dried under vacuum for one week. Methyl ethyl ketone (MEK), formic acid, and methanol were used as received.

*Syntheses of poly(MAH-*co*-VAc) and hydroxylated poly(MAH-*co*-VAc)*

Poly(MAH-*co*-VAc) was prepared in a polymerization tube with $3.00 \mathrm{mol\,l^{-1}}$ of each equimolar monomer concentration in MEK at 60°C for 72 h using AIBN as initiator. The copolymer formed was isolated by pouring the reaction mixture into *n*-hexane. The copolymer isolated was purified by two successive dissolutions in acetone and precipitated in excess of *n*-hexane. The product was dried in a vacuum oven at 30°C for 48 h. The poly(MAH-*co*-VAc)H containing hydroxyl group was obtained by two step reactions: first, poly(MAH-*co*-VAc) was saponified in MEK/methanol (2/8 v/v) with KOH as a catalyst for 5 h and then it was hydrolysed in H_2O at reflux temperature for 24 h.

Preparation of blends

Blend films were prepared by casting from 3 wt% solutions of formic acid. The resulting films were dried slowly in a petri dish at room temperature and then kept under vacuum until they reached constant weight.

N.m.r. spectroscopy

^{1}H-n.m.r. spectra of poly(MAH-*co*-VAc) and poly(MAH-*co*-VAc)H were examined by using a JEOL GSX-270 spectrophotometer. The measurement was done using DMSO-d_6 as a solvent and TMS as an internal reference.

FT*i.r. spectroscopy*

I.r. spectra were taken on an Analect FX-6160 *FT*i.r. spectrophotometer. Samples for i.r. measurements were prepared on potassium bromide (KBr) discs. Sixty-four scans at a resolution of $2 \mathrm{cm^{-1}}$ were signal averaged.

Copolymer composition and molecular weight of copolymers

The copolymer composition of poly(MAH-*co*-VAc) and poly(MAH-*co*-VAc)H were obtained by titration and ^{1}H-n.m.r. integration. Poly(MAH-*co*-VAc) was dissolved in methanol/MEK (2/8 v/v) and titrated with 0.1 N alcoholic potassium using phenolphthalein as an indicator. The actual comonomer composition in poly(MAH-*co*-VAc)H was determined by the integration of the chemical shift at $\delta = 2.01$ ppm based on that of poly(MAH-*co*-VAc). The molecular weights were measured by gel permeation chromatography (g.p.c.) (Waters 244) with Ultrastyragel 500-A linear columns. The measurement was carried out using THF as an eluent at 28°C. The apparatus was calibrated with PS standards.

Thermal analysis

Glass transition temperatures (T_g) were measured using a differential scanning calorimeter (DuPont 1090) calibrated with pure indium as a standard. In order to avoid the thermal history from the samples being packed in the aluminium pan and to eliminate any small traces of solvent, samples were heated to 473 K at heating rate of $40°\mathrm{C\,min^{-1}}$, annealed at 473 K for 5 min, and then quenched to 273 K at a rate of $80°\mathrm{C\,min^{-1}}$. Thermograms of the blends were obtained at a heating rate of $10°\mathrm{C\,min^{-1}}$. All the glass transition temperatures were recorded at half-height of the heat capacity jump.

X-ray diffractometry

The crystalline structure of polymers was examined by using a Rigaku Denki D/max-IIA X-ray diffractometer. Nickel-filtered Cu Kα radiation was applied at 30 kV and 20 mA.

RESULTS AND DISCUSSION

Characterization of copolymers

Figures 1 and *2* show the *FT*i.r. and ^{1}H-n.m.r. spectra of copolymers, respectively. The *FT*i.r. spectrum of poly(MAH-*co*-VAc) in *Figure 1a* exhibits characteristic peaks at $1853 \mathrm{cm^{-1}}$ (C=O asymmetric stretching band of MAH), $1784 \mathrm{cm^{-1}}$ (C=O symmetric stretching band of MAH), $1731 \mathrm{cm^{-1}}$ (C=O stretching band of VAc), 1230 $\mathrm{cm^{-1}}$ (C–O–C stretching band of MAH), and $1180 \mathrm{cm^{-1}}$ (–$COCH_3$ stretching band of VAc). For poly(MAH-*co*-VAc)H, as shown in *Figure 1b*, the characteristic peaks appeared at $1780 \mathrm{cm^{-1}}$ (C=O stretching band of carboxylic acid group) and around $3500 \mathrm{cm^{-1}}$ (OH stretching band of carboxylic acid group and hydroxyl group). However, it was observed that the C=O doublet stretching band of MAH around $1853 \mathrm{cm^{-1}}$ and 1784 $\mathrm{cm^{-1}}$, and the C–O–C stretching at $1230 \mathrm{cm^{-1}}$ disappeared, and the –$COCH_3$ stretching band of VAc at $1180 \mathrm{cm^{-1}}$ became much weaker due to hydroxylating of poly(MAH-*co*-VAc).

In *Figure 2a*, the ^{1}H-n.m.r. spectrum of poly(MAH-*co*-VAc) exhibits the characteristic chemical shifts at $\delta = 1.92$ ppm (CH_2 of VAc), $\delta = 2.01$ ppm (CH_3 of $COCH_3$ in VAc), and $\delta = 3$–4 ppm (CH of MAH). The ^{1}H-n.m.r. spectrum of poly(MAH-*co*-VAc)H in *Figure 2b* showed that the characteristic chemical shifts of poly(MAH-*co*-VAc)H were observed at $\delta = 1.92$ ppm (CH_2 of VAc), $\delta = 3$–4 ppm (CH of MAH), $\delta = 6.03$ ppm (hydroxyl

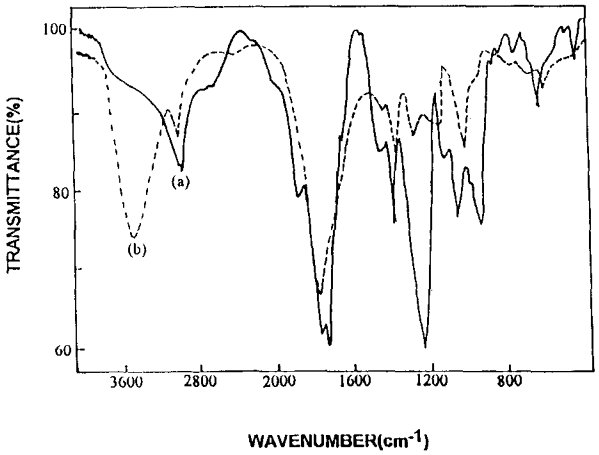

Figure 1 *FT*i.r. spectra of copolymers: (a) poly(MAH-*co*-VAc); (b) poly(MAH-*co*-VAc)H

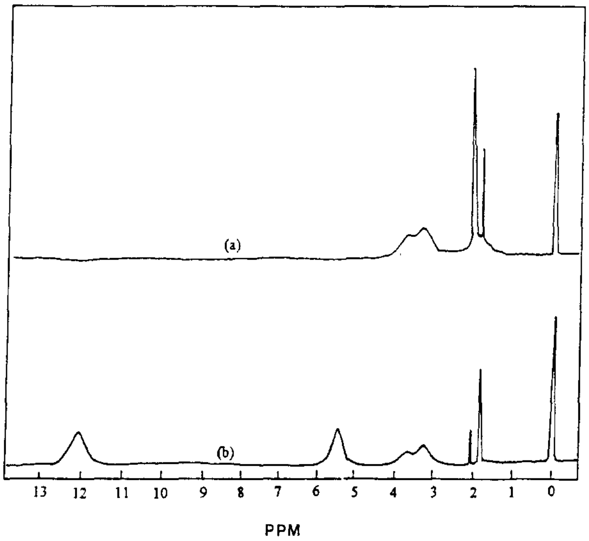

Figure 2 ^{1}H-n.m.r. spectra of copolymers: (a) poly(MAH-*co*-VAc); (b) poly(MAH-*co*-VAc)H

Table 1 Characteristics of the copolymers obtained

Copolymer	Composition^a	Molecular weight	M_w/M_n
Poly(MAH-*co*-VAc)	MAH = 39% VAc = 61%	M_n = 9000 M_w = 13 500	1.50
Poly(MAH-*co*-VAc)H	MAc = 39% VAc = 11% VA = 50%	M_n = 7800 M_w = 15 900	2.04

^{a} VA, MAc denotes vinyl alcohol and maleic acid, respectively

group), and $\delta = 12$ ppm (carboxylic acid group). The chemical shift at $\delta = 2.01$ ppm (CH_3 of $COCH_3$ in VAc) became much weaker when compared to that of poly(MAH-*co*-VAc).

Composition and molecular weight of copolymers

The comonomer compositions and the molecular weights of the copolymers are listed in *Table 1*. It was found that poly(MAH-*co*-VAc)H consists of 39% of maleic acid, 11% of vinyl acetate, and 50% of vinyl alcohol. The result means that hydrolysing poly(MAH-*co*-VAc) converted most of the VAc in the copolymer to vinyl alcohol and also all of the MAH in the copolymer to maleic acid.

It should be noted that when the polymer sample employed is not strictly monodisperse and the molecular weight differences are large, the miscibility is strongly dependent on the molecular weight characteristics of the polymers. In this work, however, the molecular weight and the molecular weight distribution of the copolymers used are comparable. Thus, in comparing the relative miscibility of the blends containing the copolymers, the conclusions drawn here may be unaffected by any minor errors due to differences in the molecular weight characteristics.

Optical clarity and T_g *behaviour*

The optical clarity and T_g of nylon 6/poly(MAH-*co*-VAc) and nylon 6/poly(MAH-*co*-VAc)H blends are summarized in *Table 2*.

For the results in *Table 2*, miscibility was determined by the criterion of the existence of a single T_g on d.s.c. thermograms as well as optical clarity of the blends. *Table 2* indicates that the nylon 6/poly(MAH-*co*-VAc) blends are immiscible over the entire blend concentrations. It should be noted, however, that the nylon 6/poly(MAH-*co*-VAc)H blends showed miscibility over blend concentrations above 75 wt% of copolymer concentrations.

Table 2 Miscibility based on optical clarity and glass transition temperature for the blends of nylon 6 with poly(MAH-*co*-VAc) and poly(MAH-*co*-VAc)H

Copolymer	Copolymer in the blends	Optical clarity^a	T_g (°C)	Miscibility
Poly(MAH-*co*-VAc)	15	O	39, 71	IM
	25	O	41, 71	IM
	50	O	41, 70	IM
	75	O	42, 68	IM
	85	T	42, 68	IM
Poly(MAH-*co*-VAc)H	15	O	42, 64	IM
	25	O	43, 64	IM
	50	T	45, 63	IM
	75	C	58	M
	85	C	62	M

^{a} O, T, C denote opaque, translucent and clear, respectively

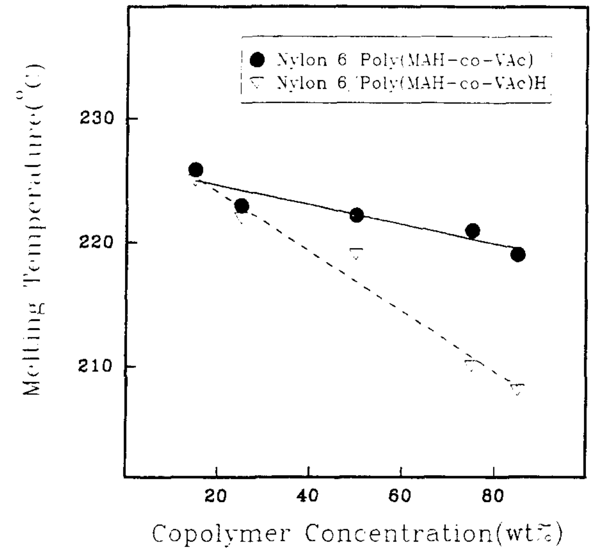

Figure 3 Melting temperature of blends as a function of copolymer concentrations (wt%)

Melting temperature depression

Figure 3 shows the melting temperatures (T_m) of nylon 6 in the blends. It is shown that T_m of nylon 6/poly(MAH-*co*-VAc)H decreases remarkably with increasing copolymer concentrations, whereas T_m of the nylon 6/poly(MAH-*co*-VAc) blends decreases slightly with increasing copolymer concentrations. The results indicate that the miscibility of poly(MAH-*co*-VAc)H with nylon 6 was much better than that of poly(MAH-*co*-VAc) with nylon 6, when the miscibility is judged from the melting point depression.

In the case of nylon 6/poly(MAH-*co*-VAc)H blends, the rapid reduction in T_m around the blend concentration above 50 wt% suggests that the miscibility of nylon 6 with poly(MAH-*co*-VAc)H is greatly enhanced at higher copolymer concentrations.

Specific interaction

Specific interactions in polymer blends were studied by *FT*i.r. spectroscopy. The application of *FT*i.r. spectroscopy to prove the specific intermolecular interactions in polymer blends is currently attracting wide research interest. For example, Lu *et al.*[28] reported on the definite spectral features sensitive to the miscibility of polystyrene (PS)/poly(vinyl methyl ether) (PVME) blends by using *FT*i.r. spectroscopy. They revealed that the vibrations most sensitive to change in the molecular environment are the C–H out-of-plane vibration of the phenyl ring (698 cm^{-1}) in PS and the $COCH_3$ vibrations of PVME (doublet at 1085 and 1107 cm^{-1}). In this work, the shifts of the relative intensity of doublet peaks at 1853 and 1784 cm^{-1} due to the anhydride group, and the singlet peak at 1780 cm^{-1} due to the carboxylic acid group were investigated.

Figures 4 and *5* indicate the shift trends of C=O stretching bands in each copolymer blend. In *Figure 4*, the peak at 1784 cm^{-1} due to the carbonyl group of anhydride in poly(MAH-*co*-VAc) was shifted to slightly lower frequency as the content of poly(MAH-*co*-VAc) was increased, whereas the peak at 1731 cm^{-1} of the carbonyl group in VAc was not shifted. *Figure 5* shows that the C=O singlet peak at 1780 cm^{-1} of poly(MAH-*co*-VAc)H due to the carboxylic acid group was shifted to low frequency as much as 30 cm^{-1} with increasing content of poly(MAH-*co*-VAc)H. The large shifts for the nylon 6/poly(MAH-*co*-VAc)H blends when compared to nylon 6/poly(MAH-*co*-VAc) blends should be noted.

The shift of the N–H deformation band in nylon 6 around 1540 cm^{-1}, which may be expected to interact with the C=O stretching band of copolymers, was also observed for the blends and is summarized in *Table 3*. In this table, one can see that the N–H bending band shifts to slightly higher frequencies as the concentration of poly(MAH-*co*-VAc) increases, and the shifts are much larger in the case of nylon 6/poly(MAH-*co*-VAc)H blends.

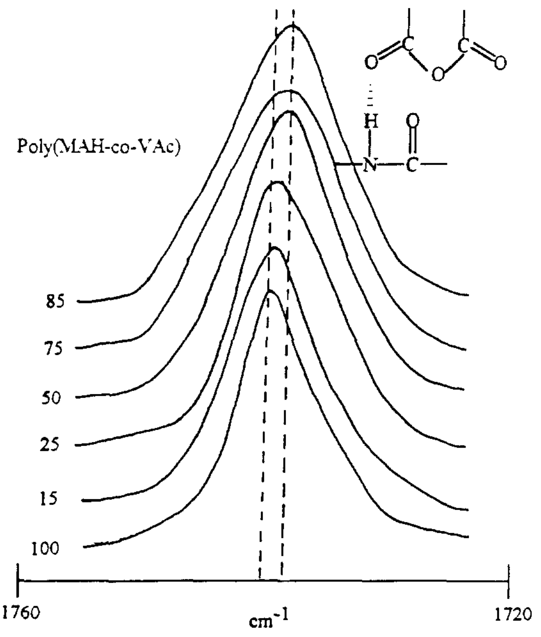

Figure 4 *FT*i.r. spectra of nylon 6/poly(MAH-*co*-VAc) blends in the 1700–1800 cm^{-1} region

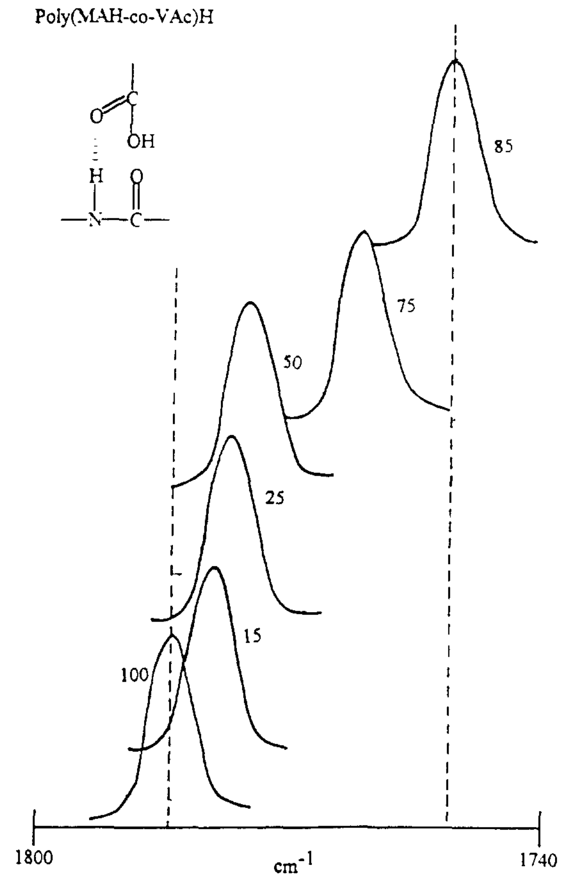

Figure 5 *FT*i.r. spectra of nylon 6/poly(MAH-*co*-VAc)H blends in the 1700–1800 cm^{-1} region

The small shifts of the N–H band to higher frequency is simply due to both anharmonicity and disorder of nylon 6 resulting from the addition of amorphous copolymers, as indicated by Painter and Coleman[29]. They reported the shift of the band to higher frequency with increasing temperature which destroys the order of the nylon 6. More interesting, however, is that the shift to higher frequency is appreciably large when the copolymer concentration in the blends is larger than 75 wt% for the nylon 6/poly(MAH-*co*-VAc)H blends. The larger shift may be due to hydrogen bonding between the N–H band of nylon 6 and the C=O band of poly(MAH-*co*-VAc)H.

Comparison of the results of *Table 3* with the *FT*i.r. results in *Figures 4* and *5* indicates that the peaks of poly(MAH-*co*-VAc)H due to the C=O stretching band and peaks of nylon 6 due to the N–H bending band are very sensitive to the miscibility of the nylon 6 containing polymer blends, and there exists hydrogen bonding between the N–H of nylon 6 and C=O in the carboxylic acid band of poly(MAH-*co*-VAc)H. The *FT*i.r. results of nylon 6/poly(MAH-*co*-VAc) blends, however, imply that the interaction between poly(MAH-*co*-VAc) and nylon 6 is not strong. Note that nylon 6 and poly(MAH-*co*-VAc) blends showed phase separation over the entire blend concentration from the results of the optical clarity and T_g behaviour.

Crystalline structure

The crystalline structures of nylon 6, poly(MAH-*co*-VAc), poly(MAH-*co*-VAc)H and their blends were investigated by X-ray diffraction. It has been reported

Table 3 Peak positions around 1540 and 1750 cm^{-1} for the blends of nylon 6 with poly(MAH-*co*-VAc) and poly(MAH-*co*-VAc)H

	Nylon 6/poly(MAH-*co*-VAc)		Nylon 6/poly(MAH-*co*-VAc)H	
Composition of nylon 6/ copolymer blends	Wavenumber of N–H in nylon 6 (cm^{-1})	Wavenumber of C=O in copolymers (cm^{-1})	Wavenumber of N–H in nylon 6 (cm^{-1})	Wavenumber of C=O in copolymers (cm^{-1})
100/0	1542	–	1541	–
85/15	1542	1740	1542	1774
72/25	1542	1739	1549	1772
50/50	1542	1738	1553	1770
25/75	1544	1738	1569	1760
15/85	1544	1738	1572	1751
0/100	–	1784	–	1780

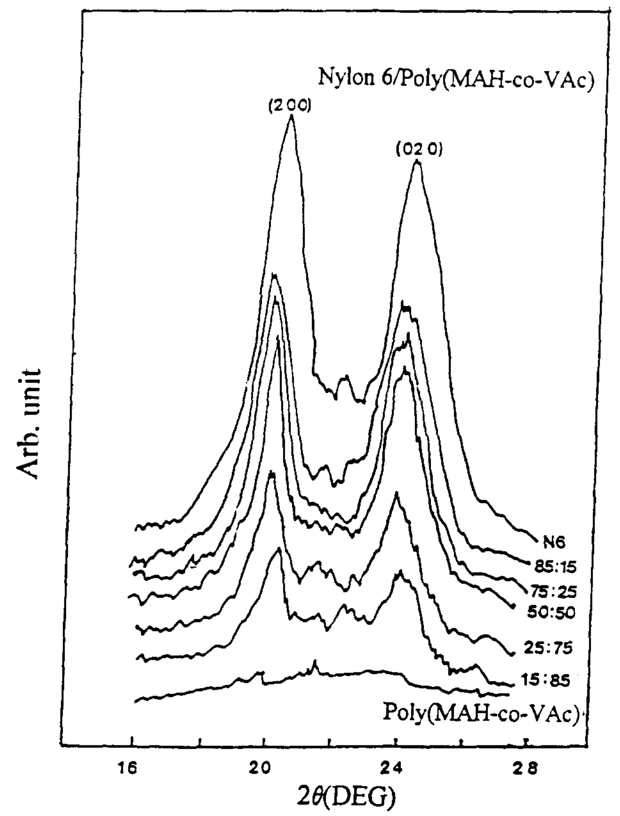

Figure 6 X-ray diffractograms of nylon 6/poly(MAH-*co*-VAc) blends

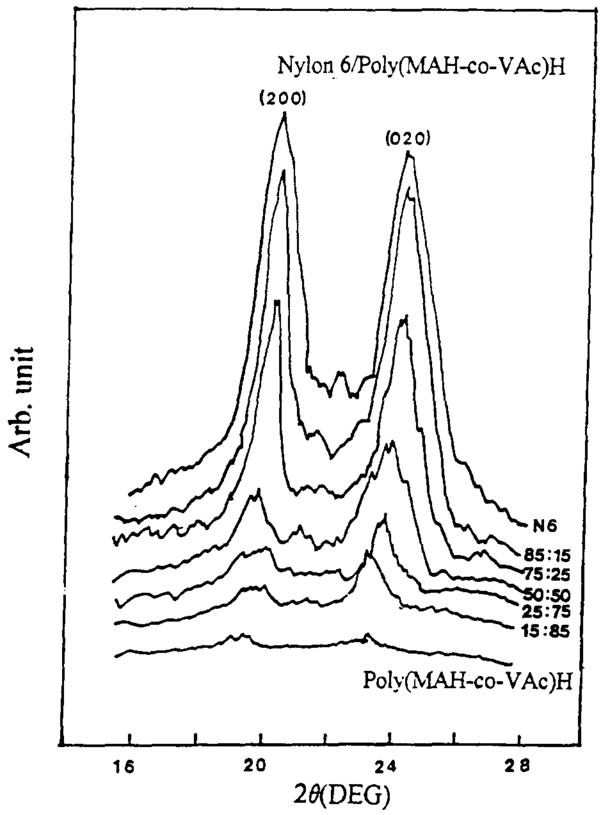

Figure 7 X-ray diffractograms of nylon 6/poly(MAH-*co*-VAc)H blends

that nylon 6 has two different structures, the α-form and the γ-form[30]. The α-form of nylon 6 has two strong diffraction peaks at the Bragg angle of $2\theta = 20.5°$ and $23.8°$ corresponding to the (200) and (020) planes, respectively. The diffraction pattern of nylon 6 used in this work shows typical α-form crystalline structure, as shown in *Figures 6* and *7*.

In the case of poly(MAH-*co*-VAc) and poly(MAH-*co*-VAc)H, the diffraction peaks were not detected, meaning that both of the copolymers are amorphous. For nylon 6/poly(MAH-*co*-VAc) blends, no significant change in the crystalline structure was found except the linear decreases in the degree of crystallinity with increasing copolymer concentrations. However, the X-ray diffractograms of the nylon 6/poly(MAH-*co*-VAc)H blends, shown in *Figure 7*, indicate that the relative intensities of the diffraction peaks at $2\theta = 20.5°$ and $23.8°$ decreased remarkably at copolymer concentrations of more than 50 wt%. The result implies that the crystal lattice spacing of the (200) planes were affected significantly by the presence of the copolymer at higher copolymer concentrations.

Taking the *FT*i.r. results into consideration, the change in the lattice spacing is mainly attributed to the hydrogen bonding between nylon 6 and poly(MAH-*co*-VAc)H, i.e. when the amount of the copolymer is small, the copolymer does not affect the lattice spacing at all. However, when more than 50 wt% of the copolymer is added to nylon 6, the strong molecular interaction acts between the component polymers due to hydrogen bonding between N–H of nylon 6 and C=O in carboxylic acid in the copolymer. Then, the nylon 6

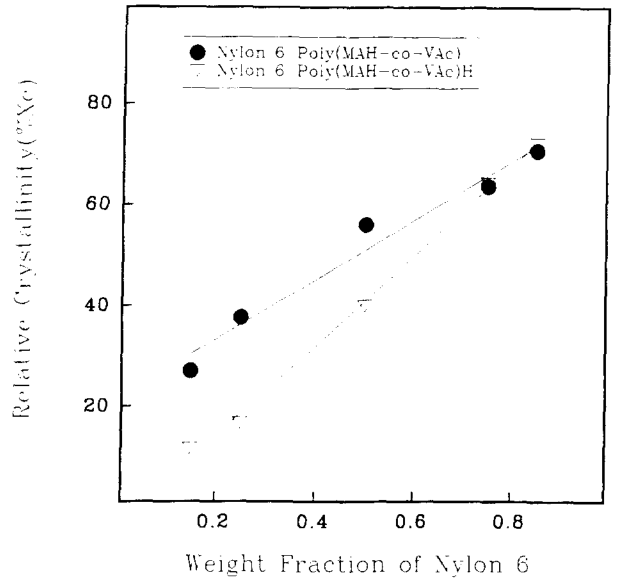

Figure 8 Relative crystallinity (% X_c) as a function of nylon 6 content for blends

cannot maintain its original crystal lattice spacing, resulting in the change of the relative intensity of the crystal peaks of the (200) and (020) planes.

Moreover, careful inspection of the diffractograms in *Figures 6* and *7* shows that for nylon 6/poly(MAH-*co*-VAc)H blends the diffraction peaks of the (020) plane are observed at lower Bragg angles as the copolymer concentrations in the blends are higher, whereas for nylon 6/poly(MAH-*co*-VAc) blends the diffraction peaks of the (020) planes are always observed at the same Bragg angle. This result suggests that in the case of the nylon 6/poly(MAH-*co*-VAc)H blends the sizes of the lattice spacing of the (020) planes become larger at higher copolymer concentrations due to the strong hydrogen bonding between the component polymers in the blends.

Figure 8 shows that the relative degree of crystallinities of nylon 6/poly(MAH-*co*-VAc) and nylon 6/poly(MAH-*co*-VAc)H blends decreased with increasing copolymer concentrations. In this figure, the relative degree of crystallinity was calculated from the X-ray diffractograms of the blends based on that of nylon 6 homopolymer. For nylon 6/poly(MAH-*co*-VAc)H blends, the degree of crystallinity showed drastic decreases around blend concentrations above 50 wt%. The result is totally in accordance with the melting point depression behaviour, as already seen in *Figure 3*. On the basis of thermal analysis, optical clarity, and *FT*i.r., the X-ray diffraction patterns of nylon 6/poly(MAH-*co*-VAc)H may be certainly due to the molecular interaction, i.e. hydrogen bonding, of the copolymer with nylon 6 at the blend concentration above 75 wt%.

CONCLUSIONS

Miscibility of nylon 6/poly(MAH-*co*-VAc) and nylon 6/poly(MAH-*co*-VAc)H blends were investigated by *FT*i.r. spectroscopy, thermal analysis, and X-ray diffraction. Poly(MAH-*co*-VAc) was synthesized by radical copolymerization and the copolymer was hydrolysed to form poly(MAH-*co*-VAc)H. Blend films were cast from formic acid solutions. It was found that the nylon 6/poly(MAH-*co*-VAc) blends showed immiscible behaviour over the entire range of copolymer concentrations, whereas nylon 6/poly(MAH-*co*-VAc)H blends showed miscible behaviour at more than 75 wt% copolymer concentrations. From the *FT*i.r. results, it was found that C=O singlet peaks at 1780 cm^{-1} due to the carboxylic acid group and the N–H peak at 1540 cm^{-1} due to the amide group were sensitive to the miscibility of nylon 6/poly(MAH-*co*-VAc)H blends. The X-ray diffraction studies showed that poly(MAH-*co*-VAc)H affected the structure of nylon 6/poly(MAH-*co*-VAc)H blends at blend concentrations above 50 wt% due to the strong hydrogen bonding interactions between the carboxylic acid group of the copolymer and the amide group of nylon 6.

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