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Miscibility of nylon 46 and ethylene–vinyl alcohol copolymer blends

Chang-Sik Ha, Myung-Geuk Ko, and Won-Jei Cho*
Department of Polymer Science and Engineering, Pusan National University, Pusan 609–735, Korea
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Miscibility of blends of nylon 46 and ethylene-*co*-vinyl alcohol copolymer (EVOH) was investigated. Blends were prepared by casting from formic acid. Miscibility of the blends was investigated by means of Fourier transform infrared (*FT*i.r.) spectroscopy and thermal analysis. Tensile properties of the nylon 46/EVOH blends were measured using a tensile tester. Based on optical clarity and melting temperature behaviours, it was shown that the nylon 46/EVOH blends are miscible at concentrations below 35 wt% of nylon 46. The blends having less than 35 wt% of nylon 46 showed strong intermolecular interaction between the C–O group of EVOH and the N–H group in nylon 46. X-ray diffraction (XRD) studies showed that the crystalline structure of nylon 46 was altered when the blend composition is 35/65 nylon 46/EVOH by wt%. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: miscibility; nylon 46; ethylene–vinyl alcohol copolymer)

Introduction

Although nylon 6 and nylon 66 have been widely used as high-strength engineering plastics, they have a few shortcomings for textiles such as their high water absorption, poor heat resistance, and rough feel to the skin. Several attempts have been made to modify nylon 6 or nylon 66 for synthesizing new polyamides or blending of nylons with other polymers[1–5]. Nylon 4 has been developed by Ney *et al.*, to solve the above problems of nylon 6 and nylon 66, from 2-pyrrolidone[6,7], although ϵ-caprolactam (CL) was anionically polymerized to give nylon 6.

For three decades, nylon 46 has attracted great interest in the textile industries in spite of the difficulty in its synthesis, since it may be expected that nylon 46 possesses balanced properties of nylon 4 and 6 by condensation polymerization of corresponding diacid and diamine[8] or anionic ring-opening copolymerization of 2-pyrrolidone and ϵ-caprolactam[9,10]. Even though nylon 46 exhibits generally good balance of mechanical properties, blending it with other polymers is still needed to improve its barrier properties and impact strength as well as to secure the price competition. Thus, we attempted to blend nylon 46 with ethylene–vinyl alcohol copolymer (EVOH) in this work, since it is well known that the blend of nylon 6 and EVOH has good barrier properties. It may be expected that the blend of EVOH and nylon 46 can be applicable as a packing material for foods, drugs, and cosmetics. Since EVOH has also been used as an impact modifier for glass fibres, the properties of the blend of nylon 46/EVOH may give insights into the development of glass fibre reinforced nylon 46/EVOH blend composites.

Usually, however, the poor miscibility of nylon 6 with other polymers has been pointed out intensively because of the too strong hydrogen bonding characteristics of nylon 6[1–4] itself. Thus, several attempts have been made to enhance the poor miscibility of nylon 6 containing blends[11]. Typical examples include the use of ethylene–propylene rubber (EPR)–*g*-maleic anhydride in the blends of nylon 6 and EPR and polypropylene-*g*-maleic anhydride in the blends of nylon 6 and polypropylene[11]. The EVOH possessing C–O group, however, is expected to have some interaction with nylon 46 having an amide group.

In this communication the miscibility of nylon 46/EVOH blends, as investigated by optical clarity, differential scanning calorimeter (d.s.c.), X-ray diffractometer (XRD), tensile tester, and Fourier transform infrared spectroscopy (*FT*i.r.), is reported.

Experimental

Materials. 2-Pyrrolidone (Aldrich) was distilled under reduced pressure after refluxing with P_2O_5. ϵ-Caprolactam (Aldrich) was used after recrystallization from a mixed solvent of petroleum ether/acetone (1 : 1 v/v). Reagent grades of potassium chloride (Aldrich), *n*-acetyl caprolactam (Aldrich) and other chemicals were used as received. Nitrogen was used after purification with an alkali solution of pyrogallol, sulfuric acid, KOH and silica gel. Ethylene–vinyl alcohol copolymer (EVOH; Aldrich, ethylene content, 27 mol%; vinyl acetate, 13 mol%) was used as received.

Nylon 46 was synthesized in our laboratory; a mixture of 0.1 mol (8.5 g) of 2-pyrrolidone, 0.016 mol (0.9 g) of KOH, and 0.1 mol (11.31 g) of ϵ-caprolactam was mixed in a 3-necked flask at 80°C. The water formed is removed by distilling off at 110°C for 30 min under 4 mmHg. The reaction mass was cooled to room temperature and dry CO_2 gas was admitted to the flask. The flask was sealed after charging with nitrogen gas and stirring at 80°C for 10 min. The reaction was heated at 130°C for 48 h. Details of the synthesis of nylon 46 will be reported elsewhere[12]. Purification of the polymers was accomplished by reprecipitation in hot water, washed with acetone, and then dried in a vacuum oven until a constant weight. Nylon 46 was identified by i.r. spectroscopy (Jasco FTIR5300 spectroscopy) and elemental

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* To whom correspondence should be addressed

analysis (Carlo Erba Elemental analyser 1180): The viscosity $[\eta]$ in *m*-cresol of nylon 46 used in this work is $2.6\,\mathrm{dl\,g^{-1}}$. From the calculated elemental analysis data (%) (C: 57.42, N: 14.59, H: 9.44), the mole ratio of nylon 4 to nylon 6 in nylon 46 was calculated as 69/31.

Preparation of blends. Films of nylon 46/EVOH blends with various concentrations were prepared by casting from 10 wt% solutions of formic acid. The films were dried slowly in a Petri dish at room temperature and then kept under a vacuum until they reached constant weight. The films underwent optical clarity and thermal analysis tests. For the *FT*i.r. analyses, films were prepared separately.

Measurements. The viscosity of nylon 46 was determined by a Cannon–Fenske viscometer (200 M331) at 25°C in *m*-cresol. Melting temperatures (T_ms) were measured using d.s.c. (DuPont 910 DSC) calibrated with pure indium as a standard. In order to avoid the thermal history from the samples packed in the aluminium pan and to eliminate any small traces of solvent, samples were heated to 423 K at a heating rate of $30^\circ\mathrm{C\,min^{-1}}$, annealed at 423 K for 5 min, and then quenched to 203 K at a rate of $80^\circ\mathrm{C\,min^{-1}}$. Thermograms of the blends were obtained at a heating rate of $10^\circ\mathrm{C\,min^{-1}}$. All the T_ms were recorded on the second heating scan. Thermal stability of samples was measured by thermogravimetric analysis (DuPont 951 TGA) at a scanning rate of $15^\circ\mathrm{C\,min^{-1}}$ under nitrogen. I.r. spectra were obtained using a Jasco 5300 spectrophotometer. Thin films of nylon 46, EVOH and blend samples were prepared by direct casting onto a potassium bromide disc from 0.5% solution of formic acid. The solvent was removed by drying in a vacuum oven at room temperature for two weeks. The thickness of the films was in the range of 2–3 μm. Forty scans at a resolution of $4\,\mathrm{cm^{-1}}$ were signal-averaged. Tensile tests were performed using an Instron Tensile Tester (Model 4204). The samples were prepared following the precedure of ASTM D1708-84. The crosshead speed was $50\,\mathrm{mm\,min^{-1}}$, and the initial gauge length was adjusted at 25 mm. X-ray diffraction patterns were obtained with the Rigaku Denki X-ray diffractometer (D/MAX-2400) using nickel filtered Cu*K*α radiation (30 kV, 20 mA).

Results and discussion

Optical clarity and T_m *behaviour.* The optical clarity and the T_ms of the nylon 46/EVOH blends are summarized in *Table 1*. In this table, the miscibility is determined by the optical clarity of the blend films. The nylon 46/EVOH blends are miscible only at below 35 wt% of nylon 46 concentration. The single T_m behaviour of the EVOH-rich blends may be thought to be related to the miscible behaviour at the concentrations. Nylon 46 showed two melting temperatures at 131°C and 247°C, meaning that nylon 46 consists of two separate blocks of a nylon 4 unit and a nylon 6 unit. It is interesting that the blend having the concentration below 50 wt% of EVOH shows two separate T_ms, one higher and one lower, where the lower T_m is increased by 30°C, being close to that of EVOH. However, the blend of more than 65 wt% of EVOH shows only one T_m, being an intermediate value between the inherent T_m of each component. The result shows that the blends having 15–50 wt% of EVOH exhibit no miscibility, whereas the blends having 85 and 65% of EVOH show miscibility. The increase of T_m of nylon 46 at 131°C in the blend with EVOH to 163°C is due to restriction on its molecular mobility due to the presence of EVOH that melts at 183°C.

Table 1 Miscibility based on the optical clarity and melting temperature for nylon 46/EVOH blends

Sample nylon 46/EVOH (wt%)	Optical clarity	T_m (°C)	Miscibility
100/0	Translucent	131,247	-
85/15	Translucent	163,246	Immiscible
65/35	Translucent	163,245	Immiscible
50/50	Translucent	163,245	Immiscible
35/65	Clear	243	Miscible
15/85	Clear	237	Miscible
0/100	Clear	183	-

FT*i.r. spectroscopy. FT*i.r. spectroscopy has been used as a tool for elucidation of specific interaction in a miscible polymer blend[13]. We have investigated the variation of the relative intensity of a doublet in the 1500–1800 $\mathrm{cm^{-1}}$ region in the *FT*i.r. spectra of nylon 46/EVOH blends.

Figure 1 shows the relative intensity of the i.r. peak around the 1700 $\mathrm{cm^{-1}}$ region for the nylon 46/EVOH blends. The peaks of the carbonyl group in EVOH shifted to lower wavenumber up to 35% of nylon 46

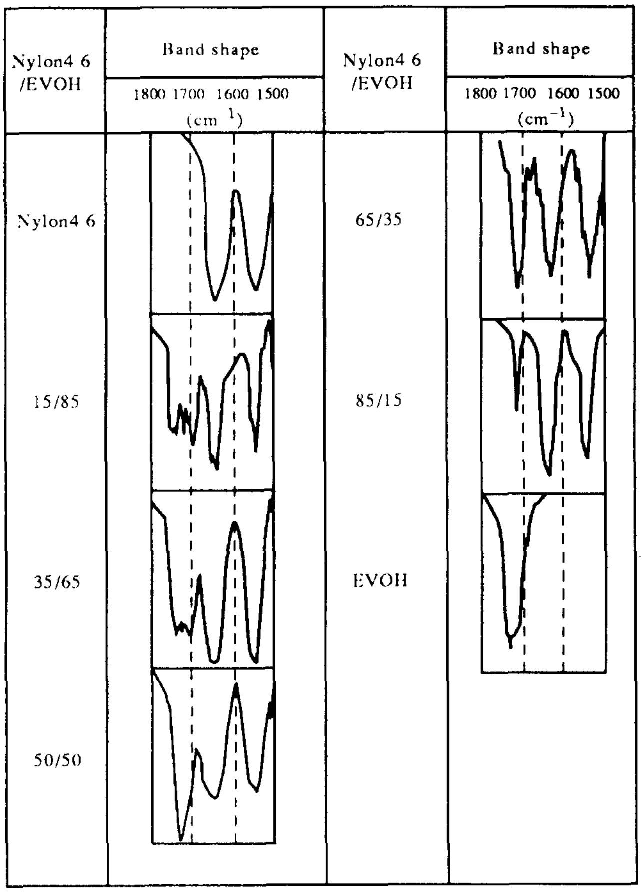

Figure 1 Relative intensity of the peak around 1700 $\mathrm{cm^{-1}}$ of nylon 46/EVOH blends on i.r. spectrum as a function of blend concentrations

contents by 10 cm^{-1} but no shift in the peaks were observed for the blends having more than 65% of nylon 46. The peak shift suggests that there exists some interaction between EVOH and nylon at higher EVOH contents. The interaction is also proved by the new peak around 1727–1747 cm^{-1} for the blends having 85 and 65% of EVOH, indicating a strong interaction between the component, whereas these peaks were not observed for both nylon 46 and EVOH. The miscibility between nylon 46 and EVOH may be strongly dependent on the strength of the interaction between the C–O group and the N–H group in amide. When the composition of the blend is more than 35% of nylon 46, the interaction between the components becomes weaker with increasing nylon 46 concentration. This suggests that a certain molecular interaction exists between the N–H group of nylon 46 and the C–O group of EVOH. It is suggested that these interactions are hydrogen bonding and/or dipole–dipole interaction between the C–O group of EVOH and the N–H group in nylon 46, and that these interactions may vary with the concentration of the blend.

When the concentration of nylon 46 is higher, the interaction may be thought to be lower, because of strong intramolecular interaction in each homopolymer such as hydrogen-bonding characteristics resulting in preventing the intermolecular interaction between nylon 46 and EVOH.

X-ray diffraction. The effect of amorphous polymer on the crystal structure of crystalline polymers has been intensively reported[14–16]. For instance, the incorporation of elastomers alters the superstructure of the crystalline polymer, such as the PP matrix, by changing the average size and number of the spherulites, and this change in the superstructure is very important in interpreting the impact modification of the elastomer with the PP matrix[15,16]. A similar tendency can be expected for the crystalline/crystalline polymer blend systems, when they show miscibility. The XRD of the nylon 46/EVOH binary blend shows two characteristic peaks due to the crystalline structure of nylon (although EVOH is semicrystalline, it shows very weak crystalline structure), in the region of the Bragg angle (2Θ) between 10° and 50° (*Figure 2*). Those strong diffraction peaks are located at the 2Θ angles of 20.3° and 24°. The two peaks correspond to the (2 0 0) and (0 2 0) planes, respectively, and are characteristic of the typical α-form monoclinic structure of nylon 6[17].

The diffractograms show that the incorporation of EVOH does not change significantly the crystal structure of nylon 46 and EVOH mixtures. Of interest in *Figure 2*, however, is that the incorporation of 65 wt% of EVOH affects the crystalline structure of nylon 46 considerably. In the XRD of 35/65 nylon 46/EVOH blend, a new sharp peak, which is related to the (3 0 0) reflection of the γ-form phase of nylon 6, appears at $2\Theta = 21.8°$. This implies that incorporation of 65% of EVOH gives rise to the formation of a new crystalline structure associated with the γ-form of the nylon 6 crystal. The essential change in the crystalline structure also suggests the increase of the amount of γ-form crystals, which existed in the nylon 46 homopolymer used in the study, if any, relative to that of major ingredients, α-form crystals. The result is thought to be closely related to the interaction between two components leading to the miscibility of the blends. In our previous result, a similar change in the crystalline structure was observed when polyethylene glycol was grafted onto nylon 6[2]. Karger-Kocsis *et al.*[15] found such an alteration in crystalline structure in the PP/ethylene–propylene rubber (EPR) blend having 75/25 composition by weight and they explained the structural changes using partial compatibility effect between two components in the molten state due to the EPR selectively extracting the defective molecules in PP. Therefore, the above XRD results indicate that nylon 46 and EVOH are miscible at 35/65 composition.

Tensile properties. Table 2 shows the tensile properties of the nylon 46/EVOH blends as a function

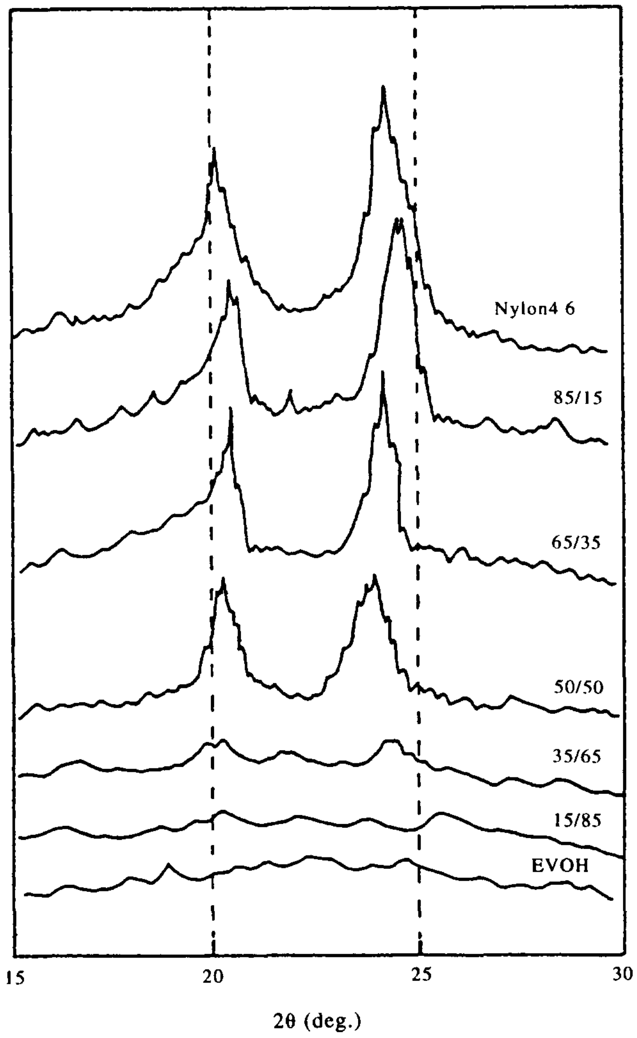

Figure 2 X-ray diffractograms of nylon 46/EVOH blends

Table 2 Comparison of tensile strength and elongation at break of nylon 46/EVOH blends

Sample Nylon 46/EVOH (wt%)	Tensile strength (kg cm^{-2})	Elongation at break (%)
15/85	4	2684
35/65	18	1715
50/50	42	318
65/35	106	138
85/15	178	173
100/0	331	213

of the blend concentrations. Tensile strength decreased monotonously with the EVOH content, but the elongation at break increased as the EVOH content increased. The reduction in tensile strength should be expected as the result of the rubbery nature of EVOH. The remarkable increase in the elongation at break should be noted, however, when 65 wt% of EVOH was added to nylon 46. This result is also related to the miscibility between EVOH and nylon 46 at the composition.

In conclusion, the optical clarity, T_m behaviour by d.s.c. showed that the blends containing more than 65 wt% of EVOH by weight showed miscibility with nylon 46. From the *FT*i.r. results, the relative intensity at 1700 cm^{-1} peak of the C–O band in EVOH and the position of the N–H group of nylon 46 were sensitive to the miscibility of the blends. An alteration was observed in the crystalline structure of nylon 46 when 65 wt% of EVOH was added.

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References

1 Iwasaki, T. and Tomita, K. *J. Soc. Fib. Sci. Jpn.* 1992, **28**, 127

2 Ha, C. S., Choi, H. Y. and Cho, W. J. *Polym. Bull.* 1991, **2**, 185

3 Ha, C. S., Lee, W. K., Roe, T. W. and Cho, W. J. *Polym. Bull.* 1993, **31**, 359

4 Paul, D. R. and Barlow, J. N. *J. Macromol. Sci. Rev. Macromol. Chem.* 1980, **C18**(1), 109

5 Ha, C. S., Lee, S. W. and Cho, W. J. *Polymer* 1996, **37**, 3347

6 Ney, Jr. W. O., Nummy, W. R. and Barnes, C. E. U.S. Patent 2,638,463, 1953

7 Ney, W. O. and Crowther, M. U.S. Patent 2,739,956, 1956

8 Roerdink, E. and Warnier, J. M. *Polymer*, 1985, **26**, 1582

9 Kobayashi, F. and Matsuya, K. *J. Polym. Sci.* 1963, **1**, 111

10 Barzakay, S., Levy, M. and Vofsi, D. *J. Polym. Sci.* 1967, **A-1**(5), 965

11 Bonner, J. G., Hope, P. S. and Jackson, A. S. in *Polymer Blends and Alloys*, Chap. 3, ed. M. J. Folkes and P. S. Hope, Blackie Academic and Prof., Glasgow, 1993

12 Ha, C. S., Ko, M. G. and Cho, W. J. in preparation

13 Coleman, M. L., Graf, J. F. and Painter, C. *Specific Interactions and the Miscibility of Polymer Blends*, Technomic Publ. Co., 1991, Chap. 5

14 Ha, C. S. and Kim, S. C. *J. Appl. Polym. Sci.* 1988, **35**, 2211

15 Karger-Kocsis, J., Kallo, A., Szafner, A., Bodor, G. and Senyei, Zs. *Polymer* 1979, **20**, 37

16 Martuscelli, E., Silvester, C. and Abate, G. *Polymer* 1982, **23**, 229

17 Parker, J. P. and Lindenmeyer, P. H. *J. Phys. Sci.* 1977, **21**, 821