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Compatibility of nylon 6 with poly(vinyl alcohol), hydroxylated poly(vinyl acetate) and poly(vinyl acetate)

Chang-Sik Ha[1], Won-Ki Lee[1], Tae-Woo Roe[2], and Won-Jei Cho[1]

[1]Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea
[2]Suhryung Materials Research Institute, Yang San, Kyung Sang Namdo, 626-800, Korea

SUMMARY

The compatibility of nylon 6 with poly(vinyl acetate)(PVAc) and poly(vinyl alcohol)(PVA) was investigated in terms of the melting-temperature depression. In order to vary the compatibility systematically, a hydroxylated poly(vinyl actate)(m-PVAc) was prepared by hydrolyzing PVAc with KOH in CH_3OH. It was found that the compatibility with nylon 6 is better in the systematic order PVA 〉 m-PVAc 〉 PVAc.

INTRODUCTION

It is well-known that nylon 6 has poor compatibility with other polymers because of its strong hydrogen bonding characteristics (1,2). Few investigation on the nylon 6-containing blends has yet been made, even though the study of polymer compatibility has undergone an enormous expansion in recent decades.

Attempts to improve the poor compatibility of nylon 6 with other polymers include the modification of nylon 6 or other component polymer by introducing polar group like hydroxyl group into the backbone of nylon 6 or amide group into the other component polymer (3-7).

Seo et al. (8) prepared poly(methyl methacrylate) (PMMA)-oligoamide graft copolymer in order to improve the poor compatibility of nylon 6 with PMMA. Ha et al. (9) synthesized nylon 6-g-poly(ethylene glycol) copolymer and reported on the compatibilizing effect of the graft copolymer in the nylon 6/poly(ethylene glycol) blend of 50/50 composition by weight.

In this work, the compatibility of nylon 6 with poly(vinyl acetate) (PVAc) and poly(vinyl alcohol) (PVA) was investigated. Compatibility was judged from the melting temperature depression. Glass transition behavior is widely accepted to be indicative of the compatibility of polymer blends. In the crystalline polymers, however, the melting temperature depression is usually used to determine the compatibility, since glass transition behavior may be subject to a variety of complications in crystallizable polymers (8). In order to investigate the compatibility of nylon 6 with PVAc and PVA systematically, we prepared one kind of hydroxylated PVAc by hydrolyzing PVAc with KOH in CH_3OH.

EXPERIMENTAL

Materials

Nylon 6 was obtained from the Research Institute of Kolon Co. Ltd. and was degassed before use at 60℃ for one week under vacuum. Poly(vinyl acetate) (PVAc) or poly(vinyl alcohol) (PVA) was a commercial product from Junsei and Kuraray Poval, respectively. The molecular weight characteristics of samples used in this work are listed in Table 1. The molecular weights were determined by GPC (Waters 244).

Preparation of Hydroxylated PVAc (m-PVAc)

Hydroxylated PVAc (m-PVAc) was prepared by hydrolyzing PVAc. 50g

Table 1. Characteristics of Polymers

Polymer	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n	Source
Nylon 6	1.73	3.45	1.99	Kolon
PVAc	6.48	9.93	1.53	Junsei
PVA	6.60	10.02	1.52	Kurarey

Table 2. Solubility characteristics of PVAc and m-PVAc

	Methanol	DMF	Formic acid	Water	THF
PVAc	S[a]	S	S	I[a]	S
m-PVAc	S	S	S	I	I

[a] S : soluble I : insoluble

of PVAc were dissolved in 400ml of methanol and then added with 8.7mmol of KOH with stirring at room temperature for 30min. Purification of the product was accomplished by reprecipitation in water from the methanol solution and then drying in a vacuum oven until kept at a constant weight. As shown in Fig.1, the m-PVAc was identified on IR spectrum by the OH band around 3430 cm^{-1} and the C-O stretching band at 1248 cm^{-1}. The OH content of the resultant m-PVAc was determined as 34% following the JIS-6730 standard. Table 2 shows the solubility characteristics of m-PVAc. It was found that the solubilities of m-PVAc in common organic solvents are similar as those of PVAc except in THF.

Blend Preparation

Blends of nylon 6 with PVAc, PVA and m-PVAc were solution-cast from formic acid. Solvent was allowed to evaporate slowly in the air at room temperature. The resulting films were further dried in vacuum at 30℃ to constant weight.

Measurements

Melting temperature, T_m, and heats of fusion, ΔH_{fus}, were measured by

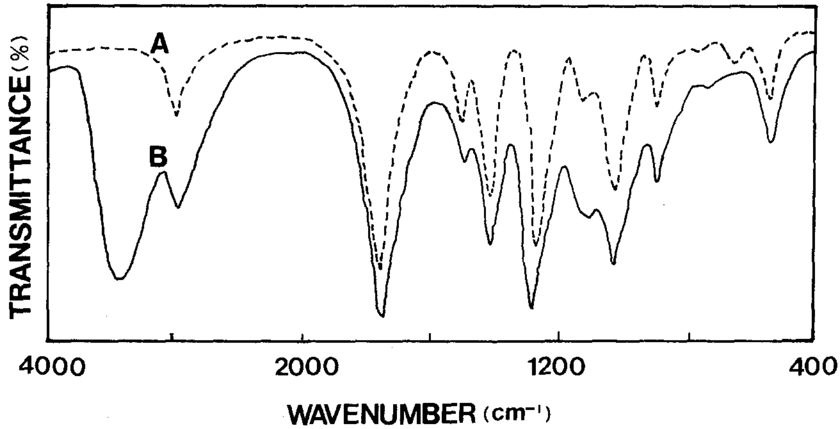

Fig.1. IR spectra of PVAc(A) and m-PVAc(B).

Differential Scanning Calorimeter(Perkin-Elmer DSC-4). The scans were made out at a heating rate of 10℃/min. The relative degree of crystallinity, X_c, was calculated from

$$X_c = \Delta H_{fus} / \Delta H_{fus}^{\circ}$$

where ΔH_{fus} and ΔH_{fus}° are the heat of fusion of the blend and the heat of fusion of the nylon 6 homopolymer used in this study, respectively. The crystalline structure was determined using X-ray diffractometer (Rigaku Denki). Nickel filtered CuKα radiation was applied at 30 kV and 20mA. Scanning electron micrographs(SEM) were obtained by JEOL 35-CF SEM. Samples were cryogenically fractured in liquid nitrogen and metallized by gold coating prior to the installation in the SEM chamber.

RESULTS AND DISCUSSION

Compatibility of Nylon 6 Blends

Fig. 2 shows the melting temperature(T_m) of nylon 6 in the blends of nylon 6 with PVAc, m-PVAc and PVA. It is shown that the T_m's of the nylon 6/PVAc blends are almost the same regardless of the blend compositions, whereas the T_m's of the nylon 6/PVA blends decrease with increasing PVA comopsitions. The result indicates that the nylon 6/PVAc blends were incompatible while the nylon 6/PVA blends are partially compatible, when the compatibility is judged from the melting point depression. Depression of melting point is usually considered to indicate a negative Flory interaction parameter, χ, meaning that the polymer blend is thermodynamically miscible in liquid state(in melt). Below the melting point, however, crystal-liquid phase separation must surely take place and the process of crystallization is essential to define the 'compatibility'. If χ is positive, the crystal-liquid phase separation below the melting point competes with liquid-liquid phase separation above it. The χ parameters at 221℃ were estimated as -0.027 - -0.055 for nylon 6/PVA blends using the quantitative analysis of the melting point depression for the polymer blends with components compatible in the melt, which had been presented by Nishi and Wang(10).

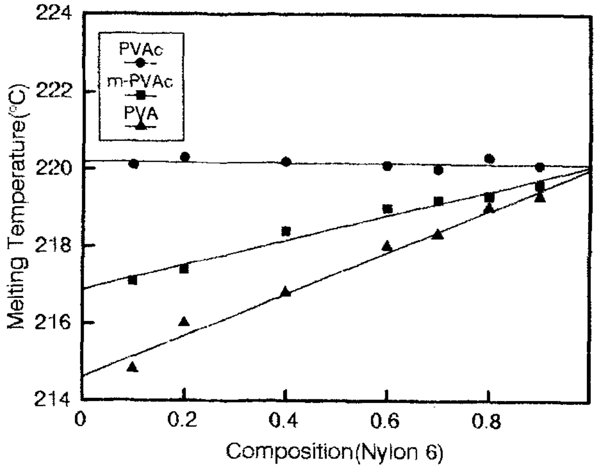

Fig.2. Plots of Tm vs. composition of nylon 6 in nylon 6-containing blends.

In this work, the χ parameter is dependent on the blend composition. (More details on this subject will be described elsewhere.) Even though the nylon 6/PVA blends exhibit melting point depression and negative χ values, it can not be assured that the blends are 'turely' thermodynamically miscible in the liquid state because the χ values are nearly close to zero(11). Moreover, it should be noted that direct use of experimental melting points in the expression describing melting point depression can potentially result in a serious underestimation of χ (12). Thus, it is believable that the 'compatibility' in this work does not mean thermodynamical miscibility but rather easiness of mixing blends in smaller size of domain, even though more precise interpretation should be necessary. This kind of speculation may be proved by the morphology of the blends. Thus, in this work, the compatibility of the blends below the melting point, where crystal-liquid phase separation takes place, attracts our interest. In order to interpret our experimental results more accurately, studies on the crystallization process of the nylon 6/PVA blend system are now undertaking.

In Fig.2, it is also interesting to note that the T_m's of nylon 6/m-PVAc blends lie between those of nylon 6/PVAc blends and those of nylon 6/PVA blends over the entire blend compositions. It is expected that the T_m depression behavior of the blend of nylon 6 with m-PVAc having higher hydroxyl contents approaches to that of the nylon 6/PVA blends to larger extent. It may be thought that the blend compatibility of nylon 6 with m-PVAc will be systematically varied from that of nylon 6 with PVAc to that of nylon 6 with PVA, depending on the

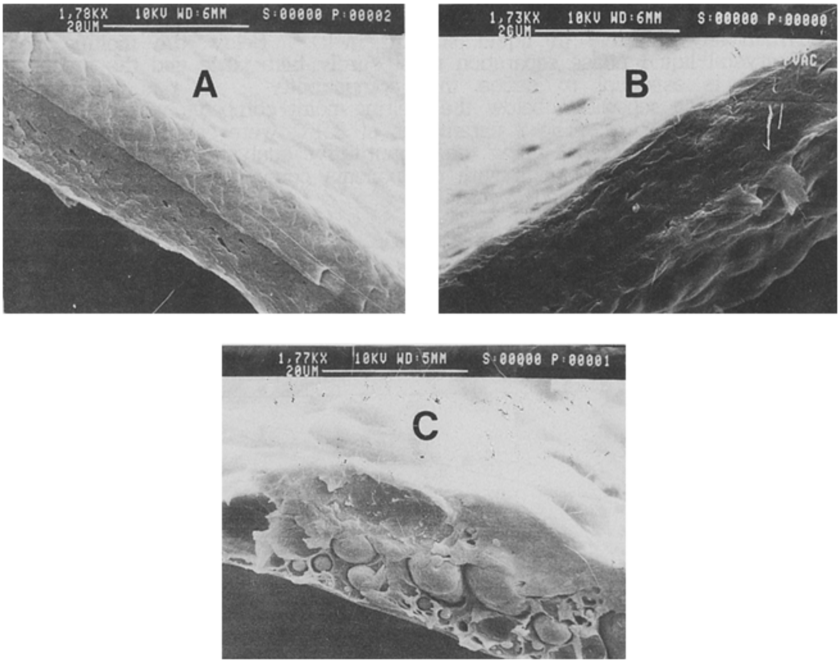

Fig.3. SEM micrographs of nylon 6-containing blends having 50/50 composition by weight.
A:nylon 6/PVAc B:nylon 6/m-PVAc C:nylon 6/PVA

hydroxyl contents in m-PVAc. The different compatibility of nylon 6 with PVAc and PVA can be also identified in the morphologies of blends by SEM. Fig. 3 shows the SEM micrographs of the nylon 6/PVAc (A), nylon 6/m-PVAc (B) and nylon 6/PVA (C) blend of 50/50 composition by weight. It is seen that two-layer-film structure with clear layer boundary due to the complete phase separation is observed for the nylon 6/PVAc blend whereas phase-interpenetrated structure due to the partial compatibility between two components is observed for the nylon 6/PVA blend. The SEM micrographs clearly show that the compatibility of nylon 6 with PVA is much better than that with PVAc. Careful inspection of the SEM micrograph of the nylon 6/PVA blend indicates, however, that nylon 6 and PVA are not compatible in the molecular level. As expected, neither two-layer-film structure nor phase-interpenetrated structure was observed for the nylon 6/m-PVAc blend. The morphology of the nylon 6/m-PVAc blend lies between that of nylon 6/PVAc blend and that of nylon 6/PVA blend.

It should be noted that the details of the compatibility behavior are significantly affected by molecular weight and molecular weight distribution. However, in this work, the molecular weights and the polydispersities of PVAc and PVA are closely comparable. Thus, in comparing the relative compatibility of PVAc and PVA with nylon 6, the conclusions drawn should be unaffected by any minor errors due to the differences in the molecular weight characteristics (13).

Crystalline Structure

Fig. 4 shows the relative degree of crystallinity of nylon 6 in the blends against the blend compositions. The relative degree of crystallinity decreased linearly with decreasing nylon 6 compositions in the blends, which simply means no change of crystallinity in the usual sense. No significant differences in the relative degree of crystallinity of nylon 6 was, however, observed among the blends of nylon 6 with PVAc, m-PVAc, and PVA. Fig. 5 shows the X-ray diffractograms of the nylon 6-containing blends. The diffraction pattern of nylon 6 used in this study shows typical γ-form structure, since the peak was appeared at the Bragg angle $2\theta = 21.6°$. It was reported that the α-form of nylon 6 has strong diffraction peaks at 2θ at $20.5°$ and $23.8°$ corrsponding to (200) and (020)

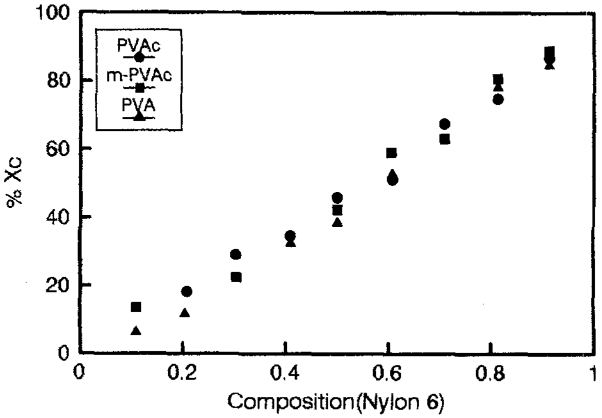

Fig.4. Relative degree of crystallinity vs. composition of nylon 6 in nylon 6-containing blends.

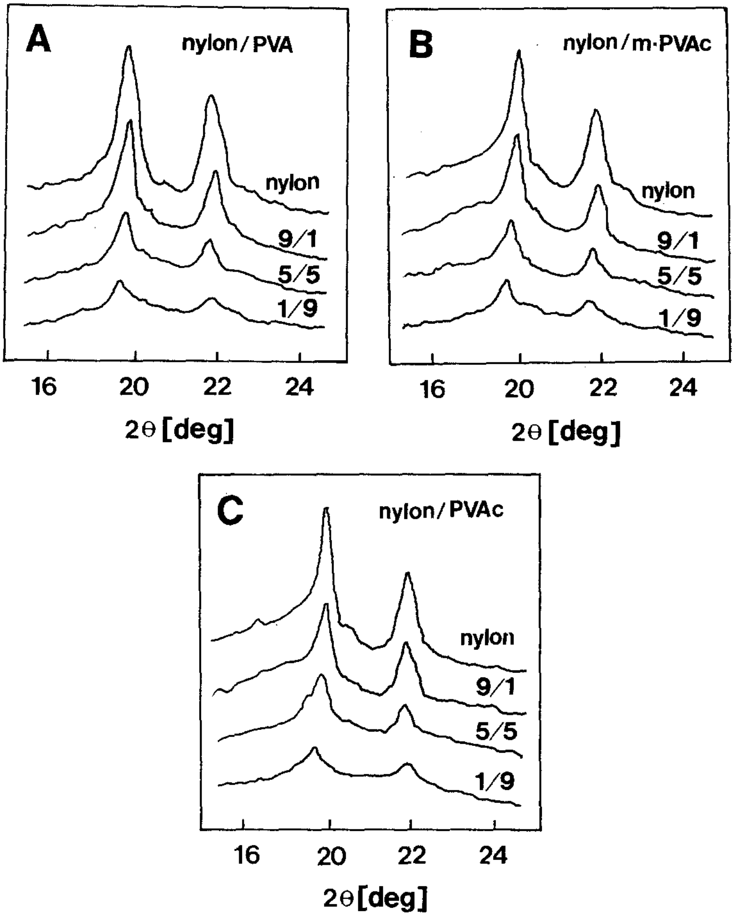

Fig.5. X-ray diffractograms of nylon 6-containing blends with various compositions.

planes(14-16). The X-ray diffractograms of the nylon 6/PVA blends, shown in Fig. 5-A, showed characteristics peaks of the nylon 6 with no additional peaks. The intensities of the peaks changed according to their blend compositions. The result is primarily due to the decrease of nylon 6 content in the blends, so that it does not imply the decrease of crystallinity in the usual sense. The trend is in accordance with the results from the DSC thermograms, as shown in Fig. 4. Similar trends were observed in the X-ray diffractograms of the blends of nylon 6 with m-PVAc and PVAc (see Figs. 5-B and 5-C). The results imply that the presence of PVAc, m-PVAc, and even PVA do not affect on the crystalline structure of nylon 6.

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