Miscibility window in nylon 6-*g*-poly(ethylene glycol)/poly(vinyl acetate) blends

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The compatibilizing effect of a new graft copolymer of poly(ethylene glycol) (PEG) on nylon 6 (nylon 6-*g*-PEG) was investigated for nylon 6/poly(vinyl acetate) (PVAc) blends by using melting-point depression and X-ray diffractograms. It was found that nylon 6-*g*-PEG exhibits no compatibilizing effect for the nylon 6/PVAc blends, but the graft copolymer itself shows a miscibility window in its blends with PVAc for blend compositions containing less than 50 wt% of the graft copolymer.

(Keywords: graft copolymer; blend; miscibility window)

Introduction

Compatibilizers or interfacial agents in polymer blends have attracted much interest from theoretical and practical standpoints[1-10]. It has been reported that a block copolymer or a graft copolymer improves the interfacial adhesion between domains and the continuous phase in a polymer blend, and thus can be used as a compatibilizer. The compatibilizing effect of block copolymers in immiscible polymer blends has been investigated extensively, but few systematic studies have been reported to date on the compatibilizing effect of graft copolymers in polymer blends[4-8].

In our previous work[4], we prepared a graft copolymer of poly(ethylene glycol) (PEG) on nylon 6 (nylon 6-*g*-PEG), and investigated its compatibilizing effect in nylon 6/PEG blends. It was observed that compatibilization of the nylon 6/PEG 50/50 (w/w) blend was achieved in the presence of the graft copolymer. Bearing in mind that nylon 6 is incompatible with poly(vinyl acetate) (PVAc) over entire blend compositions, in this work we tested the potential applications of the new graft copolymer as a compatibilizer for nylon 6/PVAc blends.

In this communication, we also report the miscibility behaviour of blends of the graft copolymer and PVAc. Differential scanning calorimetry (d.s.c.), scanning electron microscopy (SEM) and X-ray diffractometry were used to determine the miscibility.

Experimental

Nylon 6 was obtained from the Research Institute of Kolon Co. Ltd, Korea, and was degassed before use at 60°C for 1 week under vacuum. PEG with $M_w = 6000$ (Aldrich) and PVAc (Junsei) were used as received.

The nylon 6-*g*-PEG copolymer was prepared by a two-step reaction, as described elsewhere[9]: PEG was chlorinated with thionyl chloride in carbon tetrachloride and then the chlorinated PEG was grafted onto nylon 6 by reacting with triethylamine and tin chloride in *o*-chlorophenol. The wt% of PEG in the graft copolymer was determined as 36.0% from the weight loss after hydrolysis in 10% aqueous HCl solution for 24 h.

The molecular weight characteristics of polymers in this work are listed in *Table 1*. The molecular weights were determined by gel permeation chromatography (Waters 244) and are relative to polystyrene.

Two kinds of blends were prepared from nylon 6, PVAc and nylon 6-*g*-PEG by casting from formic acid: nylon 6/PVAc and nylon 6-*g*-PEG/PVAc. Compositions of the blends varied from 10/90 to 90/10 by weight. In order to investigate the compatibilizing effect of the graft copolymer in nylon 6/PVAc blends, ternary blends containing 5, 10, 15 and 20 wt% of the graft copolymer with the nylon 6/PVAc 50/50 blend were also prepared by casting from formic acid. Solvent was allowed to evaporate slowly in air at room temperature. The resultant blend films were further dried in vacuum at 35°C to constant weight.

Melting temperature, T_m, was measured by d.s.c. (Perkin–Elmer DSC-7). The scans were made at a heating rate of 10°C min^{-1}. The crystalline structure was determined using an X-ray diffractometer (Rigaku Denki). Nickel filtered CuKα radiation was applied at 30 kV and 20 mA. SEM was carried out using a Jeol 35-CF scanning electron microscope. Samples were cyrogenically fractured in liquid nitrogen and metallized by gold coating prior to the installation in the SEM chamber.

Results and discussion

Figure 1 shows the T_m values of nylon 6 in the binary blends of PVAc with nylon 6 or nylon 6-*g*-PEG and the

Table 1 Characteristics of polymers[a]

Polymer	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n	Supplier
Nylon 6	1.73	3.45	1.99	Kolon
Nylon 6-*g*-PEG	3.27	8.53	2.61	Synthesized
PVAc	6.48	9.93	1.53	Junsei

[a] Molecular weight values are relative to polystyrene

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ternary blends of nylon 6, PVAc and the graft copolymer. The T_ms of nylon 6 and the graft copolymer were measured at 225.2°C and 211.3°C, respectively. The graft copolymer showed double melting temperatures: the lower one (59.4°C) is that of PEG and the higher one (211.3°C) is that of nylon 6. The lower T_m was the same as that of PEG homopolymer, but the higher T_m of the graft copolymer was about 14°C below that of nylon 6 homopolymer. This indicates that a certain portion of PEG molecular chains prevents nylon 6 from crystallizing and gives the nylon 6 backbone chain considerable flexibility[4]. No significant difference was observed in the T_ms of PEG for both the nylon 6/PVAc/nylon 6-*g*-PEG ternary blends and the graft copolymer/PVAc binary blends. In *Figure 1*, it is seen that the T_ms of the nylon 6 in both binary and ternary blends are almost the same, regardless of the blend compositions, whereas the T_ms of the graft copolymer/PVAc blends decrease with increasing PVAc compositions in the blends. The result indicates that the nylon 6/PVAc blends are immiscible, while the graft copolymer/PVAc blends are partially miscible when the miscibility is judged from the melting point depression[11,12].

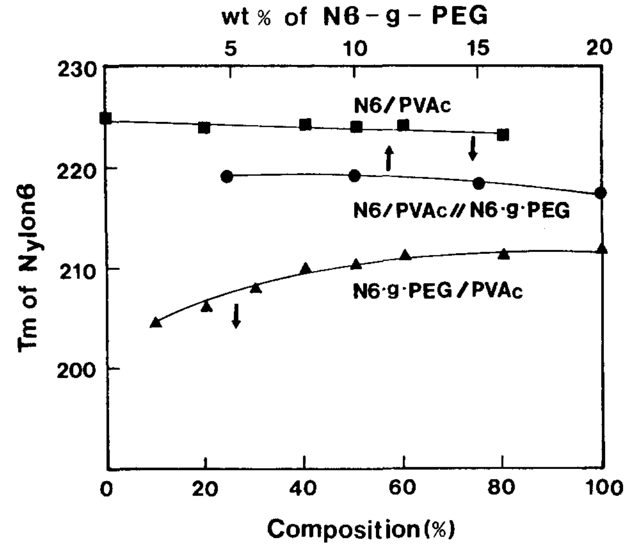

Figure 1 Melting temperatures of nylon 6 in the binary blends of PVAc with nylon 6 or nylon 6-*g*-PEG as a function of nylon 6 or graft copolymer content (wt%). Also shown are the effects of the addition of nylon 6-*g*-PEG to the nylon 6/PVAc 50/50 (w/w) blend on the melting temperature of nylon 6 in the graft copolymer. In this case, the amount of the graft copolymer varied from 5 to 20 wt%

The T_m depression behaviour was expected for the ternary blends of nylon 6, PVAc and nylon 6-*g*-PEG, taking into account that compatibilization of the nylon 6/PEG blend was achieved in the presence of the graft copolymer[4]. Unexpectedly, however, the graft copolymer did not behave as a compatibilizer between nylon 6 and PVAc. The SEM studies also revealed that there were no global morphological changes regarding miscibility in the nylon 6/PVAc blend as a result of adding copolymer, within the copolymer composition range used in this work (~0–20 wt%). *Figure 2a* illustrates the SEM micrograph of the nylon 6/PVAc 50/50 (w/w) blend and *Figure 2b* is a micrograph of the ternary blend of nylon 6/PVAc/nylon 6–PEG copolymer (10 wt% of copolymer was added to the binary nylon 6/PVAc 50/50 w/w blend). Comparison of *Figures 2a* and *2b* indicates that the miscibility of nylon 6 and PVAc was not improved by the inclusion of the copolymer.

It should be noted that the T_m depressions of nylon 6 were observed for blends of PVAc/graft copolymer containing less than 50 wt% of the graft copolymer. This result implies that the graft copolymer shows a miscibility window with PVAc within the blend compositions. The miscibility of the blends with lower graft copolymer content may be due to the interaction between PEG and PVAc. It has been reported[7,13–15] that PVAc, which has a partial positive charge on the carbonyl carbon atom, may interact favourably with PEG, which has an oxygen atom of negative charge acting as a proton acceptor, to form a miscible pair.

It is interesting to note that the interaction between the PEG segment in the graft copolymer and the PVAc segment becomes weaker and the blend of PVAc/graft copolymer shows phase separation as the graft copolymer content increases to above 50 wt%.

It may be assumed that in the graft copolymer/PVAc blends a larger portion of the molecular chains of the graft copolymer is entangled with the molecular chains of PVAc and intermixed in the molten amorphous state owing to the specific interaction between proton-accepting PEG and proton-donating PVAc. The different

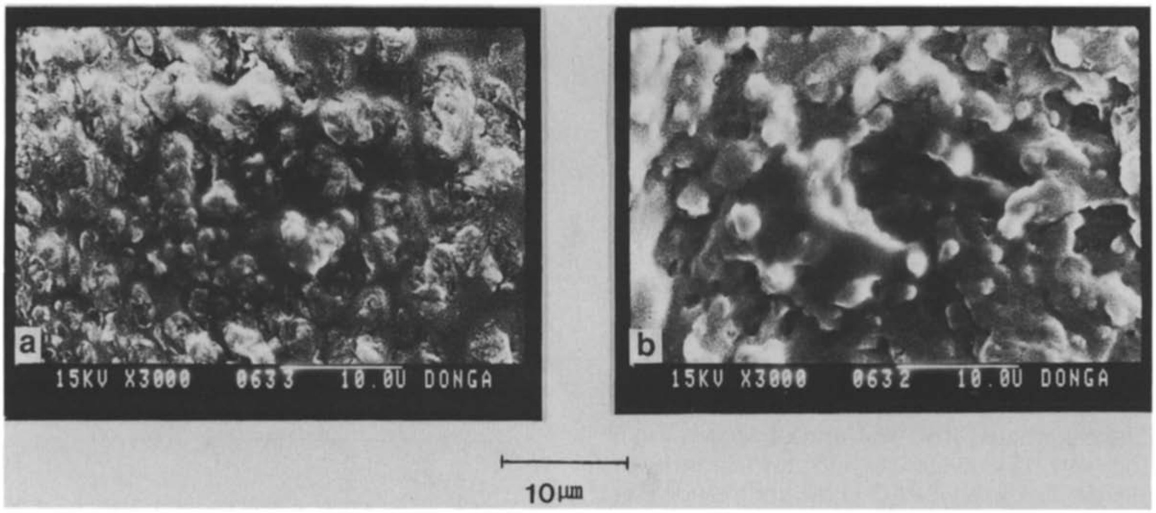

Figure 2 SEM micrographs of (a) nylon 6/PVAc 50/50 (w/w) blend and (b) ternary blend of nylon 6/PVAc/nylon 6-*g*-PEG copolymer (10 wt% of copolymer was added to the binary nylon 6/PVAc 50/50 (w/w) blend)

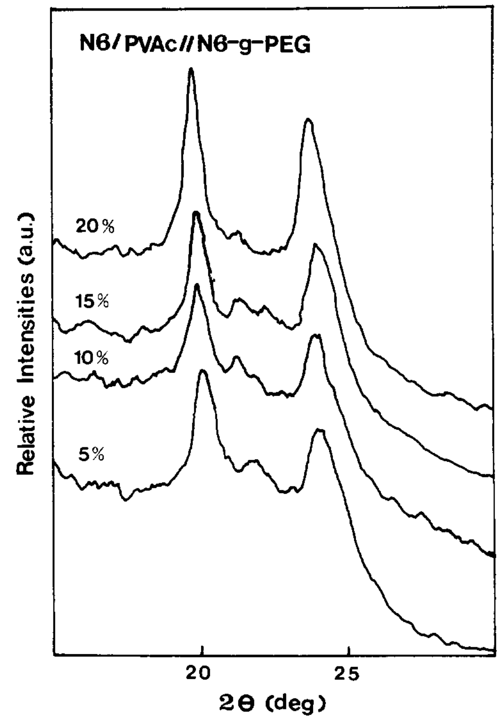

Figure 3 Effect of graft copolymer on the X-ray diffraction of the nylon 6/PVAc 50/50 (w/w) blend: the amount of the graft copolymer varied from 5 to 20 wt%

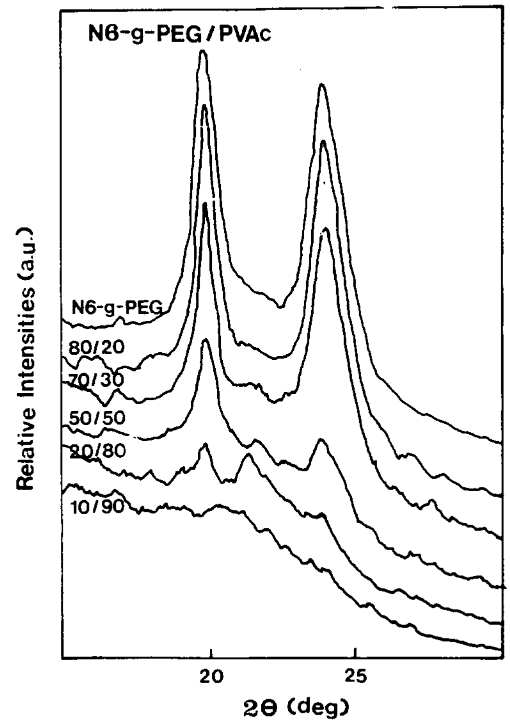

Figure 4 X-ray diffractograms of the nylon 6-*g*-PEG/PVAc blends with various compositions

miscibility behaviour of the blends containing nylon 6, PVAc and the graft copolymer also affected the crystalline structure of the blends.

Figure 3 shows the X-ray diffractograms of the nylon 6/PVAc/graft copolymer ternary blends, exhibiting the effect of the graft copolymer on the crystalline structure of the nylon 6/PVAc 50/50 (w/w) blend. The graft copolymer showed three characteristic peaks at $2\theta = 21.6°$, 22.7° and 23.8°: $2\theta = 22.7°$ corresponds to the peak of PEG crystals, and $2\theta = 21.6°$ and 23.8° correspond to (2 0 0) and (0 2 0) planes of nylon 6, respectively[9]. The diffraction pattern of nylon 6 used in this work showed typical γ-form structure. It was reported[4] that the grafting of PEG considerably affects the crystalline structure of nylon 6. Details on the crystalline structure of the graft copolymer and nylon 6 are described elsewhere[4,16,17].

In *Figure 3*, the X-ray diffractograms of the ternary blends showed superpositions of each characteristic peak of the nylon 6 and PEG homopolymers as well as the graft copolymer, with no additional peaks, even though the intensities of the peaks changed according to the composition of the graft copolymer. For the graft copolymer/PVAc blends in *Figure 4*, it should be pointed out, however, that none of the diffractograms is simply a superposition of each characteristic peak of each component. The main differences between X-ray diffractograms of the two blends, when comparing *Figures 3* and *4*, lie in the diffraction maxima at $2\theta = 22.7°$. The diffraction peaks at $2\theta = 22.7°$, due to the PEG crystals, were not observed at PVAc contents of less than 50 wt% but they increased as the PVAc content in the graft copolymer/PVAc blends increased to above 50 wt%, even though PVAc itself showed no crystalline structure. This may be related to the speculation that the molecular chains of the graft copolymer are entangled with those of PVAc and solubilized in the PVAc phase to a greater extent in the graft copolymer/PVAc blend, owing to the specific interactions between PEG and PVAc. The result is in accordance with the T_m depression behaviour. To draw a definite conclusion, however, the question should be answered of whether the miscibility behaviour of the copolymer with PVAc is attributed only to the specific interaction between PEG and PVAc, since the results of *Figure 4* are unusual in the sense that if only specific interaction between PEG and PVAc is important then one would expect the PEG crystallization peak to disappear as PVAc content increases. It may be that other effects, such as composition-dependent interaction energy for the copolymer/homopolymer, may also be important. However, the T_m of PEG is relevant in this respect rather than the T_m of nylon 6. More detailed work is being undertaken to obtain more concrete evidence for the miscibility behaviour of the graft copolymer/PVAc blends and to explain more logically the origin of the miscibility.

Conclusions

The compatibilizing effect of nylon 6-*g*-PEG for the nylon 6/PVAc 50/50 (w/w) blend was investigated, based on the melting temperature depression behaviour and X-ray diffractograms.

The graft copolymer did not show any compatibilizing effect for the binary nylon 6/PVAc blends. Instead, it was found that the graft copolymer itself shows a miscibility window in its blends with PVAc for blend compositions containing less than 50 wt% of the graft copolymer; this is due, in part, to the specific interaction between the PEG segment in the graft copolymer and PVAc.

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