Polymer Bulletin 25, 185–192 (1991)

Polymer Bulletin

Synthesis of nylon 6-g-poly(ethylene glycol) copolymer and its compatibilizing effect in nylon 6/poly(ethylene glycol) blends

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SUMMARY

A graft copolymer of poly(ethylene glycol) onto nylon 6 was prepared by two-step reactions; poly(ethylene glycol)(PEG) was chlorinated with thionyl chloride in carbon tetrachloride and the chlorinated PEG was then grafted onto nylon 6 by reacting each other with triethylamine and tin chloride in o-chlorophenol. Blends were also prepared from the graft copolymer with nylon 6 or PEG. The thermal properties and crystalline structure of the graft copolymer and the blends were studied using differential scanning calorimeter and X-ray diffractometer. It was found that the grafting of PEG onto nylon 6 changed the crystal structure of nylon 6. It was observed that compatibilization of the nylon 6/PEG blend of 50/50 composition by weight was achieved in the presence of the graft copolymer.

INTRODUCTION

Although nylon6 has been widely used as one of high-strength engineering plastics, it has a few shortcomings for end-use such as its high water absorptivity and weak compatibility with other polymers because of strong hydrogen bonding characteristics(1,2). Several attempts have been made to modify nylon 6 by synthesizing new copolymers containing polyamide group or introducing polar groups such as carboxyl or hydroxy group into the backbone of nylon 6 in order to overcome such shortcomings of nylon 6(2-4).

Grafting of vinyl monomers like vinyl acetate or styrene onto nylon 6 was attempted by Sakurada,et al. and El-Rafie,et al..etc(5-7). It has been generally expected that a graft copolymer improves the interfacial adhesion between domains and continuous phase in a polymer blend, and thus can be used as a compatibilizer. Compatibilizers or interfacial agents in polymer blends have been attracted much interests from theoretical and practical standpoints. The use of ethylene-propylene block copolymer in the blend of high-density polyethylene and polypropylene is a typical example of the attempts to compatibilize incompatible pairs in polymer blends(11). Few systematic studies, however, have been reported as yet on the compatibilizing effect of graft copolymers in polymer blends.

We prepared a graft copolymer of poly(ethylene glycol)(PEG) onto nylon6 for this work. PEG was selected because it could give some flexibility to the backbone chain of nylon 6 and improve impact strength of nylon 6. Furthermore, it was reported that since the molecular weight of PEG is easily controlled, the molecular weight of a copolymer containing PEG can be controlled without any great difficulties once if the reaction conditions are properly adjusted(12). Obviously, this must be a good merit in carrying out experiments concerning copolymerization. Blends were also prepared from the graft copolymer and nylon 6 or PEG.

The thermal properties and crystalline structure of the graft copolymer and the blends were studied and the compatibilizing effect of the graft copolymer was investigated in the blend of nylon 6 and PEG of 50/50 composition by weight.

EXPERIMENTAL

Materials

Nylon 6, kindly supplied for this work from the Research Center of Kolon Co. Ltd., was degassed at 60°C for about 6 hrs under vacuum. Poly (ethylene glycol)(PEG)(Mol. Wt.≒ 6000)(Aldrich Co.) was used as received. Other chemicals, such as carbon tetrachloride, pyridine, thionyl chloride,o-chlorophenol, tin chloride and diethyl ether, were purified by standard procedures.

Synthesis

Nylon 6-g-poly(ethylene glycol)(nylon6-g-PEG) was synthesized by two-step reactions.PEG was chlorinated with thionyl chloride in carbon tetrachloride and the chlorinated PEG was then grafted onto nylon 6 by reacting each other with triethylamine and tin chloride in o-chlorophenol.

PEG chlorination(12-14): An 1 equiv. of PEG solution of CCl_4 and 1.2 equiv. of pyridine were added to a 250 ml of three-necked round bottom flask equipped with a reflux condenser and the mixture was stirred at 70°C. Then 1.4 equiv. of thionyl chloride was added dropwise into the flask. After 6 hrs pyridine salt was removed by filtering and the product obtained was refiltered with K_2CO_3. The filterate was dissolved in methylene chloride and precipitated into tenfold excess of diethyl ether. The precipitate was collected and dried under vacuum for 10 hrs. THe chlorine content of the resultant chlorinated PEG was determined as 7.77 % by Mohr titration method with 0.003 F $AgNO_3$, using 5 % K_2CrO_4 as indicator(yield 78.3 %)(15).

Grafting of PEG onto nylon 6: The nylon 6-g-PEG copolymer was prepared by reacting nylon 6 with chlorinated PEG in o-chlorophenol in the presence of triethylamine and tin chloride at 90°C for 5 hrs. The resultant product was dissolved in formic acid. The graft copolymer was obtained by filtering unreacted chlorinated PEG with 100 ml of methanol. The weight % of PEG in the graft copolymer was calculated as 36.60 % from the weight loss after hydrolysis in 10 % of aqueous HCl solution for 24 hrs.

Preparation of blends

Three kinds of blends were prepared from nylon 6,PEG and nylon 6-g- PEG by casting from formic acid; nylon 6/PEG, nylon 6-g-PEG/nylon 6, and nylon6-g-PEG/PEG. The compositions of the blends were 20/80,40/60,50/50,60/40, and 80/20 by weight. In order to investigate the compatibilizing effect of the graft copolymer in nylon 6/PEG blends, ternary blends containing 5,10,15,and 20 wt.% of the graft copolymer with 50/50 nylon 6 and PEG were also prepared by casting from formic acid.

Measurements

The inherent viscosity was measured in 85 % formic acid at 30 ± 0.02°C with Cannon-Fenske viscometer #75. The molecular weight of polymers was determined by gel premeation chromatography(GPC)(Water-Waters244). Thermal properties of polymers were studied by DSC(Netzsch DSC444). All the DSC runs were made under a nitrogen atmosphere with a heating rate of 10°C/min. The DSC curves obtained on the second heating cycle were used to obtain all of the experimental data. The peak temperature was taken as the melting point of the samples.

The crystalline structure was determined using X-ray diffractometer(Ri-

Table 1: Characteristics of The Nylon6 and Nylon 6-g-PEG Copolymer

Samples	Inherent Viscosity(dl/g)	$M_n \times 10^{-5}$	$M_w \times 10^{-5}$	M_w/M_n	Melting Temperature(°C)
Nylon 6	0.381	0.1732	0.3452	2.00	231.0
Nylon 6-g-PEG	0.615	0.3267	0.8527	2.61	200.2/59.4

gaku Denki). Nickel filtered CuK$_\alpha$ radiation was applied at 30 kV and 20 mA.

RESULTS AND DISCUSSION

Characterization and Properties of Nylon 6-g-PEG copolymer

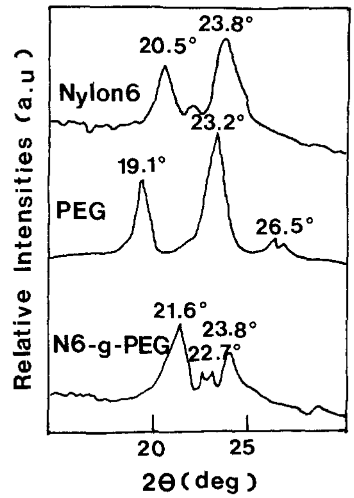
The characteristics of the nylon 6-g-PEG copolymer is summarized in Table 1. The molecular weight of the graft copolymer was almost double compared to that of nylon 6 homopolymer used for this work.The molecular weight distribution of the graft copolymer was 2.61 and slightly broader when compared to that of nylon 6. It was reported, however, that the polydispersities of copolymers formed by grafting monomers onto polymers were usually not as narrow as for the graft copolymer obtained from this work, and the values for such copolymers were usually in the range of 3.5-4.0 or larger(16).

The chlorinated PEG and the nylon 6-g-PEG copolymer were characterized by IR spectra; The chlorination of PEG could be identified on IR spectrum from the fact the OH band around 3300-3600 cm^{-1} in PEG homopolymer was almost disappeared and instead C-Cl band arund 600-700 cm^{-1} was newly appeared. The graft copolymer was identified on IR spectrum by hydroxy group band at 3300-3600 cm^{-1}, weak tertiary amine band at 1200 cm^{-1}, C-O-C stretching band at 1113 cm^{-1} and strong methylene rocking band at 947 cm^{-1}.

The graft copolymer showed double melting temperatures, as shown in Table 1. This kind of double melting points is attributed to the microphase separation, which is a characteristic property of a graft copolymer(17,22). The lower one is that of PEG and higher one is that of nylon 6. The lower melting temperature was same as that of PEG homopolymer, but higher melting temperature of the graft copolymer was about 30°C below that of nylon6 homopolymer, indicating that a certain portion of PEG molecular chains prevents nylon 6 to crystallize and gives nylon 6 backbone chain considerable flexibility.

The X-ray diffraction of PEG homopolymer shows three sharp crystalline reflection peaks, in the region of Bragg angle(2θ) between 15° and 30°(Fig. 1) Those strong diffraction peaks are located at the diffraction angles 2θ of 19.1°,23.2°, and 26.5°. It was reported that two types of crystalline structure existed in nylon 6, α-form and γ-form, and the formation of the structure depended on the processing conditions and history(18,19). The α-form of nylon 6 is characterized by tow sharp peaks at 2θ=20.5° and 23.8°, which correspond to (200) and (020) planes, respectively, whereas the γ-form crystalline structure is identified by the maximum peak at 2θ=21.6° which corresponds to (200). The diffraction pattern of nylon 6 used in the study shows typical α-form structure.

The effect of grafting of PEG onto nylon 6 on the crystal structure of nylon 6 homopolymer and PEG homopolymer is shown in the same figure. In the diffraction patterns of the graft copolymer, the diffraction intensity at 2θ=23.8° remarkably decreased and two new sharp peaks at 2θ=21.6° and 22.7° appeared, whereas the intensities of the peaks of PEG crystals at 2θ=19.1°, 23.2° and 26.5° were very weak. The weak intensities of PEG peaks are due to the relative small amount of PEG in the graft copolymer.Of interest,however, is the phenomena for the graft copolymer that the grafting of PEG affects considerably the structure of nylon 6 crystals in the graft copolymer. The

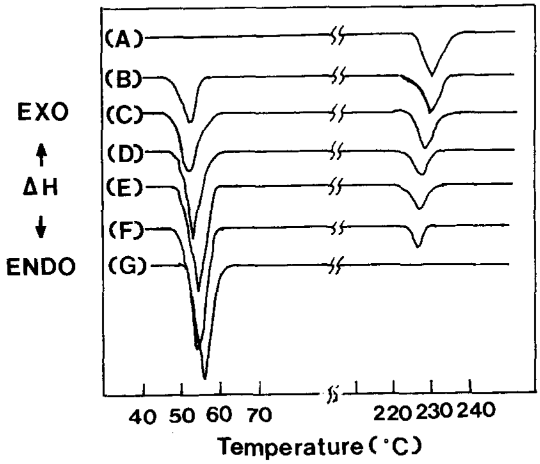


X-ray diffraction results mean that the grafting of PEG leads to an essential change in the structure of nylon6 from α-form to γ-form or increases the amount of γ-form crystals, which existed in trace within nylon 6 homopolymer used in the study, if any, relative to that of major ingredients, α-form crystals. It was presumed that the grafting of PEG might restrict the crystallization of nylon 6 homopolymer.

Fig.1. X-ray diffractograms of the Nylon 6, PEG, and Nylon 6-g-PEG(N6-g-PEG) Copolymer

<u>Compatibilizing effect of the graft copolymer</u>

The DSC thermograms of the nylon 6/PEG blends are illustrated in Fig.2. The blends showed two separate melting points due to their incompatibility of PEG and nylon 6. The melting point of PEG decreased with increasing nylon 6 content whereas that of nylon 6 increased with nylon 6 content in the blend. Taking it into consideration that the area under the heat absorption peak on the DSC thermogram is a relative measure of degree of crystallinity, the degree of crystallinity shows similar trend with increasing PEG content in the blends.



This means that PEG restricts the crystallization of nylon6 to some extent and more restrictions are brought about with increasing PEG content in the blend.

Fig.2. DSC thermograms of the Nylon 6/PEG blends ; Compositions; (A) 100/0 (B) 80/20 (C) 60/40 (D) 50/50 (E) 40/60 (F) 20/80 (G) 0/100

Table 2. Melting Temperatures of PEG and Nylon 6 in Blends(°C)

Samples	Nylon 6/PEG		Nylon 6-g-PEG/PEG		Nylon 6-g-PEG/Nylon 6	
(Compositions)	PEG	Nylon 6	PEG	Nylon 6	PEG	Nylon 6
0/100	55.5	-	-	-	-	-
20/80	54.8	225.9	60.1	198.8	58.1	230.4
40/60	54.8	226.3	59.0	198.3	58.8	229.4
50/50	53.7	227.7	58.1	198.7	58.9	229.1
60/40	52.3	228.5	58.0	199.4	58.4	228.9
80/20	51.7	229.8	59.0	199.8	59.1	227.9
100/0	-	231.0	59.4	200.2	-	-

Table 2 shows melting points of nylon 6, PEG, and nylon 6-g-PEG in the blends of the graft copolymer with nylon 6 or PEG. Two separate melting temperatures were observed in all the blends and these melting points were almost constant regardless of their compositions. It should be noted, however, that the melting point of the graft copolymer(ca. 200°C) was observed but that of nylon 6 was not observed over all the composition ranges in the blends of the graft copolymer with PEG whereas the melting point of nylon 6 was observed but that of the graft copolymer was not observed over entire composition ranges in the blends of the graft copolymer and nylon 6. In both blends, there is no substantial change in the melting points of PEG as a function of their compositions and is almost same as ca. 60°C. The result should be very important to reveal the accurate function of the graft copolymer in the blend in a morphological sense but the accurate interpretation is at the moment not easy. At this moment it may be assumed that in the

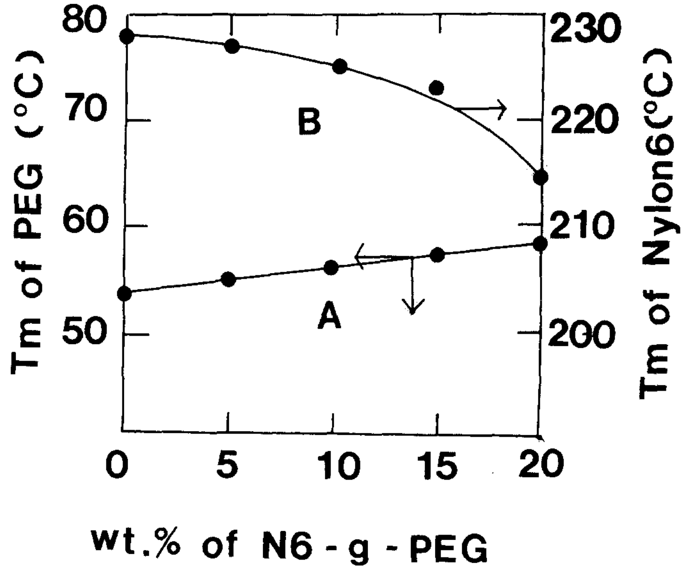


Fig.3. Effect of the addition of the Nylon 6 -g-PEG(N6-g-PEG) copolymer in the blend of Nylon 6/PEG of 50/50 composition by weight on the melting temperature of PEG and nylon6 in the graft copolymer;A,T_m of PEG;B,T_m of nylon6(°C)

graft copolymer/nylon 6 blends a larger portion of the molecular chains of the graft copolymer is entangled to the molecular chains of nylon 6 and intermixed in the molten amorphous state, and finally the graft copolymer can not possess its own morphology in the blend. But this kind of speculation should be proved with more experimental evidences. Further studies should be made in more detail.

In figure 3, the melting temperature of nylon 6 and PEG in the nylon 6/PEG blend of 50/50 composition by weight is plotted against the weight concentration of the graft copolymer. It is found that the melting temperature of nylon 6 markedly decreased with increasing concentration of the graft copolymer in the blend whereas that of PEG in the blend increased with increasing content of the graft copolymer. This trend implies that the graft copolymer synthesized in this work can be functioned in part as a compatibilizer between their constituent components, nylon 6 and PEG. The use of a block copolymer as a compatibilizer between homopolymers having each repeating unit of the copolymer has been reported. The addition of styrene-butadiene(SB) block copolymer to polystyrene/polybutadiene blends is a typical example(20,21). It can be expected that a graft copolymer can be roled as a compatibilizer in immiscible polymer blends but few results on the subject was reported.

Rudin reported that graft copolymers decreased the particle size of the dispersed phase in a binary homopolymer mixture and improved the adhesion of the dispersed and continuous phases(22). The result from DSC thermogram proves such potential use of the graft copolymer as a compatibilizer, even though more accurate interpretation should be required regarding several unknown factors including morphology changes in the ternary blends,interfacial adhesion properties,etc.

The X-ray diffractograms of the binary nylon 6/PEG blend show superpositions of each characteristic peaks of the nylon 6 and PEG homopolymer in Figure 4 with no additional peaks, even though the intensities of the peaks change according to their compositions. The general trend is in accordance with the results from DSC thermograms. An example is the fact that the degree of crystallinity,which is represented by the relative intensities of the diffraction peaks, of nylon 6 decreased with increasing PEG content in the blend. It should be pointed out,however, for the graft copolymer /PEG blends(in Fig.5) and the graft copolymer/nylon 6 blends(in Fig.6) that none of the diffractograms in Figs. 5 and 6 is just a superposition of each characteristic peak of each component, except PEG in the graft copolymer/ PEG blends. This fact implies the interaction between homopolymers and the graft copolymer in the blends and therefore the compatibilizing effect.

The main differences between X-ray diffractograms of the two blends, when compared Figs. 5 and 6, lies in the diffraction maxima at $2\Theta=20.8°$ and 26.5°. The graft copolymer/PEG blends showed distinct peaks at the Bragg angles whereas the graft copolymer/nylon 6 blends did not show peaks at the same angles. The relative intensities of the peaks were not significantly changed with compositions of each component in the blends of the graft copolymer with PEG, but decreased considerably with increasing composition of the graft copolymer. This may be related with the speculations that the molecular chains of the graft copolymer are entangled with those of nylon 6 and solubilized in nylon6 phase to larger extent in the graft copolymer/nylon 6 blend. The result is in accordance with that from DSC thermogram.

The effect of the graft copolymer on the crystal structure of the nylon 6 and PEG mixture of 50/50 composition by weight is shown in Figure 7. It is seen from the deffractograms that the diffraction maxima of PEG at $2\Theta=20.8°$ and 26.5° decreased markedly with increasing content of the graft copolymer in the blend whereas other peaks remain unchanged. Careful exam-

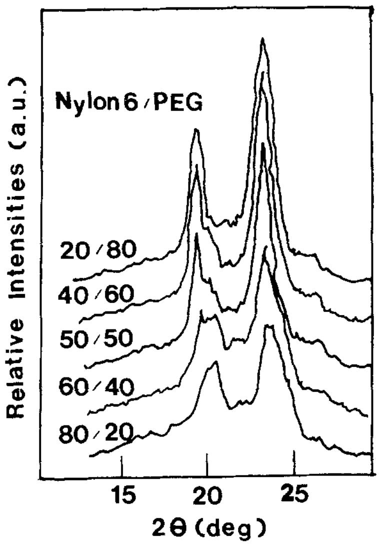


Fig.4. X-ray diffractograms of the Nylon 6/PEG blends with various compositions

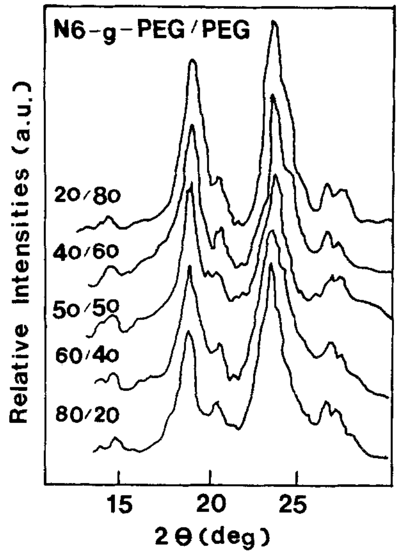


Fig.5.X-ray diffractograms of the graft copolymer(N6-g-PEG)/PEG blends with various compositions

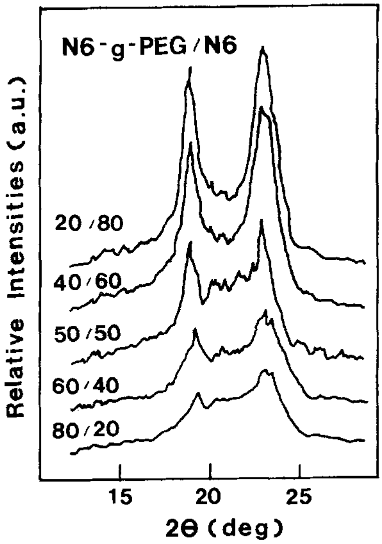


Fig.6. X-ray diffractograms of the graft copolymer(N6-g-PEG)/Nylon 6 blends with various compositions

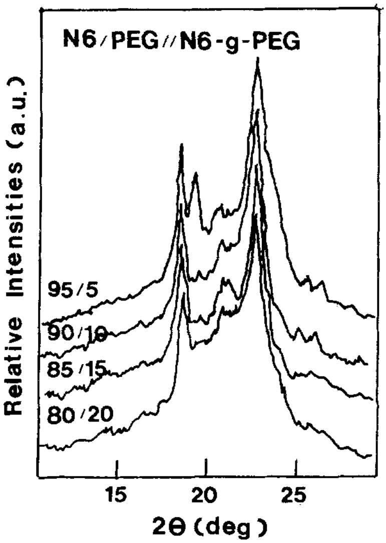


Fig.7. Effect of the graft copolymer (N6-g-PEG) on the X-ray diffraction of the 50/50 Nylon 6(N6)/PEG blend; The amount of the graft copolymer varied from 5 to 20 wt. %.

inations of those diffractograms shown in Figs.5-7 reveal that the effect of the graft copolymer on the crystal structure and degree of crystallinity of PEG in the blends is significant. Taking it into consideration that the graft copolymer affected the melting temperatures of nylon 6 and PEG from DSC results, it may be regarded that compatibilization of the nylon 6 and PEG blend was achieved in the presence of the graft copolymer. More detailed researches are undertaking and will be reported elsewhere.

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Accepted November 12, 1990 S