Effect of Maleic Anhydride Grafted Polypropylene on Structure of Polypropylene/Polyamide 6 Blend Fiber

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Abstract: The effect of maleic anhydride grafted polypropylene (hereafter "MAH-PP") on the structure of blend fibers of polypropylene (PP) and polyamide 6 (PA6) was investigated. Although undrawn fibers of pure PP or PA6 do not show crystalline orientation, undrawn blend fibers without MAH-PP show low crystalline orientation. Moreover, in undrawn blend fibers containing MAH-PP, distinct crystalline orientation of PP was observed. In the case of drawn fibers, blend fibers containing MAH-PP in an amount of 10 phr or more showed broader diffraction peaks of PA6 crystals in wide-angle X-ray diffraction than did blend fibers having an MAH-PP content of 5 phr or less or pure PA6 fibers. Small-angle X-ray diffraction clearly showed that, in all blend fibers, the long period structure does not depend on MAH-PP content. When the blend fibers were annealed at 180°C, which is higher than the melting point of PP, one scattering peak was observed in blend fibers having MAH-PP content of 10 phr or more. In contrast, two scattering peaks were observed in blend fibers having an MAH-PP content of 5 phr or less.

(Received 18 July, 2001; Accepted 21 February, 2002)

1. Introduction

The polymer blend of PP and PA normally exhibits a phase separation structure. Therefore, studies to improve the dispersibility or mechanical properties of blend polymer by use of a compatibilizer have been carried out, and dispersibility of PA6, PA66, and PA12 mixed with PP has been discussed [1-7]. Many studies have been conducted on the relation between phase structure and impact properties [8,9]. Moreover, studies using a new compatibilizer such as polyoxypropylene-amide grafted polypropylene have been reported [7,10], and studies have been conducted on the relation between phase structure and extruding conditions in a twin screw extruder [11-14]. Also, the effect of the process of mixing has been studied [15,16].

Studies on ribbon [17] and blend-fiber processing including drawing process have been conducted on blend polymers in which PP is a major component [18,19]; however, such studies have been few. These studies have pointed out that even in drawn material, addition of a compatibilizer exerts a favorable effect on the dispersibility of the PA6 phase [17,19], thereby promoting the crystallization and high orientation of PP [18].

The present report examines, by use of DSC, crystallization behavior for blend samples of PP and PA6 of different contents of MAH-PP for cooling process from the melt. Moreover, the DSC curves for heating processes are also measured for those blend polymers so as to investigate their structure. The effects of the number ratio of the functional group of MAH-PP to that of PA6 (end amino group) on the compatibility of PP and PA6 are

discussed, along with the imperfect structure of the crystalline region and the long period structure of blend fibers.

2. Experimental

2.1 Samples

The molecular characteristics of PP, PA6 and MAH-PP resins are listed in Tables 1, 2 and 3, respectively. MAH-PP (density: 0.91 g/cm³, MFR: 25.0 g/10 min and grafting ratio: 0.30 wt%) was used as the compatibilizer. The composition of the sample is listed in Table 4. The sample was prepared by mixing the pellets in a tumbler for 10 minutes and pelletizing in a 40 mm ϕ -unidirectional twin screw extruder at the extrusion temperature of 260 °C and the mass output of 150 g/min. The mixing ratio of the components PP and PA6 was represented by weight fraction.

Table 1 Molecular characteristics of iso-polypropylene sample.

Sample name	Dens. (g/cm ³)	MFR ^{*)} (g/10min)	Mw ($\times 10^4$)
PP	0.90	2.7	3.39

*1) at 230°C

2.2 Processing of fibers

a) Spinning process

A 40 mm ϕ -single screw extruder provided with a spinning

Table 2 Molecular characteristics of polyamide 6 sample.

Sample name	Dens. (g/cm ³)	Relative Viscosity	Mw (× 10 ⁴)	—NH ₂ (mol/g)
PA6	1.14	4.5	7.80	2.70 × 10 ⁻⁵

Table 3 Molecular characteristics of maleic anhydride-grafted PP sample.

Sample name	Dens. (g/cm ³)	MFR ^{*1)} (g/10min)	Mw (× 10 ⁴)	—MAH (mol/g)
MAH-PP	0.91	25.0	7.20	2.96 × 10 ⁻⁵

*1) at 230°C

Table 4 Composition of PP/PA6 blend samples.

Sample name	PP ^{*1)}	PA6 ^{*1)}	MAH-PP
C-2	40	60	0 phr ^{*2)}
G-1	40	60	5 phr
B-2	40	60	10 phr
G-2	40	60	20 phr

*1) Weight percent (%)

*2) Parts per hundred resin

nozzle (L/D:10) with 20 holes of 1.0 mm ϕ was used for the melt spinning. All the samples were extruded into a cooling water of 30 °C in tank at the spinning temperature of 260 °C, the output of 89 g/min and the air gap of 50 mm. Rolled undrawn fibers were prepared on the first roll, a take-up roll, at a speed of 25.0 m/min. At that time, the draft ratio, the ratio of extruding speed from nozzle to the first roll rolling speed, was about 4.0 [20].

b) Drawing process

The sample was drawn at two stages: first, wet drawing at 100°C, and second, heated roll drawing (roll temperature: 130 and 135 °C). This drawing was performed under the following conditions: speed of the 1st roll: 20.8 m/min; speed of 2nd and 3rd roll: 83.3 m/min; final take-up speed of 4th roll :100 m/min ; draw ratio at 1st stage: 4.0 ; draw ratio at 2nd stage: 1.2 ; namely, total draw ratio: 4.8. The fineness of the drawn fiber was set at 444 dtex [20]. Dtex (grams per 10,000m) is the unit of fiber fineness by ISO standard.

2.3 Measurement

a)Wide-angle X-ray diffraction

Wide-angle X-ray diffraction photographs were taken with an X-ray diffraction device (Rigaku Co.) using the Ni filtered Cu-K α radiation source for 1 hour at 40 kV, 30 mA. The diffraction intensity curve on the equator was obtained with a scintillation counter.

b)Small-angle X-ray scattering

Small-angle X-ray scattering intensity curve were obtained on the equator for a bundle of fibers with an X-ray scattering device (Rigaku Co.) equipped with a PSPC using the Ni-filtered Cu-K α radiation source at 40KV, 30mA.

c)Differential scanning calorimetry (DSC)

The DSC measurement was performed under nitrogen gas flow at a heating or cooling speed of 10 °C/min with a DSC200 type (Seiko Instruments Inc.). The temperature range was 60-260 °C.

The pellets of various blend samples were preheated at 260 °C for 5 minutes with a heating press machine, then compression and depression were repeated for 1 minute to degas. After compression under the pressure of 200 kg/cm² for 5 minutes, pressed films used for a blend sample were finally prepared by cooling under pressure of a cooling press at room temperature. Fiber samples were cut short. And then about 2 mg of each kind of sample was enclosed in the aluminum pan. Indium (the melting point: 156.4 °C) was used as reference material for the correction of temperature.

d)Scanning electron microscope (SEM)

The dispersion state of the blend fibers was observed with a SEM (JEOL JSM-T330A) at an accelerating voltage of 15 kV. The fibers frozen in liquid nitrogen were fractured, subsequently dipped in concentrated formic acid for 3 hours so that the PA6 component was extracted. The sample was vacuum-dried for 1 day. Then, gold was vapor-deposited in a JEOL JEC-150 equipment, and the surface of the fibers was observed.

3. Results and discussion

3.1 Dispersion state of PP and PA6 phases

Performing stable melt spinning of mere blends of PP and PA 6 was difficult, because of lack of reactivity between these components. When mixing/pelletizing was performed, the blend was found to be prone to a problem of poor cutting. However, addition of MAH-PP as a compatibilizer at a content of only 5 phr (parts per hundred resin) enabled extremely stable melt spinning. Presumably, the maleic anhydride group within MAH-PP (hereafter called the "MAH group") and the end amino group within PA6 (hereafter called the "NH₂ group") reacted with each other to improve the dispersion of the PP and PA6 phases, leading to easy melt spinning [17-19].

Functional groups in the ring closure state are generally considered to have higher reactivity than those in the ring opening state. However, in this experiment, mixing at the extrusion temperature of 260 °C presumably induced a reaction between the MAH and NH₂ groups, regardless of the ring opening ratio of the MAH group [21]. The generally-known chemical formula of graft material generated by reaction between MAH-PP and PA6 in the ring closure or ring opening state is as follows [21]:

Increasing MAH-PP content seems to raise the reacting weight of the MAH and NH₂ groups to thereby increase the affinity between PA6 and PP molecules, leading to fine dispersion of the two phases. The cross sections of undrawn blend fibers of different MAH-PP contents were observed by SEM (Fig. 1). The observed images indicate the states of the PP phase remaining after the PA6 phase was eluted with formic acid.

Fig. 1 Scanning electron micrographs of freeze-fractured and then formic acid-etched surfaces of undrawn PP/PA6 blend fibers containing MAH-PP with contents of (a) 0 phr (C-2), (b) 5 phr (G-1), (c) 10 phr (B-2) and (d) 20 phr (G-2).

In blend fibers without MAH-PP (C-2), the PP phase, serving as the dispersed phase, assumed the form of a fibril having a diameter of about 0.4–1.5 μm, whereas in blend fibers having an MAH-PP content of 5 phr (G-1), the fibril diameter is

about 0.2–0.4 μm, which is extremely small. In contrast, in blend fibers having an MAH-PP content of 10 phr (B-2) or 20 phr (G-2), PP apparently served as the matrix phase. In particular, when the MAH-PP content is 20 phr, PP becomes a complete matrix phase having holes of about 0.2–0.5 μm in diameter. In this way, increase in MAH-PP content was found to greatly change the dispersion state. The PA6 phase can be considered to be finely dispersed in blend fibers having an MAH-PP content of 10 phr or more. The PP phase apparently formed a matrix in these samples, because the PA6 component, being dispersed finely into the PP component, was difficult to elute in formic acid.

In samples having an MAH/NH₂ ratio of 0.04 or less (MAH-PP of 5 phr or less), the probability of contact between the MAH and NH₂ groups is low, and therefore fine dispersion of the PA6 and PP phases does not occur. In contrast, in samples having a ratio of 0.08 or more, the probability of contact between the MAH and NH₂ groups increases, resulting in fine dispersion of the PA6 and PP phases.

3.2 Chemical reaction between MAH-PP and PA6

Fig. 2 shows DSC curves obtained in the cooling process from the melt, measured for the pressed blend films having different PP and PA6 contents. For comparison, the results for pure PA6 and PP are also shown. For samples without MAH-PP (C-2) or having an MAH-PP content of 5 phr (G-1), the crystallization exothermic peak of the PA6 component appeared near 184 °C, which is about 6 °C higher than the temperature for pure PA6. For those samples whose MAH-PP contents were 10 phr or more (B-2, G-2), the crystallization exothermic peak of PA6 disappeared.

In contrast, as the MAH-PP content increases, the crystallization exothermic peak of the PP component tends to shift to the higher temperature side. The crystallization exothermic peak was observed at 114 °C for pure PP, and at 126 °C in the blend having an MAH-PP content of 20 phr (G-2). Even for blends without MAH-PP (C-2), the crystallization exothermic peak was found to shift about 4 °C to the higher temperature side as compared with pure PP.

As mentioned above, fine dispersion of the two phases was confirmed in samples having MAH-PP contents of 10 phr or more (Fig. 1). In these samples, a considerable mutual reaction between MAH-PP and NH₂ of PA6 prevents crystallization of PA6 in the cooling process, and therefore the crystallization exothermic peak of PA6 in these samples disappears in the DSC curve [22]. As the MAH-PP content is increased, the crystallization peak of PP phase tends to shift to the higher temperature side.

MAH-PP used in this experiment was subjected to dissolution with toluene at 110 °C after freeze-shattering, and

Fig. 2 DSC thermograms of PP, PA6 and their blends containing MAH-PP with contents of 0 phr (C-2), 5 phr (G-1), 10 phr (B-2) and 20 phr (G-2) measured in the cooling process from melt at 280°C to 50°C at a cooling rate of 10°C/min.

then pure MAH-PP was deposited with acetone. The ratio of free MAH groups was checked. As a result, the content of existent free MAH groups was found to be as high as 55.2 %. That is, only the 1.33×10^{-5} mol/g (equivalent to 44.8 %) MAH group content within MAH-PP (2.96×10^{-5} mol/g), and the 2.70×10^{-5} mol/g NH_2 group within PA6 seem to exhibit affinity. As the content of MAH-PP is increased from 0 to 5, 10, and 20 phr, the substantial content of MAH group within blends changes from 0.00 to 6.32×10^{-2} , 1.21×10^{-1} , and 2.21×10^{-1} mol/g, respectively. The content ratio of MAH groups to NH_2 groups contained in the blends (hereafter called "MAH/ NH_2 ") changes from 0.00 to 0.04, 0.08, and 0.16, respectively. Thus, in these blends, the content ratio of the MAH group within MAH-PP to the NH_2 group within PA6 can be said to be relatively small.

Fig. 3 shows a relationship between the ratio of MAH/ NH_2 and the crystallization point of each component. The crystallization point of PA6 component decreased as the MAH/ NH_2 ratio increased from 0.00 to 0.08. However, it was higher than that of pure PA6. In contrast, the crystallization point of the PP component within blends was found to rise as the MAH/ NH_2 ratio increased from 0.00 to 0.08 and to be saturated within the range of 0.08 to 0.16. This point was also higher than that of pure PP.

Fig. 3 Crystallization point obtained from Fig. 2 plotted against MAH/ NH_2 ratio for PP, PA6 and their blends: (□) PA6 component and (●) PP component.

Fig. 4 shows a relation between the MAH/ NH_2 ratio and the heat of crystallization of each component. The heat of crystallization of the PA6 component at an MAH/ NH_2 ratio of 0.00 was almost equivalent to that of pure PA6. As the MAH/ NH_2 ratio increased, the heat of crystallization decreased considerably and became nearly zero at a ratio of 0.08 or higher. This is probably due to the amounts of MAH and NH_2 groups approaching to the stoichiometric ratio, thereby increasing the probability of contact between the functional groups and improving their affinity. That is, a fine dispersion [21] of the PA6 phase seems to suppress crystallization of the PA6 component.

Fig. 4 Heat of crystallization estimated from Fig. 2 plotted against MAH/ NH_2 ratio for PP, PA6 and their blends: (□) PA6 component and (●) PP component.

In contrast, the heat of crystallization of the PP component increased with MAH/ NH_2 ratio, particularly between 0.04 and 0.08. Although the heat of crystallization was almost equivalent

to that of pure PP for samples having an MAH/NH₂ ratio of 0.04 or less, it was found to be about 45 J/g higher than that of pure PP for samples having an MAH/NH₂ ratio of 0.08 or more. This is probably because a portion of PA6, whose crystallization had been suppressed by MAH-PP and molten PP, was crystallized near the temperature at which the crystallization of PP started. Thereby, the heat of crystallization of the PP component appeared to increase.

DSC curves for two kinds of blend samples (pressed films), having an MAH-PP content of 10 phr and without MAH-PP, were measured at various cooling speeds. The results are shown in Figs. 5 and 6. Although the temperature of the crystallization exothermic peak of PA6 in the blend sample without MAH-PP (C-2) decreased slightly with increasing cooling speed, the crystallization peak of PA6 does not disappear, even at a cooling rate of 40°C/min. In contrast, in the blend samples having an MAH-PP content of 10 phr, the crystallization peak of PA6 was not observed, even at a cooling speed of 1°C/min. This indicates that the PA6 phase is relatively stable when dispersed into molten PP with MAH-PP, so that the PA6 phase barely begins to crystallize at the crystallization point of PP in the cooling process.

Fig. 5 DSC thermograms of C-2 blend samples (PP/PA6=40/60 by wt%) without MAH-PP measured in the cooling process from melt at 280 °C to 50 °C at different cooling rates.

Fig. 6 DSC thermograms of B-2 blend samples (PP/PA6=40/60 by wt%) with an MAH-PP content of 10 phr measured in the cooling process from melt at 280 °C to 50 °C at different cooling rates.

The samples obtained in the experiment as shown in Fig. 2 were reheated so as to measure DSC curves in the heating process. The results are shown in Fig. 7. The endothermic peak of PA6 was observed even in samples (B-2, G-2) having MAH-PP contents of 10 phr or more, which show no crystallization exothermic peak of PA6 in Fig. 2. Note that the DSC curves of both samples (B-2 and G-2) having no crystallization exothermic peak of PA6 during the cooling process include a caving region (enclosed by a broken circle) just before melting of PA6, which seems to appear due to recrystallization of PA6. The probable reasons for the appearance of the melting endothermic peak of the PA6 component in these samples are recrystallization of PA6 in this reheating process and the crystallization of PA6 having occurred simultaneously with that of PP in the preceding cooling process.

3.3 Crystal orientation in blend fibers

Polymer blends were melt-spun while the MAH-PP content was varied between 0, 5, 10, and 20 phr. Fig. 8 shows wide-angle X-ray diffraction patterns of undrawn blend fibers in the order of increasing MAH-PP content. For comparison, the X-ray diffraction patterns of pure PA6 and PP fibers are also shown. For all fibers, the draft ratio, or the ratio of linear speed of the first roll speed to extruding speed from the nozzle, is about 4.0.

Fig. 7 DSC thermograms of PP, PA6 and their blends containing MAH-PP with contents of 0 phr (C-2), 5 phr (G-1), 10 phr (B-2) and 20 phr (G-2) measured in the heating process at a heating rate of 10 °C/min. The enclosed area in a broken circle shows partial recrystallization of PA6.

When the draft ratio is held constant, X-ray diffraction patterns of undrawn fibers are very strongly influenced by the addition of MAH-PP. For blend fibers with MAH-PP (G-1, B-2, G-2), diffraction peaks of PP crystal corresponding to the (110), (040), and (130) planes appeared on the equator and a diffraction peak of (041) appeared at the azimuthal angle of 40.2°, indicating c-axis orientation. The a*-axis orientation of PP crystallites was also observed on the meridian. Orientation of PP crystallites was observed in blend fibers produced by addition of MAH-PP, even when the speed of the first roll was reduced in order to decrease the draft ratio to about 2.0. Thus, for blend fibers having an MAH-PP content of 5 phr or more, even extremely small draft ratios were found to induce c-axis orientation of PP crystallites.

In contrast, for blend fibers without MAH-PP (C-2), the (040) diffraction peak of PP crystal appeared on the equator to indicate a*-axis orientation. However, c-axis orientation was not observed, indicating that the degree of crystal orientation was considerably lower than those of blends to which MAH-PP had been added. In this way, the results show that even when the blend ratio is held constant, addition of MAH-PP drastically changed the c-axis orientation of PP crystallites in blend fibers of PA6 and PP.

Fig. 8 Wide-angle X-ray diffraction patterns of (f) PP, (e) PA6 and their undrawn blend fibers containing MAH-PP with contents of (a) 0 phr (C-2), (b) 5 phr (G-1), (c) 10 phr (B-2) and (d) 20 phr (G-2).

Preferential orientation was not observed at all for undrawn fibers of pure PP and PA6 produced at a draft ratio of about 4.0. PP fibers, when the draft ratio was increased to about 6.0, showed a slight increase in the (110) reflection intensity on the equator. However, such obvious crystal orientation as in blend fibers was not observed. Crystal orientation was not observed at all for PA6 fibers, even when the draft ratio was increased to about 20.

As shown in Fig. 2, in MAH-PP-added blends, crystallization of the PP phase started at higher temperature as compared with blends having no MAH-PP or with pure PP. Therefore, in MAH-PP-added blends, the solidification point in melt spinning seems to move closer to the nozzle position than in the case of pure PP or blends without MAH-PP, by increasing the strain rate of blend fibers on the spinning line before solidification and leading to higher c-axis orientation of PP crystallites of undrawn blend fiber.

Fig. 9 shows a relation between viscosity and shear rate at

260 °C, which is the spinning temperature. This figure indicates that although MAH-PP has the lowest viscosity, the MAH-PP-added blends (G-1, B-2, G-2) have higher viscosities than C-2 without MAH-PP. The figure also indicates that the viscosities of these blend samples increase with increasing MAH-PP content. This is attributable to increased probability of reaction between the MAH and NH₂ groups.

Fig. 9 Viscosity of (●) PP, (■) PA6, (▲) MAH-PP and their blends containing MAH-PP with contents of (□) 0 phr (C-2), (△) 5 phr (G-1), (○) 10 phr (B-2) and (◇) 20 phr (G-2) plotted against shear rate at 260 °C.

In a wide range of shear rate, only the viscosity of the blend without MAH-PP (C-2) was lower than that of pure PP. As reported in a previous paper, for blends without MAH-PP the respective phases seem to be easily transformed at different shear rates, because of lack of compatibility between the PP and PA6 phases [23]. For samples used in this experiment, the viscosity of PP is lower than that of PA6. Therefore, for C-2, greater shear deformation tends to occur in the PP phase at lower viscosity than in the PA6 phase. Thus, the viscosity of C-2

Fig. 10 Viscosity of PP, PA6 and their blends plotted against MAH/NH₂ ratio for different shear rate : (●) 6.08 sec⁻¹; (○) 9.12 × 10² sec⁻¹; (▲) 6.08 × 10³ sec⁻¹

shown in Fig. 8, the preferential orientation of PP crystallites is appeared to be lower than that of pure PP [23]. As a result, as observed in C-2, although no crystal orientation is observed in undrawn fibers of pure PP.

Fig. 10 shows a relation between MAH/NH₂ ratio and viscosity. At a relatively small shear rate (6.08 sec⁻¹), viscosity of blend samples increased with increasing MAH/NH₂ ratio. Samples having an MAH/NH₂ ratio of 0.04 or more are found to have viscosity greater than that of pure PA6 or PP.

At a shear rate of 9.12 × 10² sec⁻¹, viscosity of blend samples increases with increasing MAH/NH₂ ratio. However, the rate of increase becomes relatively low as the ratio exceeds 0.08. For each blend sample, viscosity is low in comparison with that of pure PA6. In contrast, the viscosity of the blend having an MAH/NH₂ ratio of 0.00 is almost the same as that of pure PP, whereas samples having a ratio of 0.04 or more have viscosity greater than that of pure PP. At the highest shear rate of 6.08 × 10³ sec⁻¹, blends having a ratio of 0.04 or more show nearly constant viscosity. In this way, at shear rates of 9.12 × 10² sec⁻¹ and 6.08 × 10³ sec⁻¹, viscosity values of blends fall between those of pure PA6 and PP, because the affinity between the two components increased with increasing MAH/NH₂ ratio.

Fig. 11 Wide-angle X-ray diffraction diagrams of PP, PA6 and their blend fibers drawn to a ratio of 4.8 containing MAH-PP with contents of 5 phr (G-1), 10 phr (B-2) and 20 phr (G-2).

Blend fibers drawn to the ratio of 4.8 were subjected to X-ray diffraction measurement. Wide-angle X-ray diffraction photographs indicated no difference in diffraction patterns of blend fibers having different MAH-PP contents. Subsequently, the diffraction intensity profiles on the equator were measured

with a scintillation counter. For comparison, the results for pure PP and PA6 fibers are also shown (Fig. 11).

For the diffraction of PP crystal in drawn blend fibers, (110) and (040) diffraction peaks of PP crystals were found to be relatively small as compared with those of pure PP fibers. Almost no difference in diffraction of PP crystals was observed among blend samples of different MAH-PP contents. In contrast, strong diffractions of (200) and (002) appeared in pure PA6 fibers, whereas blend fibers show relatively broad diffractions. In particular, for blend fibers having an MAH-PP content of 10 phr or more (B-2, G-2), the diffraction intensity for (002) of the PA6 crystal was relatively small. This is probably because, in blend fibers having an MAH-PP content of 10 phr or more, fine dispersion of the two phases suppressed the crystallization of PA6 to make the diffraction peak of PA6 crystal relatively broad.

3.4 Long-period structure of blend fibers

The long-period structure of blend fibers drawn to a ratio of 4.8 was investigated, using small-angle X-ray scattering. As shown in Fig. 12, symmetric single peaks were observed in each scattering profile for blend fibers. The long period of these blend fibers was about 150 Å. Also, when the MAH-PP content increased, the peak intensity was found to decrease slightly. The peak slightly shifted to the low-angle side with increasing MAH-PP content, indicating a slight increase of the long period. These findings are probably attributable to fine dispersion of the PP and PA6 components, due to MAH-PP, making formation of the long-period structure difficult. However, the level of influence of MAH-PP content can not be said to be very large on the whole.

Fig. 12 Small-angle X-ray scattering diagrams of PP/PA6 blend fibers drawn to a ratio of 4.8 containing MAH-PP with contents of 0 phr (C-2), 5 phr (G-1), 10 phr (B-2) and 20 phr (G-2) without annealing.

In the next step, these blend fibers were annealed under free

ends at 180°C, which exceeds the melting point of PP. Fig. 13 shows the scattering profile after annealing. Here, blend fibers having MAH-PP contents of 10 phr and 20 phr exhibit symmetric single scattering peaks, whereas those having contents of 0 phr and 5 phr exhibit double peaks. That is, in blend fibers having MAH-PP contents of 5 phr or less, annealing separated the PP and PA6 components because of poor compatibility between the two components, causing the long period of each component to appear. In contrast, in blend fibers having MAH-PP contents of 10 phr or more, the PP and PA6 components can be considered to be difficult to separate by annealing because of relatively fine dispersion, based on the result that only one scattering maximum is observed even after annealing. In any of the blend fibers, the scattering maximum was found to be smaller than that before annealing.

Fig. 13 Small-angle X-ray scattering diagrams of PP/PA6 blend fibers drawn to a ratio of 4.8 containing MAH-PP with contents of 0 phr (C-2), 5 phr (G-1), 10 phr (B-2) and 20 phr (G-2) after annealed at 180°C.

3.5 Change in the melting behavior of blend fibers due to drawing

DSC curves were recorded for blend fibers of different contents of MAH-PP, as well as for pure PA6 and pure PP fibers. Fig. 14 shows the results of measurements of undrawn fibers. The melting peaks of the PA6 and PP components in the undrawn fibers were found to be almost as same as those of pure ones.

Fig. 15 shows the melting endothermic curves of blend fibers drawn to a ratio of 4.8. In each blend fiber, the melting endothermic peak of the PP component became sharper than that of the undrawn fiber and was shifted to the higher temperature side. This is probably because drawing at 130 °C promoted the crystallization and growth of PP crystallites. Melting points of PP components within the blend fibers were found to be almost the same as that of pure PP.

Fig. 14 DSC curves of PP, PA6 and their undrawn blend fibers containing MAH-PP with contents of 0 phr (C-2), 5 phr (G-1), 10 phr (B-2) and 20 phr (G-2) measured in the heating process at a heating rate of 10 °C/min.

Fig. 15 DSC curves of PP, PA6 and their blend fibers drawn to a ratio of 4.8 containing MAH-PP with contents of 5 phr (G-1), 10 phr (B-2) and 20 phr (G-2) measured in the heating process at a heating rate of 10 °C/min.

Meanwhile, a peculiar phenomenon was observed in the melting endothermic curves of the PA6 component in drawn blend fibers. That is, the addition of MAH-PP caused formation of two melting endothermic peaks of the PA6 component. The melting endothermic peak of the PP component was shifted to the higher temperature side by drawing, whereas the melting endothermic peak of the higher temperature side of the PA6 component changed little to show almost the same temperature as that of pure PA6 fibers, even when MAH-PP content was changed from 0 phr (C-2) to 20 phr (G-2). The lower temperature side peak of the PA6 component was not observed in fibers without MAH-PP (C-2) and appeared in a shoulder shape in the blend fibers having an MAH-PP content of 5 phr (G-1). Furthermore, when the content was increased from 10phr (B-2) to 20phr (G-2), the lower temperature side peak of the PA6 component became clear. In the blend fibers having a content of 20phr (G-2), the height of the lower temperature side peak was comparable to that of higher temperature side peak.

The results of various experiments indicate that the peak at the lower temperature side for the PA6 component was not observed in the blend fiber produced at a draw ratio of 4.0 and it appeared in sample drawn to a ratio of 4.8 [14]. This lower temperature side peak of the PA6 component can be considered to correspond to the melting of PA6 crystallites of smaller sizes. That is, as the content of MAH-PP was increased from 10phr (MAH/NH₂ ratio of 0.08), a greater amount of the PP component seemed to be easily mixed with the PA6 component, enabling generation of PA6 crystallites of smaller sizes with drawing [13-15].

4. Conclusions

PP/PA6 blended fibers having different contents of MAH-PP were prepared in order to examine the effect of MAH-PP content on their structures.

(1) Observation of undrawn blend fibers under a SEM indicated that for C-2, which contains no MAH-PP, the PP phase showed the formation of fibrils having a diameter of about 0.4-1.5 μ m, whereas for G-1, having an MAH-PP content of 5 phr (MAH/NH₂ ratio of 0.04), the diameter of the fibrils was reduced to about 0.2-0.4 μ m.

(2) The crystallization exothermic peak of the PA6 component was not observed in DSC curves of samples having an MAH-PP content of 10 phr (MAH/NH₂ ratio of 0.08) or more. Subsequently, even in samples that exhibited no crystallization exothermic peak of the PA6 component in the cooling process, the melting endothermic peak of the PA6 component appeared in the reheating process.

(3) Undrawn fibers of pure PA6 and PP indicated no preferential

orientation of crystallites. An a*-axis orientation of PP crystallites was observed in blend fibers without MAH-PP (C-1), even at a draft ratio of about 2.0-4.0. Furthermore, in blend fibers having MAH-PP contents of 5 phr or more, c-axis orientation of PP crystallites was clearly observed, with diffraction patterns overlapping those of a*-axis orientation.

(4) The drawn fibers (draw ratio: 4.8) were investigated by wide-angle X-ray diffraction. The diffraction peaks of PA6 crystal for pure PA6 fibers were distinct, whereas those of blend fibers having a content of 10 phr (MAH/NH₂ ratio of 0.08) or more were relatively broad.

(5) The long-period structure of drawn blend fibers was investigated after annealing at 180°C. Blend fibers having MAH-PP contents of 5 phr or less were found to exhibit double scattering peaks. Presumably, because of poor compatibility between the two components, annealing separated the PP and PA6 components, causing the long period of each component to appear.

(6) DSC curves of drawn fibers (draw ratio: 4.8) were obtained. As a result, the lower temperature side peak of the PA6 component was found to appear in blend fibers having a content of 10 phr (B-2). This peak can be considered to correspond to the melting of incomplete or small crystallites of PA6.

Acknowledgments

The author wishes to express his sincere appreciation for the advice and guidance provided by Professor Emeritus A. Konda of Shinshu University.

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