

Study of the Crystal Structure of P(HBA/HNA)/PET Blend Fibers

CHANGFA XIAO,¹ YUFENG ZHANG,¹ SHIZHEN WU,¹ TOSHISADA TAKAHASHI²

¹ Department of Materials Science, Tianjin Polytechnic University, Tianjin 300160, People's Republic of China

² Faculty of Engineering, Fukui University, Bunkyo 3-9-1, Fukui 910, Japan

Received 25 October 2000; accepted 19 April 2001

ABSTRACT: The crystal structure of *p*-hydroxybenzoate/2-hydroxy-6-naphthoic acid copolyester [P(HBA/HNA)]/poly(ethylene terephthalate) (PET) blend (ACPET) fiber was studied with wide-angle X-ray diffraction and differential scanning calorimetry. The results showed that crystallites of P(HBA/HNA) and PET were formed in ACPET fibers; that is, some crystallites of ACPET fiber were composed of PET chains, and others were composed of P(HBA/HNA) chains. The thermal behaviors of the crystals of each component in the blend fiber were different from those of each corresponding pure component. For the fibers heat-treated at 300 and 350°C, the degree of supercooling of P(HBA/HNA) segments in the blend fibers was the same as that of P(HBA/HNA) fiber, but the degree of supercooling of PET in the blend fibers was distinctly higher than that of pure PET fibers. Evidently, the aforementioned changes were attributable to the blending of PET with P(HBA/HNA). © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 394–400, 2002

Key words: *p*-hydroxybenzoate/2-hydroxy-6-naphthoic acid copolyester; poly(ethylene terephthalate); blend fibers; crystal structures; differential scanning calorimetry (DSC)

INTRODUCTION

After the success of a wholly aromatic polyamide fiber (Kevlar) being made from a lyotropic liquid-crystal polymer system, there have been significant advances in research on wholly aromatic polyester (i.e., polyarylate) fibers made from thermotropic liquid-crystal systems. Although there are many kinds of thermotropic liquid-crystal polymers, only *p*-hydroxybenzoate/2-hydroxy-6-naphthoic acid copolyester [P(HBA/HNA)] has been commercially used to produce high-performance fibers at present.^{1–3} Moreover, poly(ethylene terephthalate) (PET) is a typical aromatic-

aliphatic polyester and is widely used to produce synthetic fibers, films, bottles, and so forth.

Our previous studies of P(HBA/HNA) fibers showed that the structure of the as-spun fiber was in an oriented, amorphous state. After heat treatment, the macromolecules in the fiber were ordered, and cocrystals of the two components, *p*-hydroxybenzoate (HBA) and 2-hydroxy-6-naphthoic acid (HAN), were formed. The degree of crystallinity increased with increasing heat-treatment temperature.⁴ P(HBA/HNA) fibers with excellent mechanical properties could be obtained accordingly.

In general, irregular chemical or geometric structures of macromolecules affect their aggregated structure. In comparison with flexible molecules, rigid macromolecules have less freedom to move, so their conformation cannot be changed

Correspondence to: Changfa Xiao (cfxiao@public.tpt.tj.cn).

Journal of Applied Polymer Science, Vol. 83, 394–400 (2002)
© 2002 John Wiley & Sons, Inc.

easily. The incorporation of PET with polyarylate by copolymerization or blending can improve the melt spinnability of polyarylate and some properties, such as fatigue resistance, of the fiber. Such fibers can be applied to manufacturing so-called self-reinforced engineering materials. Compared with copolymerization, polymer blending possesses so many peculiarities, such as modification in evidence, actualization on an industrial scale, and relative briefness, that it has already been applied to the modification of polymeric materials.⁵⁻⁸

This work is concerned with the crystalline structure of P(HBA/HNA)/PET blend (ACPET) fibers as determined by wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC). The results showed that the crystallization of P(HBA/HNA) and PET occurred in ACPET fibers; that is, some crystals in ACPET fibers were composed of PET chains, and others were composed of P(HBA/HNA) chains. The crystalline orientation of P(HBA/HNA) or PET in ACPET fibers was different from that of pure P(HBA/HNA) or PET, respectively.

EXPERIMENTAL

As-spun P(HBA/HNA) and ACPET fibers were prepared by melt spinning and were kindly supplied by Kuraray Co. (Japan). The molar ratio of HBA/HNA in P(HBA/HNA) was about 70/30. The ACPET fiber was composed of P(HBA/HNA) and PET with a mass ratio of 70/30. The tensile strengths of the P(HBA/HNA) and ACPET fibers were 9.8 and 7.7 cN/dtex, their tensile moduli were 494 and 454 cN/dtex, and their breaking extensions were 2.0 and 2.1%, respectively. For comparison, a regular PET fiber was also employed, the tensile strength, tensile modulus, and breaking extension of which were 8.2 cN/dtex, 145 cN/dtex, and 12%, respectively.

The heat treatment of fibers was performed in two ways: (1) heated at a certain temperature for 10 min in a vacuum oven and then naturally cooled to room temperature and (2) heated at a certain temperature for 16 h in a silicon oil bath and then naturally cooled to room temperature.

WAXD patterns were obtained through the transmission mode with a Rigaku-Denki X-ray diffractometer using nickel-filtered Cu K α radiation. The distance of the film to the X-ray source was corrected with silicon powder.

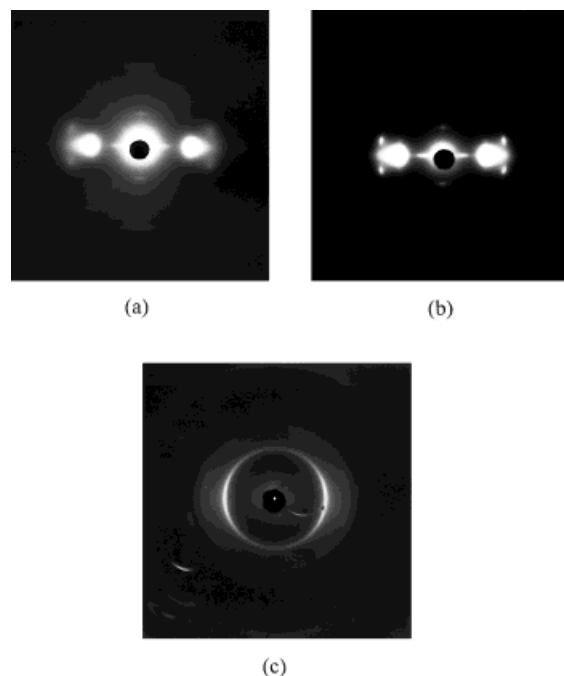


Figure 1 WAXD patterns of P(HBA/HNA) fibers: (a) as-spun fiber, (b) fiber heat-treated at 265°C for 10 min, and (c) fiber heat-treated at 300°C for 10 min.

DSC was carried out with a PerkinElmer DSC-7C under a nitrogen atmosphere. An empty sample pan was taken as the reference sample. Fiber specimens were cut into small pieces and weighed accurately. The heating and cooling rates were 10°C/min. Some of the fiber specimens were specially heat-treated for a certain time in the DSC instrument before the DSC measurements.

RESULTS AND DISCUSSION

P(HBA/HNA) is a typical wholly aromatic polyester with rigid chains and has characteristics of nematic liquid crystals. Therefore, P(HBA/HNA) can be made into a polyarylate fiber with a strong orientation along the fiber axis and the structure of orthorhombic crystal. In WAXD patterns of as-spun P(HBA/HNA) fiber, equatorial (110) and (200) and meridional (002), (004), and (006) crystalline reflections can be observed.⁴

The WAXD patterns of heat-treated as-spun P(HBA/HNA) fibers are shown in Figure 1. The intensities of the reflections on the equator and the first layer line become stronger when the fibers are heat-treated below the melting point

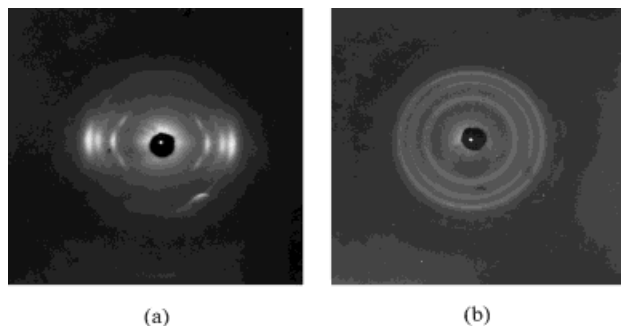


Figure 2 WAXD patterns of PET fibers: (a) regular fiber and (b) fiber heat-treated at 265°C for 10 min.

(T_m) of P(HBA/HNA), for example, below 265°C. This result shows that the three-dimensional order of the heat-treated fibers has been enhanced. The WAXD patterns of P(HBA/HNA) fiber heat-treated above the P(HBA/HNA) T_m are shown in Figure 1(c). Only the reflection arc remaining at $d \approx 0.451$ nm near the equator can be observed.

In general, nematic liquid-crystal molecules in an oriented state hardly produce orientation relaxation, even if they have been molten. It is evident that although the P(HBA/HNA) fiber is heat-treated at a temperature above T_m of P(HBA/HNA) for 10 min, the orientation of the rigid molecules cannot be fully relaxed within a limited time as the orientation of flexible molecules is. As shown in Figure 1(c), the reflection near the equator is still strong, indicating that the molecules of P(HBA/HNA) fiber are still located on a hexagonally packed structure. These phenomena can also be observed in the ACPET fibers discussed later.

PET is a kind of aromatic–aliphatic polyester. PET fiber can be made by melt spinning as well as poststretching and heat treatment. In general, the crystal of PET fiber belongs to a triclinic crystalline system. In the WAXD patterns of PET fibers, as shown in Figure 2(a), (010) ($d \approx 0.501$ nm), (100) ($d \approx 0.345$ nm), and (T10) ($d \approx 0.391$ nm) reflections on the equator, as well as (0T1) and (T11) reflections on the layer line, can be observed. If the heat-treatment temperature is above the PET T_m , only an isotropic amorphous halo can be observed on WAXD patterns of heat-treated PET fibers, as shown in Figure 2(b).

Figure 3 shows the WAXD patterns of ACPET fibers. Figure 3(a) shows the pattern for an as-spun fiber, and Figure 3(b) is the schematic representation of Figure 3(a). It is evident that the reflections of the PET and P(HBA/HNA) compo-

nents on the equator are superposed and difficult to separate. We can determine by comparing Figures 1 and 2 that the reflection on the low-angle side of the meridian is the (002) reflection of the P(HBA/HNA) component and that the one on the low-angle side of the first layer line is the (0T1) reflection of the PET component in ACPET fiber.

Thus, (1) the ACPET fiber has a kind of mixed crystal structure made up of crystals of PET and P(HBA/HNA) components in the fiber; (2) the (002) reflection on the meridian in Figure 3 seems to be a spot shape, indicating that the liquid-crystal P(HBA/HNA) component exhibits a higher degree of crystalline orientation along the fiber axis; and (3) although the PET component in the ACPET fiber also orients to a certain extent, the orientation is weaker compared with that of the P(HBA/HNA) component.

The crystalline orientation of the PET component in ACPET fiber is different from that of the PET component in PET/P(HBA/HNA) sheath/core-type bicomponent fiber.⁹ The solidification of the PET component happens after P(HBA/HNA) solidifies during the fiber-spinning process, so the oriented PET component in the sheath/core-type

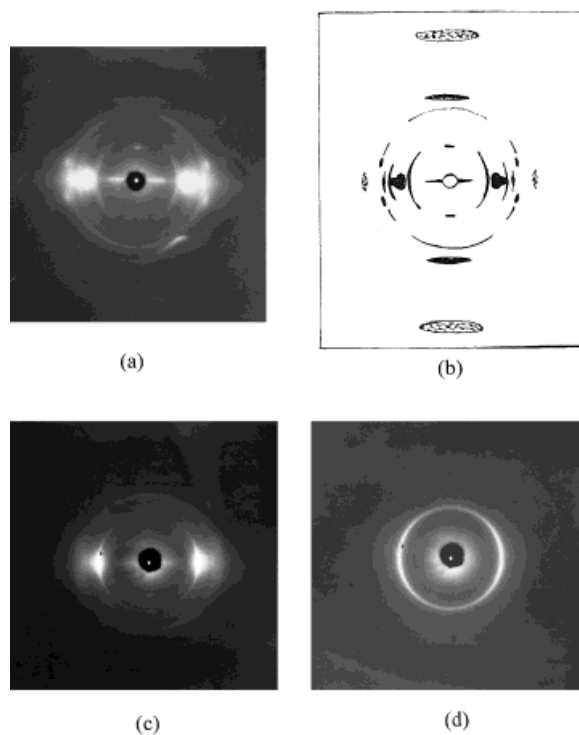


Figure 3 WAXD patterns of ACPET fibers: (a) as-spun fiber, (b) scheme of the as-spun fiber, (c) fiber heat-treated at 265°C for 10 min, and (d) fiber heat-treated at 300°C for 10 min.

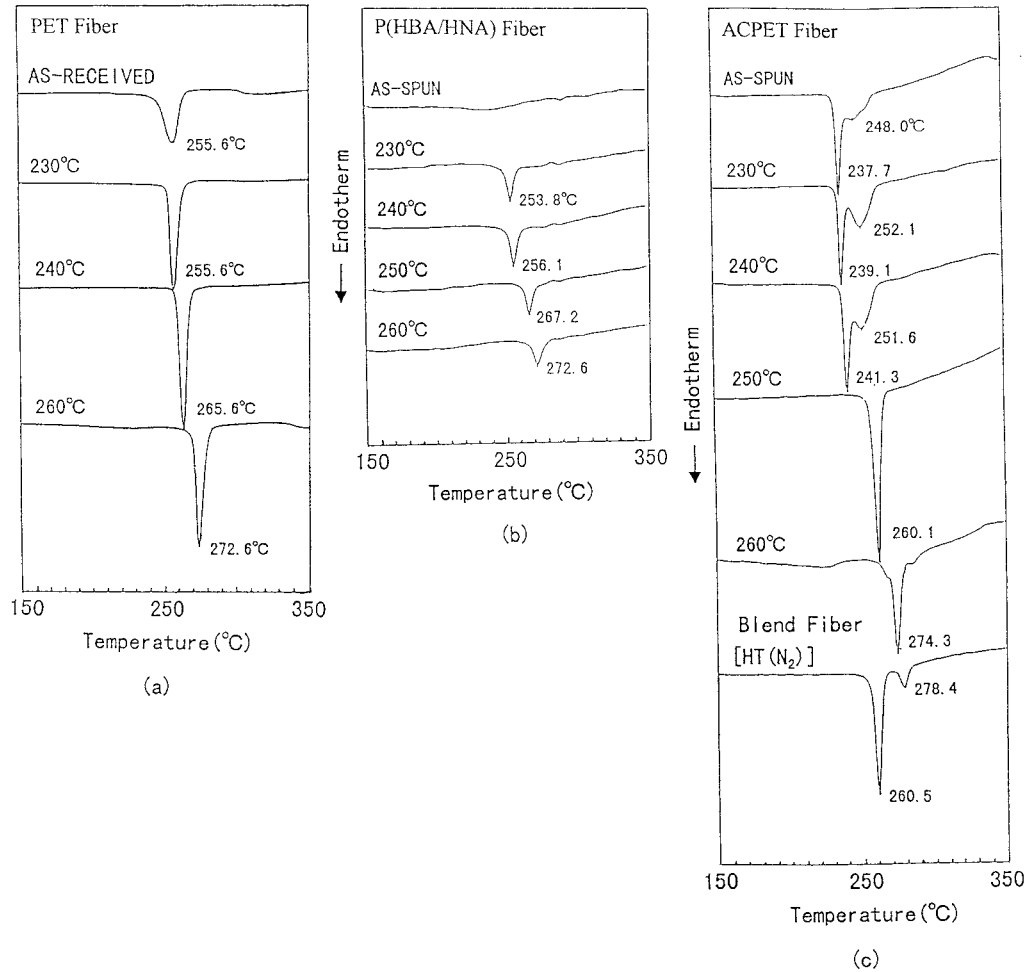


Figure 4 DSC heating thermograms of fibers: (a) regular PET fiber, (b) P(HBA/HNA) fiber, and (c) ACPET fibers.

bicomponent fiber may produce easily orientation relaxation. Dispersed in a rigid P(HBA/HNA) matrix highly oriented along the fiber axis, with orientation relaxation hardly occurring, the PET component in the formed ACPET fiber still maintains a proper crystallinity and degree of orientation. As shown in Figure 3(c), if the blend fiber is heat-treated near the PET T_m , for example, 265°C, the $(hk0)$ reflections present an arc shape due to the melting crystallization of the PET component in the ACPET fiber. The reflections of (110) ($d \approx 0.449$ nm), (200) ($d \approx 0.391$ nm), and (210) ($d \approx 0.314$ nm) on the equator, as well as the (002), (004), and (006) reflections on the meridian, which are attributed to the P(HBA/HNA) component in the ACPET fiber, are also observed. Figure 3(c) shows that the crystalline orientation of PET has evidently been destroyed, but P(HBA/HNA) still retains fairly good crystalline orienta-

tion in the ACPET fiber. The results of the heat-treatment temperature further rising are shown in Figure 3(d). It is evident that although the heat-treatment temperature is higher than T_m of P(HBA/HNA), because of the rigidity of P(HBA/HNA) molecules, some arc reflection rather than an amorphous halo on the equator can still be seen.

As previously discussed, the crystalline behaviors of PET and P(HBA/HNA) are mutually independent, and a structure of mixed crystal in ACPET fiber forms. Next are discussed the thermal behaviors of the two components in the blend fiber via DSC analysis.

DSC thermograms of the fibers heat-treated in a silicon oil bath for 16 h are shown in Figure 4, where T_m is the melting point of PET and T_{C-N} is the crystal/liquid-crystal transition temperature of P(HBA/HNA). It is evident that the T_m of the

Table I T_m and T_{C-N} of Various Fibers Heat-Treated at 240°C

Fiber	T_m (°C)	T_{C-N} (°C)
PET	256.1	260.5
ACPET	241.3	251.6

PET component in the ACPET fiber heat-treated under 250°C is lower than that of the PET fiber. Moreover, T_{C-N} of ACPET fiber is lower than that of P(HBA/HNA) fiber heat-treated at the same temperature. T_m and T_{C-N} of various fibers heat-treated at 240°C are listed in Table I.

It is known from WAXD results that crystals of P(HBA/HNA) and PET coexist in ACPET fiber. T_m and T_{C-N} of ACPET fiber are lower than the corresponding values of PET and P(HBA/HNA) fibers. These results indicate that there are some mutual influences between the two components in ACPET fiber during crystallization.

Fiber samples were heat-treated in the DSC device at 230, 265, 300, and 350°C for 5 min before their cooling DSC measurements. No changes were observed in the DSC cooling thermograms when the heat-treatment temperature was lower than T_m of PET and T_{C-N} of P(HBA/HNA) (e.g., 230°C). A clear change in the DSC cooling thermograms of fibers heat-treated at 265 and 300°C appears, as shown in Figure 5. In Figure 5(a), no changes can be observed in the DSC cooling thermograms of P(HBA/HNA) fiber heat-treated at a temperature lower than its T_{C-N} but a little higher than T_m . Because the heat-treatment temperature was higher than T_m , an exothermic peak corresponding to the melting recrystallization of PET at 214°C can be observed. Moreover, an exothermic double peak corresponding to the crystallization of PET component at 175 and 196°C can be observed. Figure 5(b) shows DSC cooling thermograms of fibers heat-treated at 300°C, which is higher than T_m and T_{C-N} . The exothermic peak of crystallization for PET fiber appears at 208°C. The liquid-crystal/crystal transition temperature for P(HBA/HNA) fiber appears at 238°C.

In addition, in the DSC cooling thermograms of the ACPET fiber, an exothermic peak for the crystallization of PET component that appears at 177 and 188°C is a double peak, and the one for the liquid-crystal/crystal transition of P(HBA/HNA) can be observed at about 238°C.

The aforementioned results indicate that as the disperse phase, the PET component suffers

the repression of the P(HBA/HNA) component, the matrix phase, when the melting recrystallization of PET occurs at a heat-treatment temperature higher than T_m but lower than T_{C-N} , so the crystalline temperature of PET shifts to the lower side. This is possibly due to steric hindrance of the motion of PET molecules in the blend fiber.

After heat treatment at a temperature higher than T_m and T_{C-N} , the liquid-crystal/crystal transition of P(HBA/HNA) first occurs during the cooling process and follows the crystallization of PET.

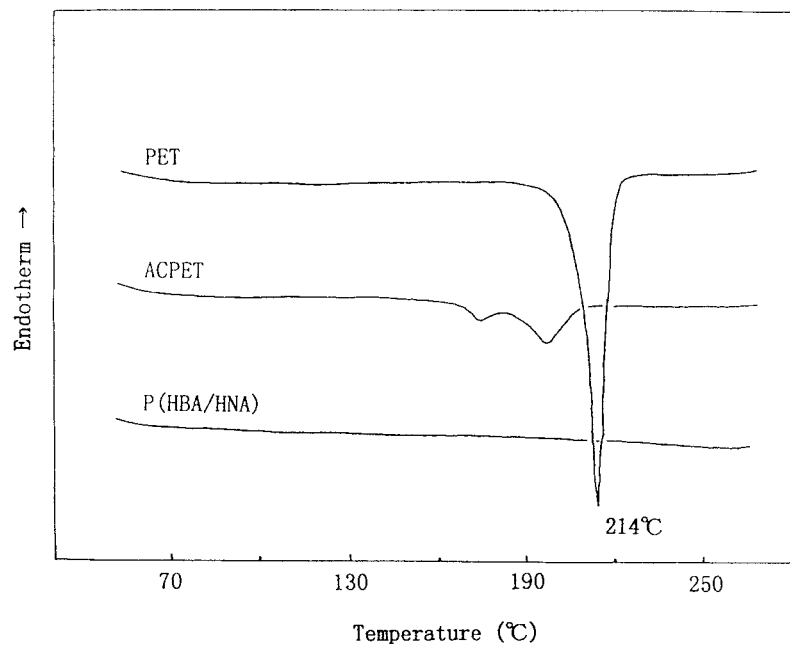
It is known from the WAXD results that the concerned structure, similar to that of pure P(HBA/HNA), still remains in ACPET fiber, even after heat treatment above 300°C. The existence of this structure could certainly influence the crystallization of the PET component, and vice versa. Moreover, the crystal peak is a single peak in the DSC cooling thermograms of PET fiber, but the peak in the DSC cooling thermograms of the blend fiber related to the crystallization of the PET component is a double one. This possibly indicates the existence of two kinds of PET crystals with differently sized unit structures in the blend fiber.

In general, the difference value of the temperature (ΔT) corresponding to the crystal peak on the DSC cooling thermograms (T_C) and T_m is defined as the degree of supercooling, namely, $\Delta T = T_m - T_C$. Moreover, the higher T_C is or the smaller ΔT is, the more easily the sample crystallizes. For PET fibers heat-treated at 265, 300, and 350°C, as shown in Figure 6, ΔT is 43, 49, and 56°C, respectively; that is, the higher the heat-treatment temperature is, the more difficult the crystallization is in the cooling process.

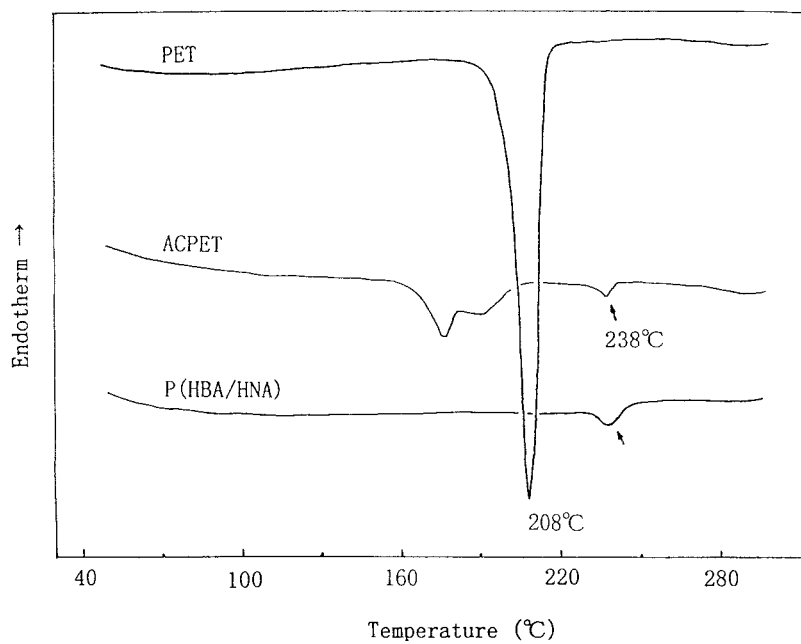
For fiber heat-treated at 265°C, only about 10°C higher than the PET T_m , even if it melts, the PET crystal still possesses a certain memory, and as crystal nuclear in cooling process, the remnant of such an ordered structure easily induces crystallization, so that the temperature of the crystal peak in the DSC cooling thermograms will shift to the higher temperature side, and ΔT will be reduced.

For the P(HBA/HNA) fibers heat-treated at 300 and 350°C, ΔT is 43 and 46°C, respectively, and the change is not large. Unlike the situation with PET fiber, the heat history has less effect on the liquid-crystal/crystal transition of P(HBA/HNA) fiber.

For the P(HBA/HNA) component in ACPET fiber heat-treated at 300 and 350°C, ΔT is 42 and 45°C, respectively, almost identical to the values of P(HBA/HNA) fiber. However, for the PET com-



(a)



(b)

Figure 5 DSC cooling thermograms of fibers: (a) fibers heat-treated at 265°C for 5 min and (b) fibers heat-treated at 300°C for 5 min.

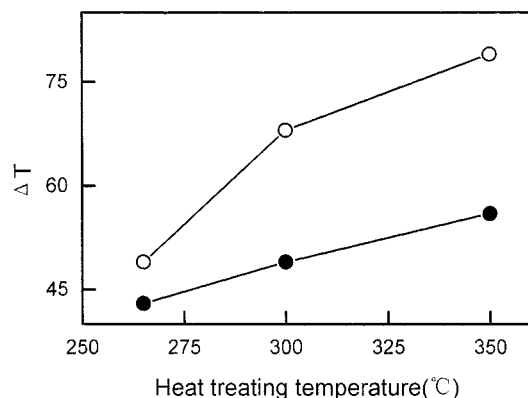


Figure 6 ΔT plotted against the heat-treatment temperature of ACPET (○) and PET (●) fibers.

ponent in ACPET fiber, as shown in Figure 6, ΔT of fibers heat-treated at 265, 300, and 350°C is 49, 68, and 79°C, respectively. The trend is similar to that for PET fiber, but the level of change is greater. Obviously, the reason for this change depends on the blending of PET with P(HBA/HNA). The PET component melts, and the original structure of the P(HBA/HNA) component is retained when the ACPET fiber is heat-treated at 265°C. Therefore, it is known that the melting-crystallization behavior of the PET component in the ACPET fiber is similar to that of the PET fiber. When the heat-treatment temperature rises above 300°C, P(HBA/HNA) also melts in addition to PET. Compatibility of the two components, P(HBA/HNA) and PET, to a certain level might be considered to result in the crystallization behaviors of the two components deviating from those of their pure state.

CONCLUSIONS

The crystal structure of ACPET fibers was studied with WAXD and DSC techniques.

WAXD studies of the fibers show that the crystal structure of ACPET fiber is a kind of mixed crystal composed of crystals of PET and P(HBA/HNA) components. After ACPET fiber cools from a melting state, the crystalline orientation behaviors of the two components are relatively independent; the crystalline orientation degree of liquid-crystal P(HBA/HNA) is high, but that of PET is low.

The results of DSC indicate that the PET T_m and P(HBA/HNA) T_{C-N} in ACPET fiber are lower than the temperatures for the components by themselves; this indicates that the two components affect each other in the blend fiber.

For ACPET fibers heat-treated at 300 and 350°C, ΔT of P(HBA/HNA) is almost the same as that of P(HBA/HNA) fiber. However, for the PET component in ACPET fiber, as for PET fiber, ΔT increases with an increasing heat-treatment temperature, but more than that of PET fiber. Obviously, this is attributable to the blending of PET with P(HBA/HNA).

REFERENCES

1. Cheng, S. Z. D. *Macromolecules* 1988, 21, 2475.
2. Troughton, M. J.; Davies, G. R.; Ward, I. M. *Polymer* 1989, 30, 58.
3. Xiao, C. F. *China Synth Fiber Ind* 1992, 15, 39.
4. Xiao, C. F.; Takahashi, T. *Sei-i Gakaishi* 1990, 46, 49.
5. Sun, L. M.; Sakoda, T.; Ueta, U.; Koga, K. *Polym J* 1994, 26, 961.
6. Martinez, J. M.; Nazabal, J.; Eguiazabal, J. I. *J Appl Polym Sci* 1994, 51, 223.
7. Fernandez-Berridi, M. J.; Iruin, J. J.; Maiza, I. *Polymer* 1995, 36, 1357.
8. Han, M.; Park, J.; Kim, W. N. *Polym Bull* 2000, 45, 151.
9. Furuta, T.; Rahakrishnan, J.; Ito, H.; Kikutani, T.; Okui, N. *Seikeikakou* 1997, 9, 920.