

Effects of Molecular Weight on Phase Structure of Poly(ethylene terephthalate)/Poly(ethylene 2,6-naphthalate) Blends

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ABSTRACT: The phase structure of poly(ethylene terephthalate)/poly(ethylene 2,6-naphthalate) (PET/PEN) blends was studied in relation to the molecular weight. The samples were prepared by both solution blends, which showed two glass-transition temperatures (T_g), and melt blends (MQ), which showed a single T_g , depending on the composition of the blends. The T_g of the MQ series was independent of the molecular weight of the homopolymer, although the degree of transesterification in the blends was affected by the molecular weight. The MQ series showed two exotherms dur-

ing the heating process of a differential scanning calorimetry scan. The peak temperature and the heat flow of the exotherms were affected by the molecular weight of the homopolymers. The strain-induced crystallization of the MQ series suggested the independent crystallization of PET and PEN. Based on the results, a microdomain structure of each homopolymer was suggested. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 2428–2438, 2005

Key words: polyester; blend; phase

INTRODUCTION

Poly(ethylene terephthalate) (PET) and poly(ethylene 2,6-naphthalate) (PEN) are both crystallizable polyesters with high thermal and mechanical properties. Thus, the blends of PET and PEN have been attracting increasing interest from both scientific and commercial viewpoints. The PET/PEN blends are basically immiscible, independent of the blend composition.¹ Transesterification in the melt blending of PET and PEN leads to the formation of block copolymers first and then random copolymers, which enhances the miscibility of the blend.² Thus, extensive work has been devoted to the relation between transesterification and structure development of the blends. The phase structure of PET/PEN blends has been evaluated from the glass-transition temperature (T_g), crystallization behavior, and tensile properties of the blends. The width of the glass-transition region (ΔT_g) in cases where only one T_g was observed in a differential scanning calorimetry (DSC) scan was related to the extent of miscibility of PET/PEN blends.³ The difference of the crystallization mode between thermal and strain-induced crystallization also gives us information on the phase structure of PET/PEN blends.^{4,5} Stewart et al. investigated the effects of transesterifi-

cation on the miscibility of the blends with a visual observation of the haziness of the extrudate and reported that 10% transesterification is necessary to show miscibility.² By contrast, Ihm et al. reported that the blends show a single T_g between those starting polymers and they are not crystallizable when the extent of transesterification reaches 50%.⁶ Such studies suggest that the definition of miscibility, which is closely related to the size of the heterogeneities in the blends, is important to understand the phase structure of PET/PEN blends. The size of the heterogeneities would be a function of the degree of transesterification, the conditions for blending, and the molecular weights of the homopolymers that were used.

In this work, immiscible blends of PET/PEN, which were prepared by solution blends, were used as starting materials to exclude the effects of transesterification on the phase structure of the blends. Then, the immiscible blends were heat treated to react with each other through transesterification. The effects of the molecular weight on the heterogeneities were evaluated by using high molecular weight PET and PEN, which were prepared by a solid-state polymerization of commercially available PET and PEN.

Temperature modulated DSC (TMDSC) provides excellent resolution of the T_g by separating the heat capacity from other nonreversing processes such as enthalpy relaxation and crystallization.⁷ In this study, TMDSC was utilized for thermal analysis of the samples in an effort to provide improved resolution of the

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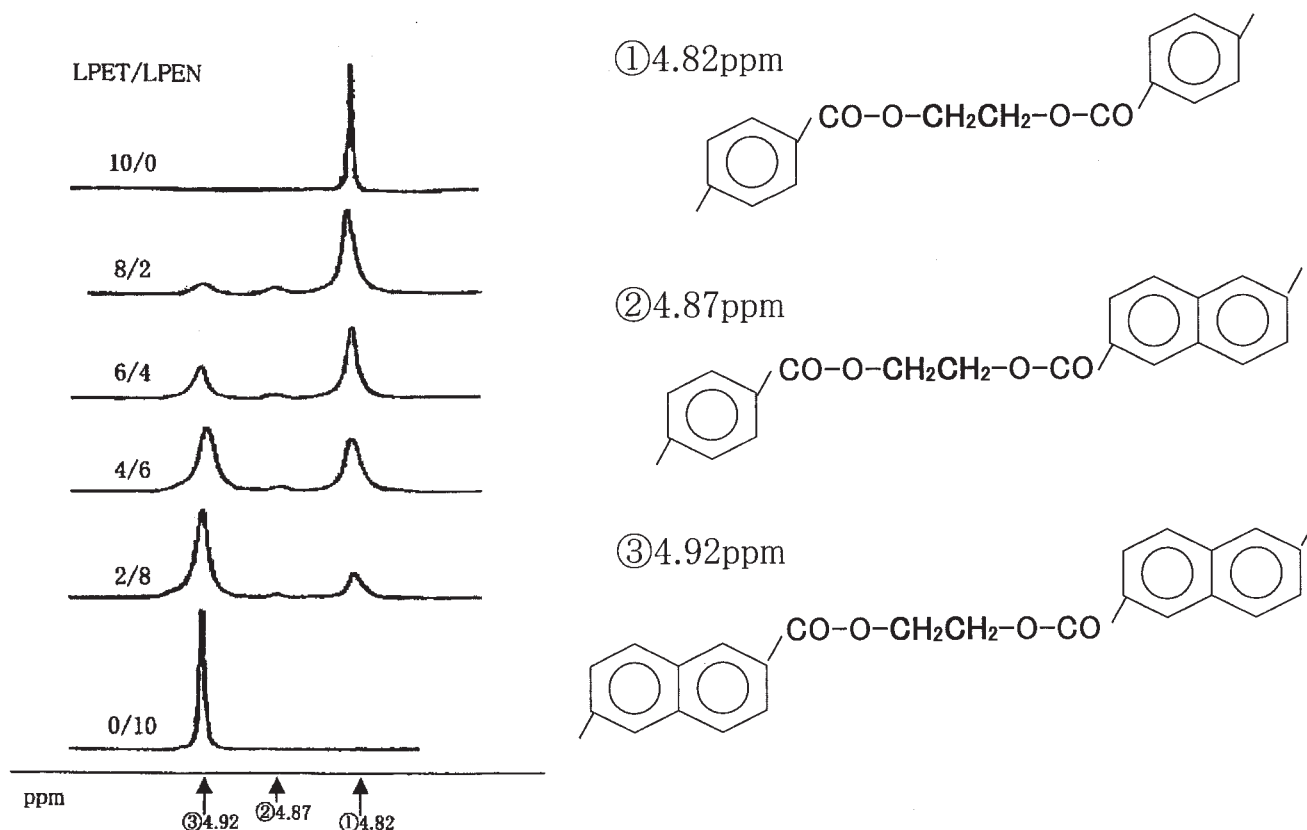


Figure 1 $^1\text{H-NMR}$ spectra of the ethylene unit region for PET, PEN, and their blend.

T_g as well as the cold crystallization behavior of PET/PEN blends.

EXPERIMENTAL

Samples

Commercially available PET [intrinsic viscosity (IV) = 0.63 dL/g] and PEN (IV = 0.65 dL/g) pellets were

used as starting materials. Each polymer was solid-state polymerized to obtain high molecular weight materials. Details of the polymerization are described elsewhere.⁸ The IV values after the polymerization were 3.5 and 3.0 dL/g for PET and PEN, respectively. Each homopolymer with a different molecular weight was denoted by the following abbreviations; LPET (IV = 0.63 dL/g), LPEN (IV = 0.65 dL/g), HPET (IV = 3.5 dL/g), and HPEN (IV = 3.0 dL/g). The blending of PET with PEN was done in two stages by the combination of LPET/LPEN, LPET/HPEN, and HPET/LPEN. In the first stage, each homopolymer with the desired molecular weight was dissolved individually in a mixed solvent of trifluoroacetic acid and dichloromethane (50/50, v/v) at room temperature. A desired volume of PET solution (3 wt %) was mixed with a desired volume of PEN solution (3 wt %). The mixture containing requisite amounts of PET and PEN components was poured into methanol to attain polymer precipitates. In the second stage, the dried precipitates were compression molded at room temperature (MD) and at 290°C for 5 min under pressure, followed by quenching in ice water (MQ). The films of the pure components were molded under similar conditions. The blend ratio was expressed by a weight ratio of the two components, PET/PEN (g/g).

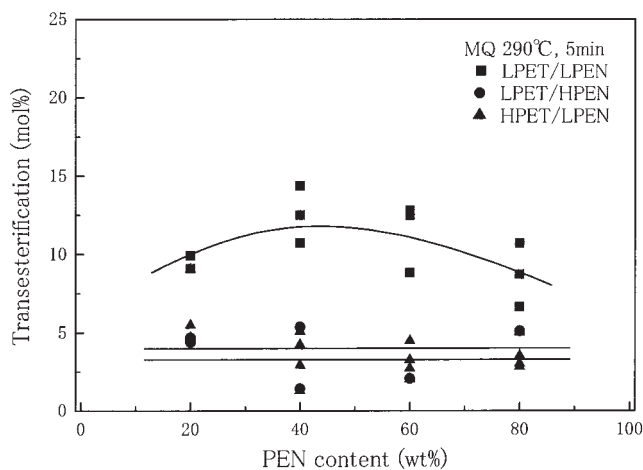


Figure 2 The dependence of the PEN content in the blends on the molar percentage of transesterification.

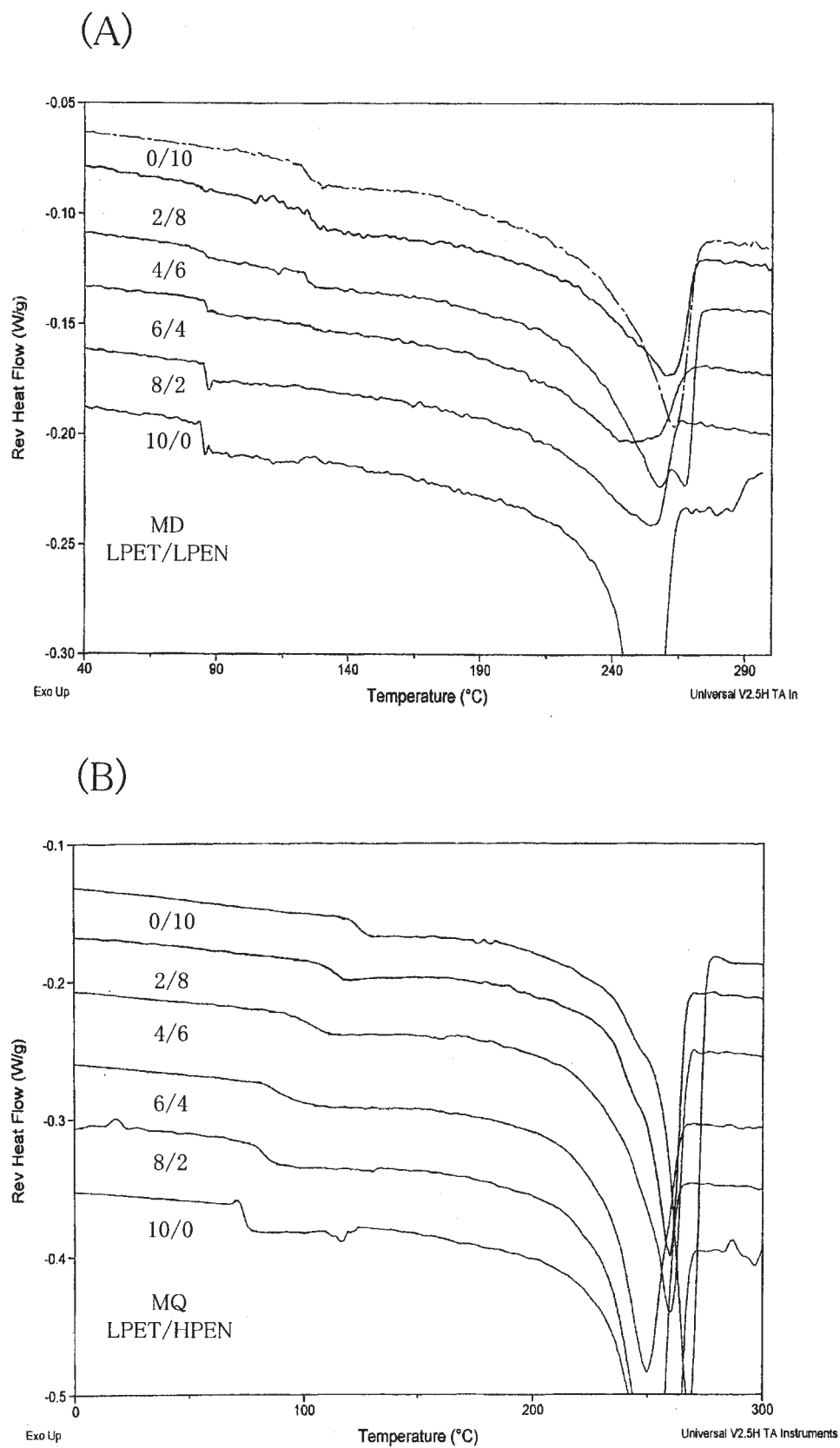


Figure 3 The reversing heat flow of (A) MD and (B) MQ blends.

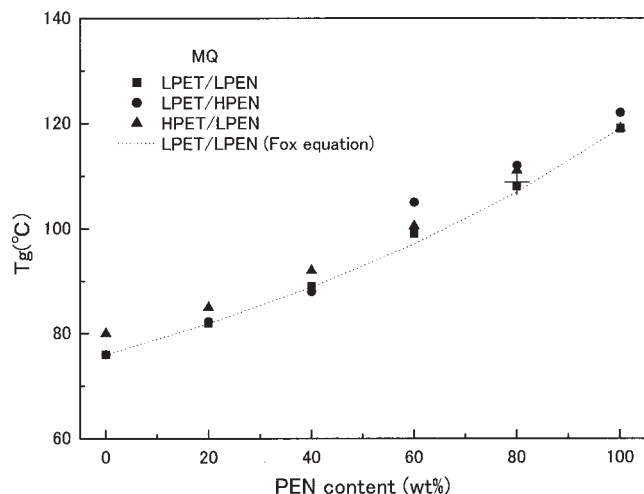


Figure 4 The relation between the T_g and PEN content of MQ blends.

Uniaxial drawing was carried out by solid-state co-extrusion near the T_g for the MQ. The extrusion draw ratio (EDR) of each sample was fixed at 5.

Measurements

The extent of transesterification of the PET/PEN blends was estimated by using the $^1\text{H-NMR}$ spectra corresponding to the ethylene moiety.⁹ The samples for the NMR measurements were prepared by dissolving the blends in a mixture of trifluoroacetic acid/deuterated chloroform (10/20, v/v). The measurements were carried out at 25°C on a Jeol JNM-LA 400 at a field strength of 400 MHz for the proton observations. The chemical shift was referenced by tetramethyl silane.

The thermal behavior of the samples was examined with a Seiko Instrument DSC calorimeter (model SSC-5200) in a dry nitrogen atmosphere at a heating rate of 10°C/min. TMDSC measurements were carried out by using a TA Instruments (New Castle, DE) 2920 DSC at heating ramps of 2°C/min with a modulation amplitude of 0.265°C and a period of 50 s.

Wide-angle X-ray diffraction (WAXD) patterns of the samples were obtained at room temperature with Cu $K\alpha$ radiation generated at 50 kV and 50 mA on a Rigaku RU-200 and monochromatized with a graphite crystal.

The tensile modulus and strength on the fiber axis of the samples were measured at strain rates of 10^{-3} and 10^{-2} s^{-1} , respectively, at room temperature. The modulus was determined from the initial slope of the stress-strain curve at low strain (<0.1%). The gauge length for all samples was adjusted to 5 cm. The cross-sectional area of a sample was determined by the combination of optical microscope and micrometer measurements.

RESULTS AND DISCUSSION

Characterization of as-prepared samples

The $^1\text{H-NMR}$ spectra of the MQ series (LPET, LPEN, LPET/LPEN) in the ethylene unit region are shown in Figure 1. The peaks at 4.82 and 4.92 ppm are attributed to the ethylene units of PET and PEN, respectively, and the one at 4.87 ppm is attributed to those that exist between terephthalic and naphthalic groups in the polymer backbone, which was not observed in the MD. Shi and Jabarin used these three peak to determine the extent of transesterification according to the literature.⁹ The results for LPET/LPEN, LPET/HPEN, and HPET/LPEN are shown as a function of the blend ratio in Figure 2. At a given blend ratio, the blend of LPET/LPEN showed the highest percentage with a maximum around a blend ratio of 40–60 wt % PEN. However, the extent of transesterification for the blends of LPET/HPEN and HPET/LPEN is quite low, almost independent of the blend composition. For PET/PEN blends, the kinetics and mechanism of the transesterification reaction have been discussed for a long time. However, no final agreement has been reached in the literature. In this work, discussion on the mechanism of transesterification is not the focus; however, the results shown in Figure 2 indicate that the end groups of both polyesters have an important role in the transesterification reaction. As will be shown later, the MD series that was used for the transesterification had a phase separated system and the domain size of each phase was suggested to be dependent on the molecular weight. In this work, the extent of transesterification was evaluated from the amount of PET/PEN copolymer in the blends that might be produced at the interface between the PET and PEN phases. Thus, the influence of the phase structure on the degree of the transesterification might not be negligible. These are under investigation.

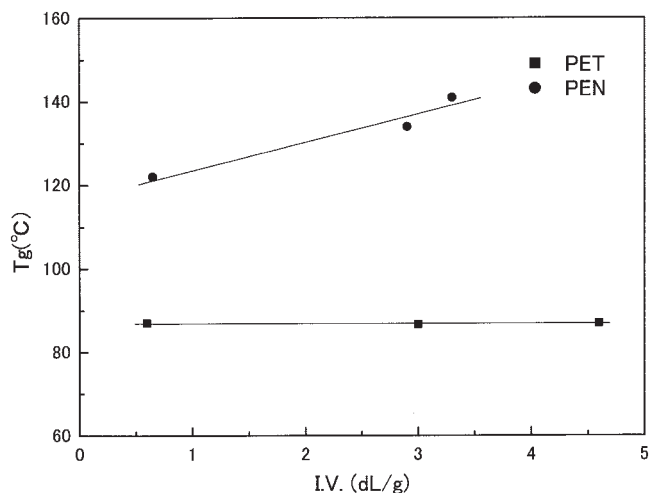


Figure 5 The relation between the intrinsic viscosity (IV) and T_g of PET and PEN.

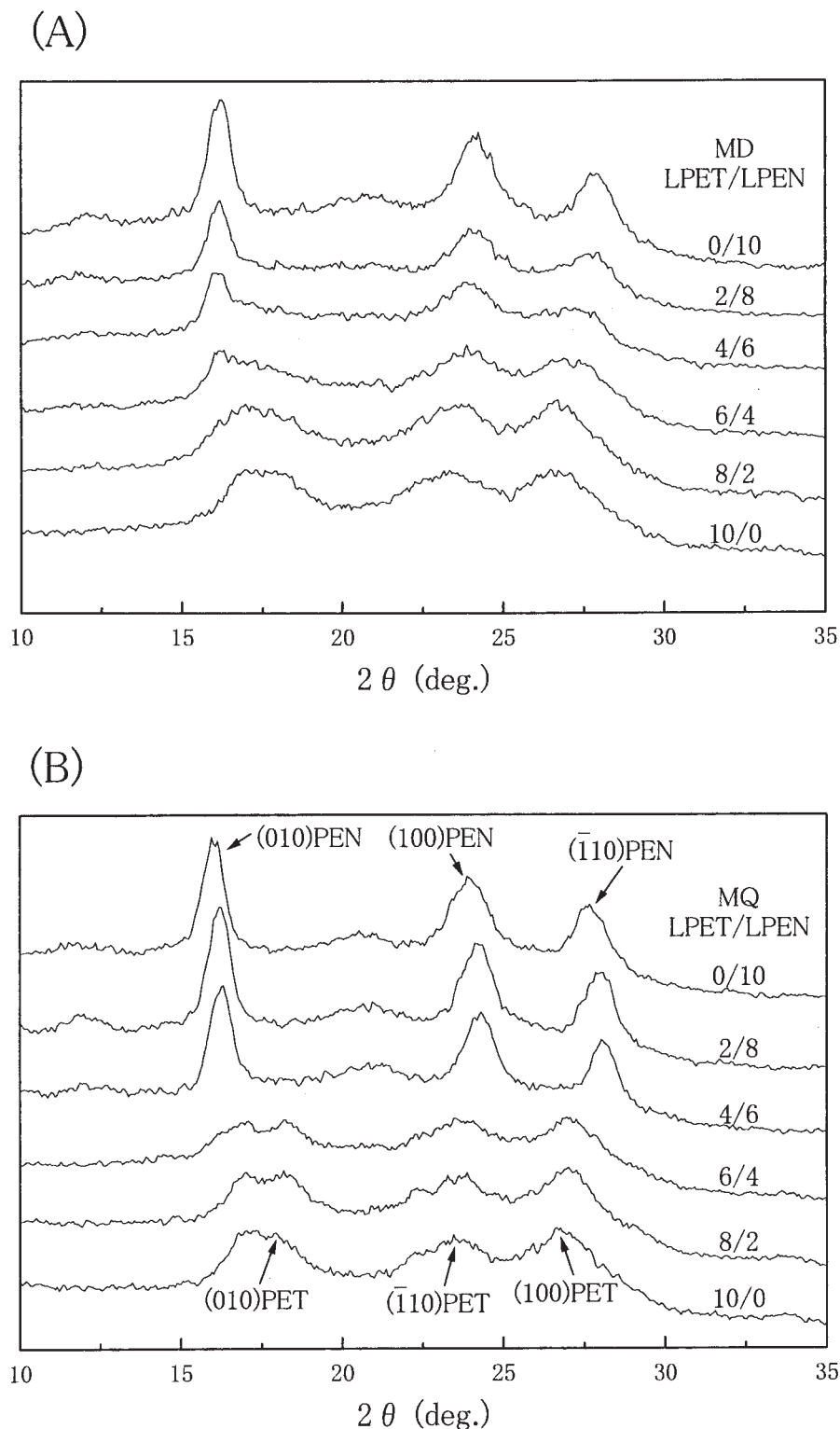


Figure 6 WAXD profiles of the (A) MD series and (B) MQ series annealed at 180°C for 4 h.

Figure 3 shows the reversing heat flow of TMDSC data with a 2°C/min heating rate for the blends of MD (LPET/LPEN) and MQ (LPET/HPEN). For MD blends a clear transition is observed at around 80°C, which is close to the T_g of PET. The blends with high

PEN content showed another transition around the T_g of PEN. Both HPET/LPEN and LPET/HPEN of MD blends also showed similar behavior (data not shown). The results clearly indicate that the MD is a completely immiscible system. In contrast, the blends of

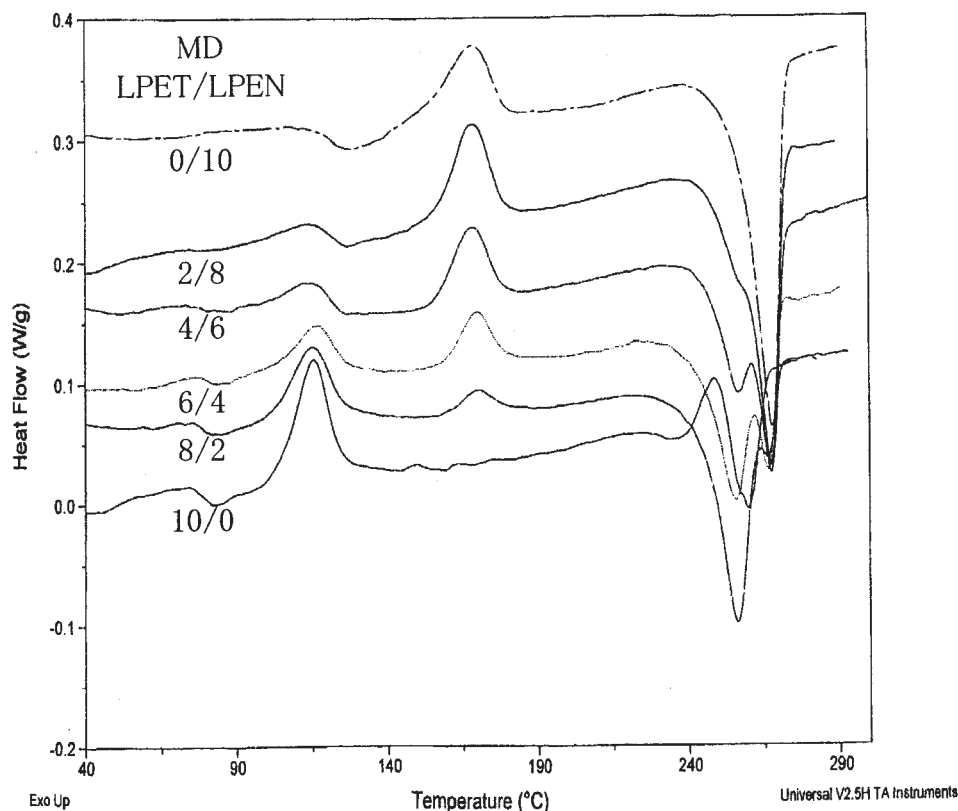


Figure 7 The heat flow of the MD series in the heating process.

MQ showed a single T_g , depending on the blend composition. Further, the transition temperature is rather broad compared with that for the MD series. The observed T_g for a whole series of MQs is plotted as a function of the PEN content in Figure 4. In the case of miscible blends of polymers or random copolymers, the T_g of the blends or copolymer can be expressed by the empirical Fox equation.¹⁰ The T_g s of the LPET/LPEN blends were calculated by the Fox equation and the results are shown in Figure 4. The Fox equation gives good fits to the experimentally obtained T_g values for LPET/LPEN blends, indicating the formation of miscible blends or random copolymers of LPET and LPEN. For LPET/HPEN, the observed T_g deviated slightly from the Fox equation around higher PEN content. This was due to the molecular weight dependence of the T_g for PEN. Figure 5 plots the T_g s of melt quenched PET and PEN as a function of the IV of the polymers. Although the T_g of PET was almost independent of the IV, PEN showed a steady increase of the T_g with the IV. As described, the T_g s of LPET and LPEN were used for the calculation of the T_g of the blends by the Fox equation. When the T_g of HPEN was used for the calculation of the T_g [results (+), Fig. 4], the experimentally obtained T_g and the calculated one approached each other. From these results it is concluded that the MQ has a miscible phase that reflects on the T_g ; further, the miscibility was not affected by

the molecular weight, although the extent of transesterification was affected by the molecular weight.

Thermal crystallization

PET and PEN are both crystallizable polymers. Thus, the crystallization behavior of the blends would give us useful information on the phase structure of their precrystallized state. Figure 6 shows the relative intensities of the WAXD patterns for the thermally crystallized MD and MQ series. For the MD series, the diffraction profiles of the blends with lower PEN content were PET-like profiles. Conversely, the blends with lower PET content showed PEN-like (α -form) diffraction profiles.¹¹ As described, the MD series is an immiscible system. Thus, it is reasonable that PET and PEN can crystallize independently. The diffraction profiles of the MQ series are basically similar to those for the MD series, although the MQ series shows the single T_g . Similar WAXD profiles of annealed PET/PEN blends were already reported by Patchek and Jabarin.⁴ They suggest that the crystallization of PET and PEN blends proceeds with the segregation of the miscible state. Kampert and Sauer studied the crystallization behavior of PET/PEN blends by DSC and report⁷ the progression from completely incompatible, but well dispersed, PET and PEN homopolymers to miscible blocky (crystallizable) copolymers formed at

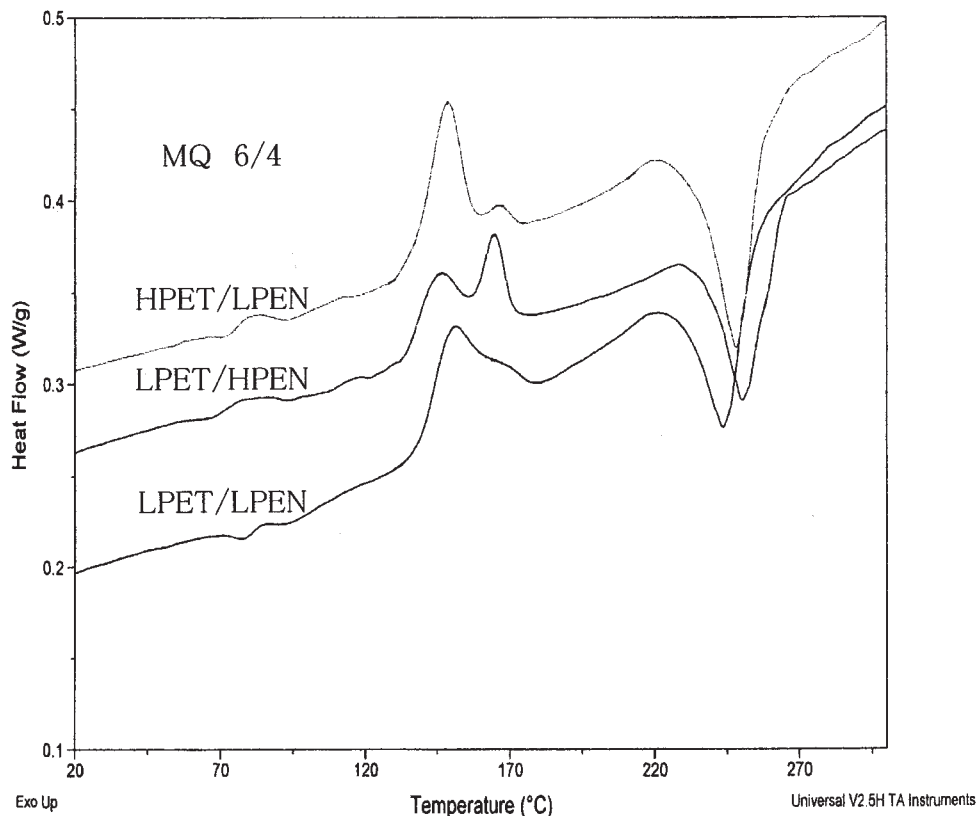


Figure 8 The heat flow of the MQ series in the heating process.

different rates, depending on temperature, because of transesterification, to finally noncrystallizable more random copolymers. We also performed thermal analyses for both MQ and MD series. Figure 7 shows the heat flow during the heating process on the MD series. All the samples showed two exotherms due to cold crystallization of PET for the lower exotherm and of PEN for the higher exotherm. The peak temperatures for both exotherms were independent of the blend composition and corresponded to the exothermic peak temperatures of each homopolymer. In addition, the total heat flow of each exotherm was a function of the blend composition. With increasing content of each phase, the total heat flow for the crystallization of each component increased. These results indicate that PET and PEN can crystallize independently, in accordance with the WAXD results. Figure 8 shows the heat flow in the heating process for MQ of HPET/LPEN (6/4), LPET/HPEN (6/4), and LPET/LPEN (6/4). Three samples exhibited double exotherms around 170°C that are due to cold crystallization of PET for the lower exotherm and of PEN for the higher exotherm. However, both peak temperatures were slightly different from those of homopolymers, as shown in Figure 7. The temperature for the lower exotherm was higher than that of PET, and the temperature for the higher exotherm was lower than that of PEN. This means that the cold crystallization in each component is affected

by the existence of the other component of the blends. The interesting fact is that the total heat flow necessary for the cold crystallization of each component (ΔH , J/g) was affected by the molecular weight. In this work, the ΔH for each component of the three blends was calculated from the deconvoluted thermograms by using the results shown in Figure 8. For LPET/LPEN and HPET/LPEN, the fractions of ΔH for the cold crystallization of PET in the total heat flow were 0.72 and 0.84, respectively. In contrast, for LPET/LPEN and LPET/HPEN, the fractions of ΔH for the cold crystallization of PEN in the total heat flow were 0.28 and 0.47, respectively. The results suggest that, at a given blend ratio, the increase of the molecular weight enhances the cold crystallization of each component on heating. We also studied the effects of the molecular weight of the PET homopolymer on the cold crystallization behavior in the heating process of the DSC scan. The results showed (data not shown) that the total heat flow for the cold crystallization decreased with increasing molecular weight, although the peak temperature was not affected by the molecular weight. As described, for the crystallization of miscible PET/PEN blends, the segregation of each component was proposed.⁴ If this is true, the segregation rate might decrease with the increase of the molecular weight because of the increase of the relaxation time of the molecular chain, which might reduce the

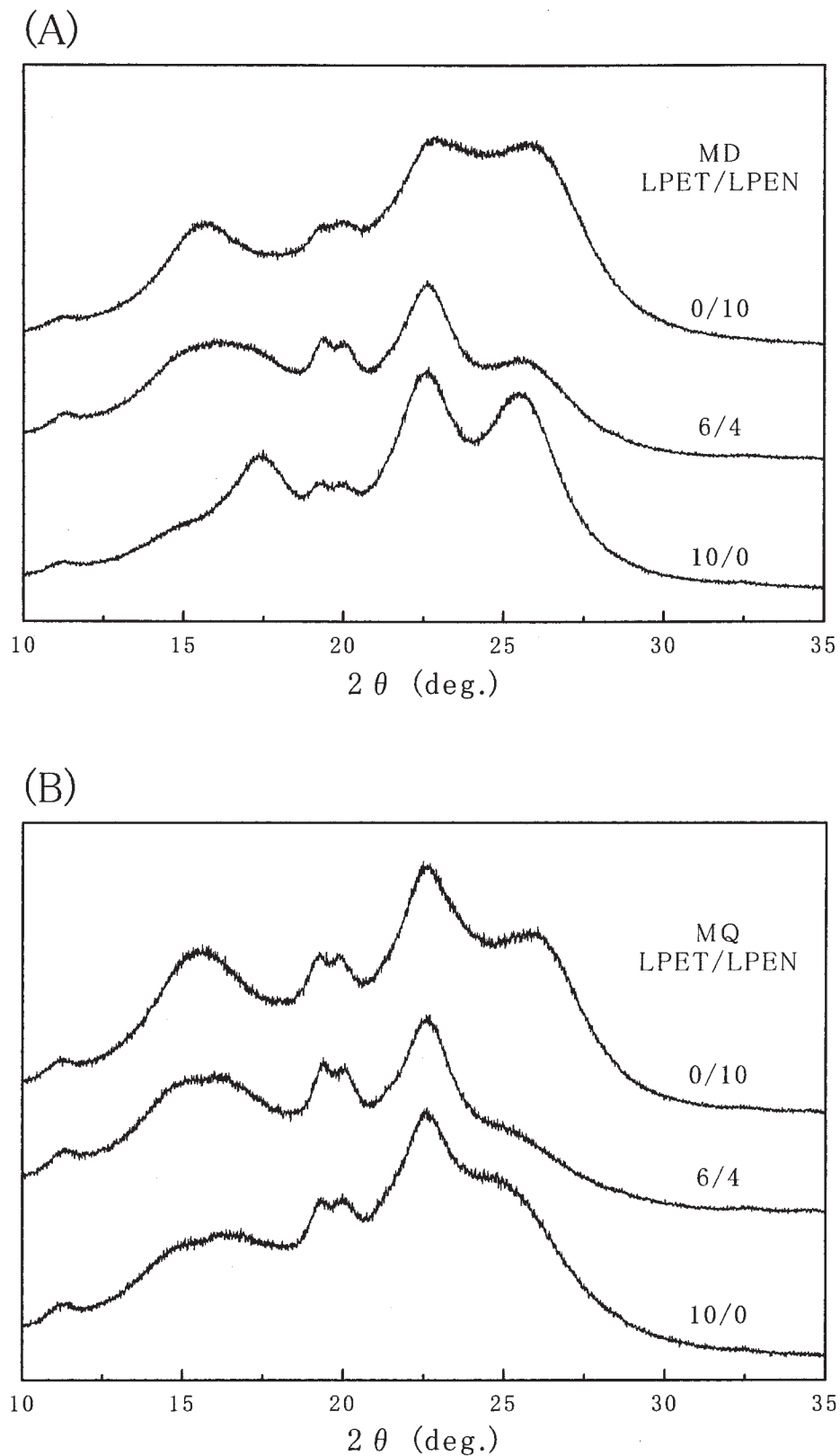


Figure 9 WAXD profiles on the equator of the extrudates (EDR = 5) from (A) MD and (B) MQ blends.

crystallization rate, contrary to the results shown in Figure 8. Taking those into consideration, the present results suggest that the MQ series is not a completely

miscible state at a molecular level, but involves the microdomain structure of each homopolymer for which the size is not large enough to influence the T_g

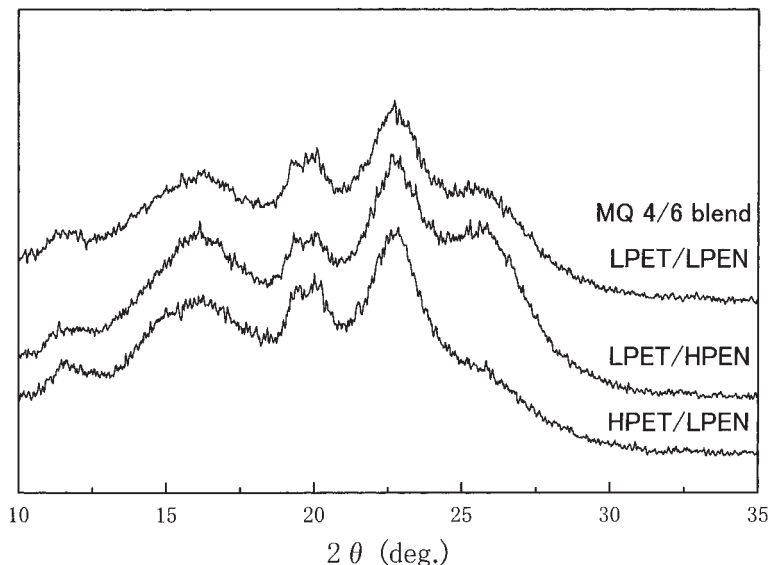


Figure 10 WAXD profiles on the equator of the extrudates ($EDR = 5$) from MQ blends with different molecular weights.

but is large enough to crystallize independently. The size might be increased with increasing molecular weight. At present, we have no information on the size of the microdomain. However, the size might be considerably smaller than ~ 10 nm, which is considered to be a minimum size to observe the T_g by a conventional method.¹²

Strain-induced crystallization

It is well known that the rate of strain-induced crystallization is much faster than that of thermal crystallization. Thus, for the strain-induced crystallization, the blends do not have enough time for segregation. In order to confirm the possibility of segregation during thermal crystallization, as described in the previous section, a comparison of thermal crystallization with strain-induced crystallization was carried out. Figure 9 shows WAXD profiles on the equator of the drawn samples with a constant EDR of 5 and prepared from both MQ and MD. Although the profiles are diffuse and broad because of the low deformation temperature (80 – 110°C), it is clear that the WAXD patterns of MD are quite similar to those of MQ. Further, the profiles of the blends seem to be the sum of the diffractions of PET and PEN. This is recognized especially in the low angle regions. These results suggest that thermal crystallization proceeded without segregation, as suggested by Patchek and Jabarin.⁴ This was further confirmed by the molecular weight dependence on the strain-induced crystallization because the rate of segregation might be affected by the chain length. Figure 10 shows the WAXD profiles on the equator of the extrudates ($EDR = 5$) from MQ blends with different combinations of molecular

weight. It is seen that the molecular weight dependence on the diffraction profiles is less, suggesting a lack of segregation during the crystallization. These results support our consideration that the MQ blends are composed of microdomains of each homopolymer as described in the previous section. Lu and Windle studied the strain-induced crystallization behavior of a PET/PEN random copolymer and found that both PET and PEN units were cocrystallizable.^{13,14} Patchek and Jabarin⁴ also suggest the possibility of cocrystallization of PET and PEN during the strain-induced crystallization of miscible blends of PET/PEN. Both PET and PEN have similar crystals of a triclinic structure, which made it difficult to judge the possibility of cocrystallization. A detailed study might be necessary to draw conclusions.

The tensile modulus and strength of drawn samples are greatly affected by the strain-induced crystallization. Figure 11 shows the tensile modulus and strength of drawn samples with an EDR of 5 from MD and MQ series as a function of the PEN content. The tensile modulus of the samples from MQ blends was found to decrease with increasing PEN content and reached a minimum at 40–60 wt % PEN, then increased as the PEN content increased further. The results can be explained by the relation between the blend ratio and the degree of strain-induced crystallization of drawn samples.⁵ In this work, similar results were obtained for the samples from MQ. By contrast, for the samples from MD, the modulus increased gradually with increasing PEN content. As described in the previous section, both PET and PEN components could crystallize independently during annealing. Such independent crystallization might happen during deformation, and the degree of strain-induced

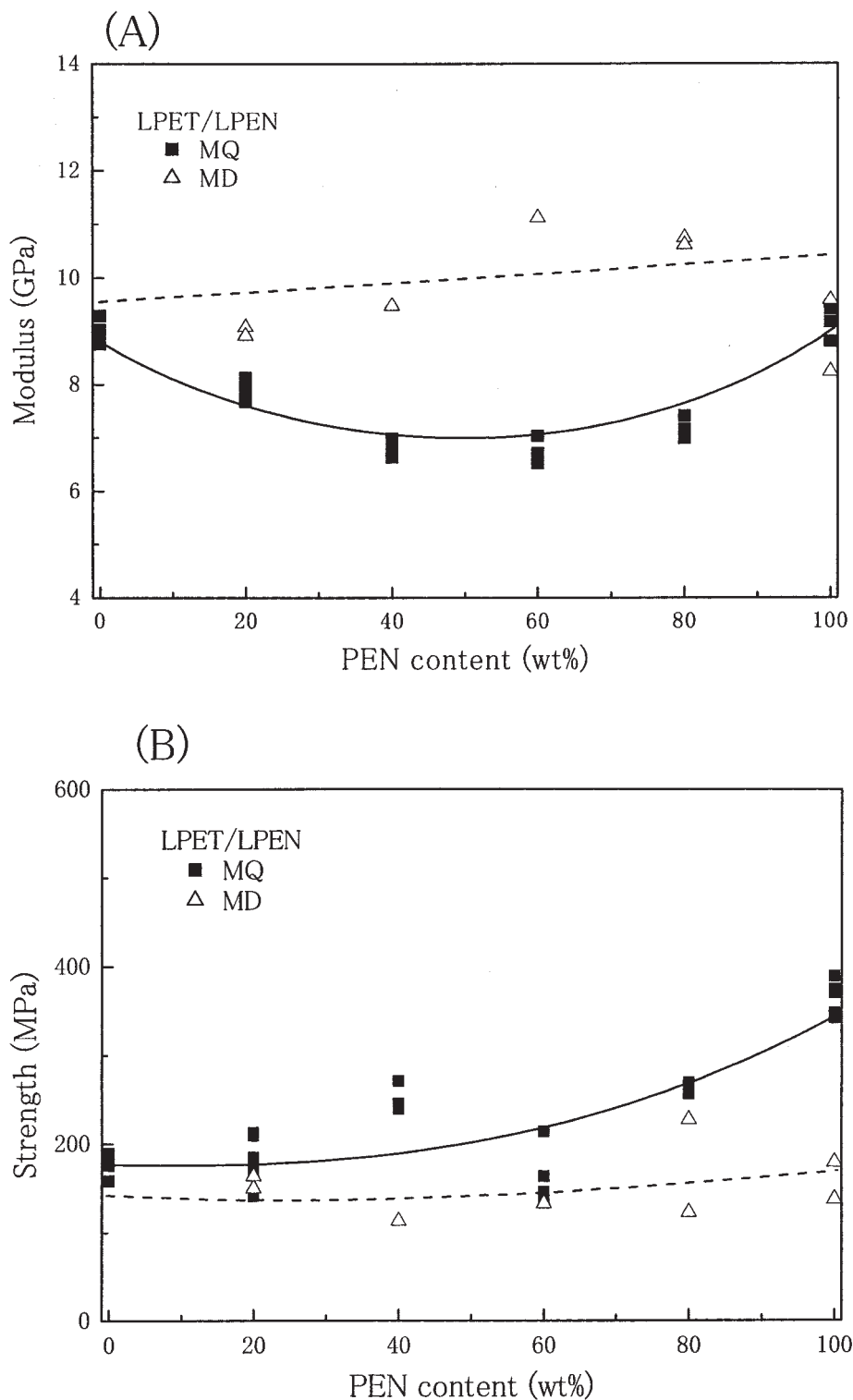


Figure 11 The (A) tensile modulus and (B) tensile strength of the extrudates (EDR = 5) as a function of the PEN content.

crystallization is primarily governed by the strain and deformation temperature. The crystal modulus of PEN along the chain direction was determined to be 145 GPa by the WAXD method,¹⁵ which is about 40% higher than that of PET (108 GPa).¹⁶ Thus, the tensile modulus of drawn samples might be expected to in-

crease with increasing PEN content if similar levels of chain extension, orientation, and crystallization are achieved in both PET and PEN molecules, in agreement with the present results. The interesting fact is that the blends from MD are deformable around the T_g of the samples, although the blends were immiscible.

The results suggest that the blends are compatible, and the domain size of each component is small enough to bear the tear-off at the interface during deformation.

The tensile strength of drawn samples from MQ gradually increased with increasing PEN content. For the measurements of the tensile strength, a large structural change sometimes takes place, especially for a sample with low crystallinity. For the drawn samples with low crystallinity, a part of the extended noncrystalline molecules might be partly relaxed during and after the drawing, which leads to a lower tensile modulus. Such partly relaxed chain molecules are forced to extend during the measurements of the tensile strength, leading to the increase of the tensile strength of the samples with low crystallinity. The tensile strength of drawn samples from MD is almost independent of the PEN content. This is reasonable because the sample crystallinity of drawn samples from MD was around 40%, independent of the PEN content, with a rough estimation from the DSC thermograms of drawn samples.⁵

In the whole range of PEN contents, the strength for MD blends was lower than that for MQ blends. As discussed, the MD blends are not miscible but compatible. Thus, we must consider the interface between the two components as where stress concentration might happen, leading to the decrease of the tensile strength.

CONCLUSION

The phase structure of PET/PEN blends was studied in relation to the molecular weight of the homopolymer, mainly by WAXD and DSC. The following conclusions were obtained from the experimental results.

1. Melt blends of PET/PEN (MQ) showed a single T_g , independent of the molecular weight, although the degree of transesterification in the blends was affected by the molecular weight of the homopolymer.
2. The MQ blends showed two exotherms during the heating process of the DSC scan. The peak temperature and the heat flow of the exotherms were affected by the molecular weight of the homopolymer.
3. Independent crystallization was suggested by the strain-induced crystallization in the MQ series.
4. These results suggest that the MQ series is not a completely miscible state at the molecular level, but involves microdomain structure of each homopolymer for which the size is not large enough to exhibit an independent T_g but large enough to crystallize independently.

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