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Phase structure and deformation behavior of polyester blends

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Abstract

The supermolecular structure, deformation behavior and tensile properties were studied for the blends of a high molecular weight (HMW) poly(ethylene 2,6-naphthalate) (PEN) and a commercially available low molecular weight (LMW) PEN. The HMW with an intrinsic viscosity (IV) of 3.30 dl/g was obtained by solid-state polymerization of the LMW with IV of 0.65 dl/g. The mixture of HMW and LMW prepared by a freeze-dried method from the polymer solutions showed two T_gs, independent of the blend ratio. These T_gs corresponded to those for the HMW and the LMW. After melting or even annealing above the T_g of HMW, these blends showed a single T_g, which was dependent on the blend ratio. The deformation behavior of the blends and the tensile properties of the resultant drawn films were greatly affected by the draw temperature (T_d). For the drawing above the T_g of HMW ($T_d = 150$°C), the LMW behaved as a plasticizer of the HMW. In that case, the draw efficiency evaluated from the Young's modulus of the samples increased systematically with increasing the fraction of HMW in the blends. For the drawing around the T_g of LMW ($T_d = 120$°C), the deformation behavior and tensile properties of the resultant drawn films were primarily governed by those for the component polymer with higher fractions in the blends. The results were discussed in connection with the phase structure of the blends. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene 2,6-naphthalate); Blend; Miscibility

1. Introduction

Poly(ethylene 2,6-naphthalate) (PEN) is a new family of commercially available polyesters containing naphthalene rings. Because of the increased stiffness of polymer backbone, PEN exhibits excellent thermal and mechanical properties compared with poly(ethylene terephthalate) (PET). Detailed thermal analysis has revealed that the equilibrium melting temperature of this polymer is 337°C and the glass transition temperature (T_g) of a completely amorphous sample is 117°C [1]. These values are significantly higher than those of PET. The crystal modulus of PEN along the chain direction has been determined to be 145 GPa by wide angle X-ray diffraction (WAXD) method [2], which is about 40% higher than that of PET.

The tensile properties of drawn PEN depend on several factors including molecular weight, draw ratio and draw conditions [3]. At a given draw ratio, the higher the molecular weight, the higher the tensile strength that can be achieved. However, there exists a serious problem for the processing of high molecular weight (HMW) PEN due to its extremely high shear viscosity. One possibility to overcome this difficulty may be utilization of a low molecular weight (LMW) PEN as a plasticizer.

The phase behavior of polyester/polyester blends in which chemical structure of a component polymer is similar to that of the other polymer has been studied extensively for the blends obtained by melt blending [4–10]. The results revealed that ester interchange reaction took place in melt blending, which induced miscibility in the blends. On the other hand, Guo and Zachmann reported that polyester/polyester blends obtained by solution precipitation were phase separated [11].

In this study, a commercially available PEN (IV = 0.65 dl/g) (LMW) was examined as a plasticizer of a PEN (HMW) with IV = 3.30 dl/g. For this purpose, two sets of blends with various blend ratios were prepared. One series was the freeze-dried (FD) films prepared from polymer solutions and the other one was the melt-quenched (MQ) films. The deformation behavior and tensile properties of the resultant drawn films were discussed in connection with the phase structure of these blends.

2. Experimental

2.1. Samples

Commercially available PEN pellets (LMW), with an intrinsic viscosity (IV) of 0.65 dl/g, were used as a starting

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material. A PEN (HMW) was obtained by solid-state polymerization of the LMW. The details are described elsewhere [3]. The IV of HMW was 3.30 dl/g.

The blending was performed in solution. The LMW and HMW samples were dissolved in a mixed solvent of hexafluoro-2-propanol and dichloro-metnane(50/50, v/v) at room temperature. Two sets of undrawn films with different blend ratios were prepared from polymer solutions (~3 wt%). One series was the FD films and the other one was the MQ films. The preparation of the FD films was as follows: a polymer solution containing requisite amounts of the LMW and HMW components was casted onto a glass plate, which was rapidly cooled to about −100°C by using liquid nitrogen, followed by evaporation of the solvent in vacuo at −50°C. For the preparation of a MQ film of a blend, the components in the polymer solution were precipitated into methanol. After drying the precipitates in vacuo at room temperature for 48 h, they were melted at 300°C for 10 min under pressure, followed by quenching in an ice water. The films of the pure components were prepared in similar ways used for the preparations of the FD and MQ. The composition of a blend was expressed by a weight ratio of the two components, HMW/LMW, g/g.

2.2. Drawing

The MQ and FD films were uniaxially drawn by a tensile force under an initial strain rate of 1.0 min^{-1} at 120 and 150°C. After the drawing, the samples were cooled to room temperature under a constant length. The draw ratio was determined by measuring the separation between lateral ink marks on the sample before and after drawing. The maximum draw ratio ($\mathrm{DR}_{\max}$) was defined as follows: three pieces of undrawn films were set on the tensile tester and drawn. When two pieces were broken during drawing, the drawing of the rest stopped and the draw ratio was determined by the method described above, which was defined as $\mathrm{DR}_{\max}$.

2.3. Measurements

The IV of a sample was measured in a mixed solvent of trifluoroacetic acid and dichloromethane (50/50,V/V) at 30°C.

The thermal behavior of the samples was examined with a Seiko Instruments differential scanning calorimeter (DSC) model SSC-5200 in a dry nitrogen atmosphere at a heating rate of 10°C/min.

The stress–strain curves of the samples were measured at draw temperatures (T_ds) of 120 and 150°C in an air oven equipped with an Orientec Tensilon tensile tester HTM-100 at a constant cross-head speed corresponding to an initial strain rate of 1 min^{-1}. The tensile modulus on the fiber axis was measured at a strain rate of 0.001 s^{-1} at room temperature. The modulus was determined from the initial slope of the stress–strain curve at a low strain (<0.1%). The gauge length for all samples was adjusted to 10 cm regardless of draw ratio of the samples. The cross-sectional area of the samples was determined by the combination of optical microscope and micrometer.

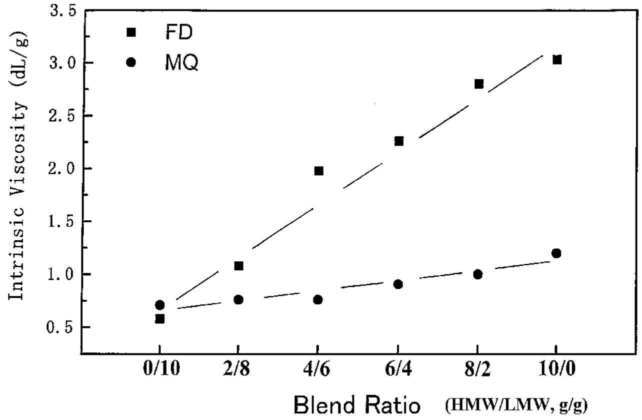

Fig. 1. Intrinsic viscosity (dl/g) of blends as a function of blend ratio.

Wide angle X-ray diffraction patterns of the samples were obtained at room temperature with CuK_α radiation generated at 40 kV and 25 mA on a Rigaku Gigerflex RAD-3A, monochromatized by a graphite monochrometer and flat-plate camera. The distance from the sample to the camera was 45 mm.

3. Results and discussion

3.1. Structure of undrawn films

As was described, two sets of undrawn films with different blend ratios of LMW and HMW PENs were prepared in this work. One was the FD films and the other was the MQ films. It is well known that an ester-interchange reaction (transesterification) takes place upon melt blending of polyester/polyester blends [12]. Further, a HMW polyester is easily degraded into a lower molecular weight during melting [13].

In Fig. 1, the IV of the blends is plotted as a function of blend ratio for the FD and MQ films. For the FD films, the IV increased almost linearly with increasing the fraction of HMW. At 100% of HMW (10/0), the IV was 3.3 dl/g, which was comparable to that for the starting IV of HMW. These results indicate that for the FD films, a molecular weight retention is perfect. For the MQ films, the IV of 100% HMW was 1.2 dl/g, which means that the IV retention after the processing was only 36%. As a result, the IV of the blends with higher fraction of HMW showed a quite low value compared with that for the FD films. The IV retention was dependent on the moisture content of the precipitates, which were used for the preparation of MQ films. As described in Section 2, the precipitates were dried in vacuo at room temperature for 48 h. More severe dry condition might be necessary to improve the IV retention. We confirmed that the degradation was almost negligible below 180°C.

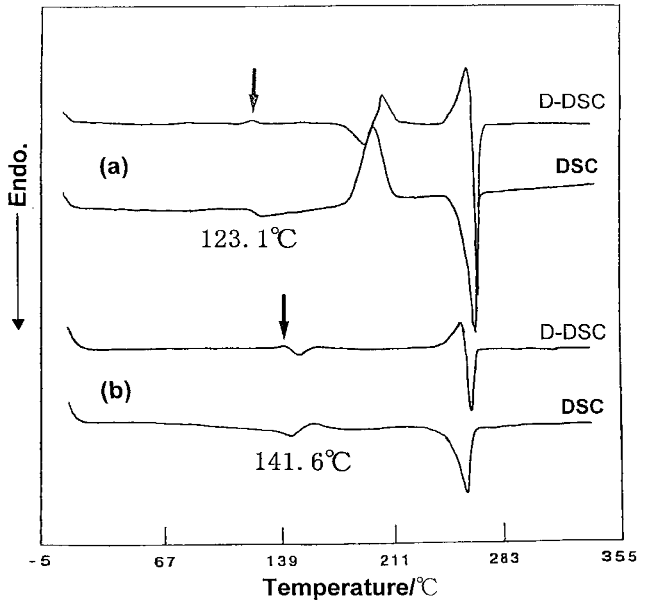

Fig. 2. DSC and D-DSC thermograms for LMW from MQ (a) and HMW from FD (b).

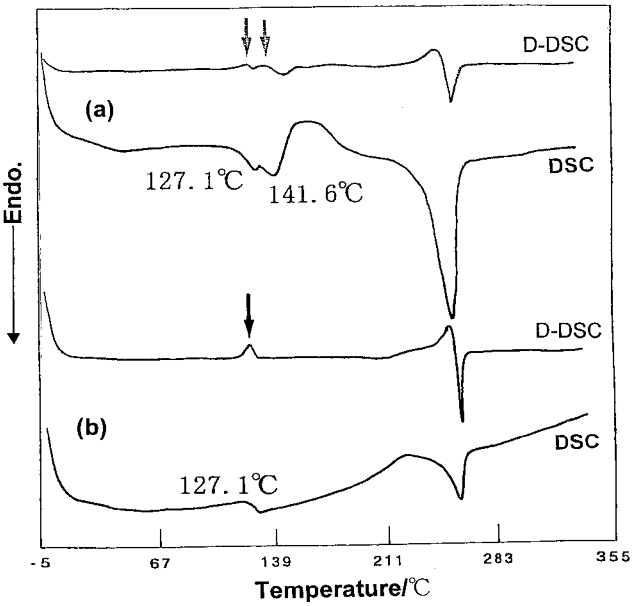

Fig. 3. DSC and D-DSC thermograms for blends (HMW/LMW, 6/4) from FD (a) and MQ (b).

The supermolecular structure of the blends was evaluated from the WAXD patterns and thermal properties of the samples. The WAXD profiles indicated that all undrawn films studied were almost amorphous (data not shown).

Fig. 2 shows two sets of DSC and differential DSC (D-DSC) thermograms for MQ film of LMW and the FD film of HMW. In this work, an inflection point method was used to determine the T_g of the sample. As can be seen in the figure, the inflection point was easily found in the D-DSC thermogram as a peak. The T_g of LMW determined by this method was 123.1°C, which was about 6°C higher than that previously reported for the completely amorphous PEN with normal molecular weight (IV = 0.593 dl/g) [1]. However, the difference was not so important as for the discussion on the phase behavior of the blends. The T_g of HMW from the FD film was 141.6°C, which was about 18° higher than that of LMW. It is well known for amorphous polymers that a molecular weight dependence of T_g becomes less prominent when the molecular weight exceeds ~10,000. Such behavior was also observed in poly(ethylene terephthalate) (PET) [14]· We measured the T_g of amorphous PETs as a function of molecular weight in the IV range of 0.6–4.5 dl/g. The T_g determined by DSC was around 70°C, independent of the molecular weight. At present, the reason for the increase in T_g with molecular weight for PEN is not clear. The increased chain stiffness likely influences the molecular weight–T_g relations.

The difference of T_g between the two PEN components was large enough to discuss on the miscibility of the blends based on the relation between T_g of the blends and blend ratio.

Fig. 3 shows DSC and D-DSC thermograms of the blends with a blend ratio of 6/4 prepared by the FD (a) and MQ (b) methods. The blend from the MQ film showed a single T_g around 127°C, which was about 4° higher than that for the LMW component. On the other hand, the blend from the FD film showed two T_gs. In Fig. 4, the T_g is plotted as a function of the blend ratio for both FD and MQ films. All blends from the FD films showed two T_gs. The higher T_g was ~141°C, independent of the blend ratio. This value is comparable to that for the HMW component (Fig. 2). Although the lower T_g of the blends was slightly higher (~4°C) than that of the LMW component, the value again kept almost constant irrespective of the large changes in the blend ratios. These results indicate that the LMW and the HMW are apparently immiscible in the FD series of blends. In this study, no difference of solubility in the solvent was observed between LMW and HMW. The dissolution time necessary for the preparation of homogeneous polymer solution with the concentration of ~3 wt% was less than 1 h at room

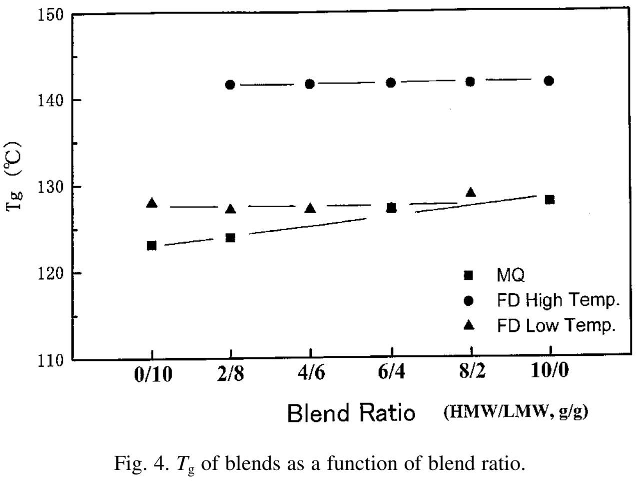

Fig. 4. T_g of blends as a function of blend ratio.

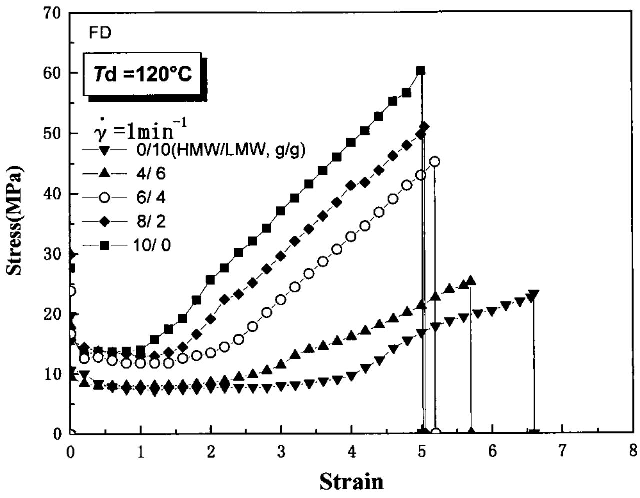

Fig. 5. Stress–strain curves at 120°C for FD with different blend ratios. Strain rate (γ) is 1/min.

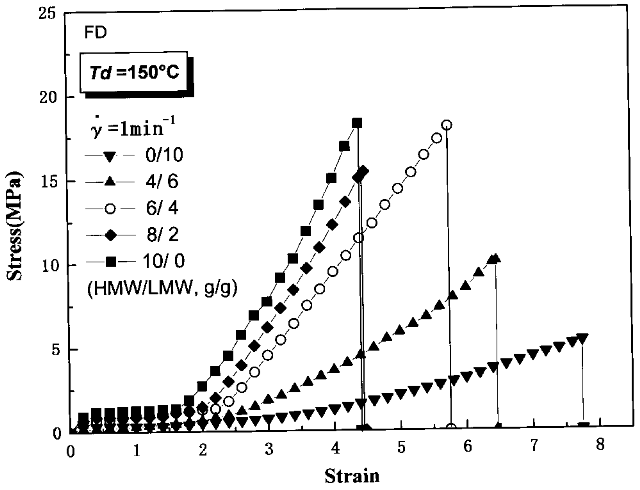

Fig. 6. Stress–strain curves at 150°C for FD with different blend ratios.

temperature, independent of the molecular weights. Also, the polymer solution was apparently one phase and homogeneous. The polymer solution was rapidly cooled to −100°C by using liquid nitrogen. During this stage, a solidification of the polymer solution occurred. Then the solvent was removed from the solidified polymer solution at −50°C under a reduced pressure. Thus, the possibility of fractional precipitation during quenching the solution followed by vacuum drying seems to be less.

Guo and Zachmann [11] reported that a PEN/PET 50/50 blend prepared by solution precipitation was phase-separated. However, their study was performed on the powder precipitated from solution. Therefore, it might be possible to speculate in their study that the phase separation is a consequence of fractionation during precipitation as they suggested. As described in Section 2, the FD films were prepared at low temperatures by using mixed solvent. At present we do not have any information on the phase behavior of this quaternary mixture. Thus, there is a possibility that the FD films are in a thermodynamically metastable state. These are currently studied.

All blends of the MQ series showed a single T_g. Further, the value increased slightly with increasing the fraction of HMW. It is well known that an ester-interchange reaction (transesterification) often takes place in the melt blending for the polyester/polyester blends [12]. In this work, the interchange reaction might occur between HMW and LMW to some extent on melt processing, which might enhance the miscibility of the two-component polymers. As was shown in Fig. 1, the molecular weight retention of HMW after the melt processing was extremely low. Therefore, a rather lower T_g of the blends for the MQ series is likely due to the thermal degradation of HMW.

3.2. Deformation behavior

As was described in the previous section, a transesterification and molecular degradation had likely occurred in the blends of the MQ series. Thus, most of the deformation work was carried out for the blends of the FD series.

Fig. 5 shows the nominal stress–strain curves at a strain rate of 1 min^{-1} for the FD films with various blend ratios. The T_d was 120°C, which was close to the T_g of LMW (123.1°C). For the samples with high fractions of LMW, the stress on draw was quite low and the strain at a break, which corresponded to the maximum achieved draw ratio (DR_{max}), was fairly high. On the other hand, for the samples with higher fractions of HMW, the stress on draw was very high and the DR_{max} was small. In addition, the changes in DR_{max} with blend ratio. as well as the stress on draw at a given strain, were not systematic. The effect of blend ratio on the stress–strain curves changed with T_d. The stress–strain curves for the FD films recorded at 150°C are shown in Fig. 6. The stress on draw decreased and the DR_{max} increased steadily with increasing the fraction of LMW. Such changes with blend ratio were rather systematic compared with those at $T_d = 120$°C. The stress–strain curves shown in Figs. 5 and 6 were quite reproducible. We repeated the measurements five times. The results showed that the experimental errors were within ±5%. As was discussed, the blends from the FD films were apparently immiscible systems. However, the stress–strain behavior shown in Fig. 6 suggests that the LMW was dispersed homogeneously at a molecular level and behaved as a plasticizer of the HMW component. These results suggest that the immiscible systems might have transformed into miscible one when the T_d increased from 120 to 150°C. This was confirmed by the DSC results shown in Fig. 7. As described in the previous section, the blends from the FD films showed two T_gs. This sample was heated up to 150°C and held for 10 min, followed by a rapid cooling to −50°C. Then the second heating run was carried out. The DSC thermogram showed a single T_g (see Fig. 7). A similar DSC measurement was done at the holding temperature of 120°C. However, no

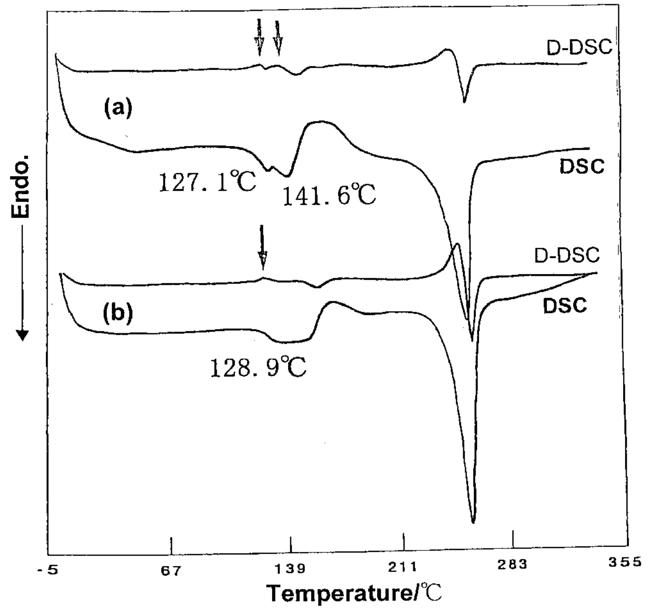

Fig. 7. DSC and D-DSC thermograms of blend (HMW/LMW, 6/4) from FD: (a) first run and (b) second run.

annealing effect was observed in the DSC thermogram. That is, the immiscible system changed into a miscible one by the heat treatment at 150°C. On the stress–strain measurements, the samples were heated up from room temperature to T_d of 120 or 150°C with the heating rate about 20°C/min. The drawing started when the temperature in the air oven reached T_d. The draw time was dependent on the strain attained. Since initial sample length (5 cm) and strain rate (1 min^{-1}) were constant for each measurement. The DR_{max} obtained in this work was around 8. In that case, the sample was exposed to the T_d for about 8 min. After drawing, the samples were cooled to room temperature with an approximate cooling rate of 5°C/min under a constant sample length. These thermal histories during drawing were similar to those for DSC measurements. As described, there is a possibility that the FD films are in a thermodynamically metastable state. During the drawing at 150°C, thermodynamically unstable and immiscible system might change into stable miscible one. Such immiscible–miscible change was also supported by the following results.

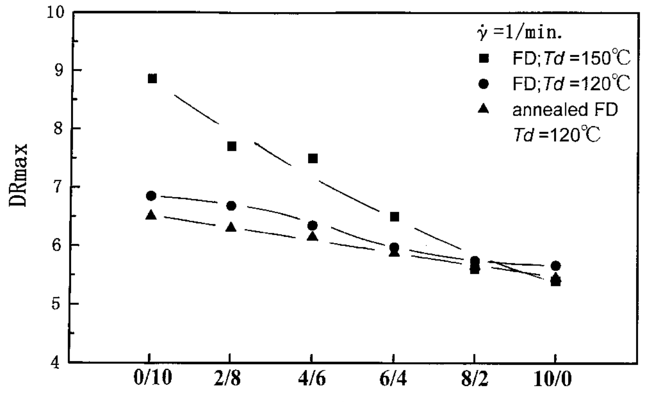

Fig. 8. DR_{max} of blends from FD, MQ and annealed FD at 120 and 150°C as a function of blend ratio.

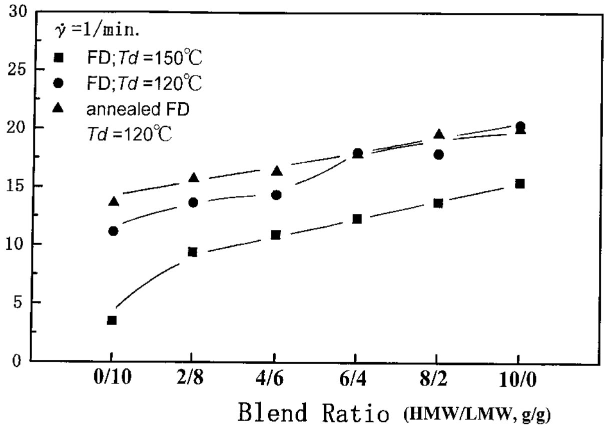

Fig. 9. Young's modulus as a function of blend ratio.

In Fig. 8, the DR_{max} at T_d of 120 and 150°C is plotted as a function of blend ratio for the FD film and its annealed one (annealing temperature of 150°C). The strain rate was 1 min^{-1}. At a T_d of 120°C, the DR_{max} for the FD films decreased gradually with increasing the fraction of HMW. In addition, the decrease around blend ratio of 4/6–6/4 seemed to be large compared with that for the other blend ratio. As stated, the FD blends were immiscible system. In that case, the apparent deformability is primarily governed by the deformability of the matrix phase. For the blends with higher fractions of LMW, the matrix phase is composed of LMW. On the other hand, when the fraction of HMW exceeds 60%, the matrix phase changes from LMW to HMW. As has been suggested [3], the apparent deformability of PEN is affected by the disentanglement and chain slippage occurring during deformation, which are influenced by the chain length. Thus, apparent deformability and hence the DR_{max} is higher for LMW than for HMW [3].

The DR_{max} and blend ratio relation for the drawing of the FD at $T_d = 150°C$ was qualitatively similar to that for the drawing of annealed FD at $T_d = 120°C$. The DR_{max} decreased almost linearly with increasing the fraction of HMW, which suggests that the LMW performed as a plasticizer of HMW.

3.3. Tensile properties

Fig. 9 shows the blend ratio dependnence of the Young's modulus at the DR_{max} for a series of FD and its annealed one obtained at $T_d = 120$ and 150°C. For three sets of drawn samples, the moduli increased with increasing the fraction of HMW although the DR_{max} decreased (see Fig. 8). The results clearly indicate that disentanglements and chain slippages occurred during tensile drawing and suggest that the draw efficiency is markedly affected by the

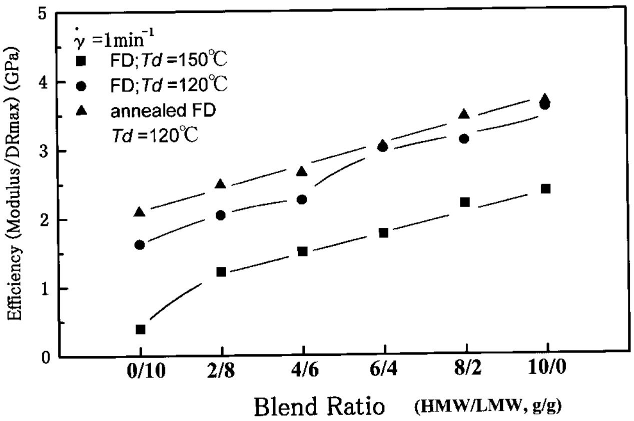

Fig. 10. Draw efficiency as a function of blend ratio.

blend ratio, supermolecular structure of undrawn films and draw conditions. For PEN, the Young's modulus increased almost linearly with increasing the draw ratio [3]. Thus, each modulus at DR_{max} was divided by the DR_{max} for the evaluation of draw efficiency and the results are plotted as a function of blend ratio for the FD films and their annealed one in Fig. 10. For the drawing of FD films at a higher T_d of 150°C, the efficiency gradually increased with increasing the fraction of HMW, again suggesting a homogeneous distribution of LMW in HMW. The interesting fact is that the increase of efficiency is more prominent for the samples with lower fractions of HMW. This implies that the existence of small amount of long chain molecules is extremely effective for the transmission of draw stress and hence for the achievement of high chain extension and orientation.

For the drawing of FD films at a T_d of 120°C, the efficiency was lower for the blends with higher fractions of LMW (0/10–4/6) than for the blends with higher fractions of HMW (6/4–10/0). That is, the efficiency seems to have a small boundary around blend ratios of 4/6–6/4. The draw efficiency seems to be higher for the samples of which matrix phase is composed of HMW than for LMW. This is reasonable since the draw efficiency is higher for HMW than for LMW [3].

Fig. 11 shows a series of WAXD patterns of the FD samples drawn to the DR_{max} at 120°C. As was suggested, the draw efficiency was primarily governed by the molecular weight of the matrix phase in the blends. The higher the molecular weight, the higher is the draw efficiency that can be achieved. This suggests that the draw efficiency is different between the discontinuous and continuous matrix phases. However, all the reflections are circular spots in each of the diffraction patterns shown in Fig. 11 indicating that the crystal orientation function is a single component. A large part of the chain extension and orientation in the discontinuous phase might not be high enough to enhance the stress-induced crystallization because the direct coupling between the continuous matrix and the discontinuous phases might be weak. Thus, the tensile force is not transmitted effectively to the discontinuous phase. The details are currently studied.

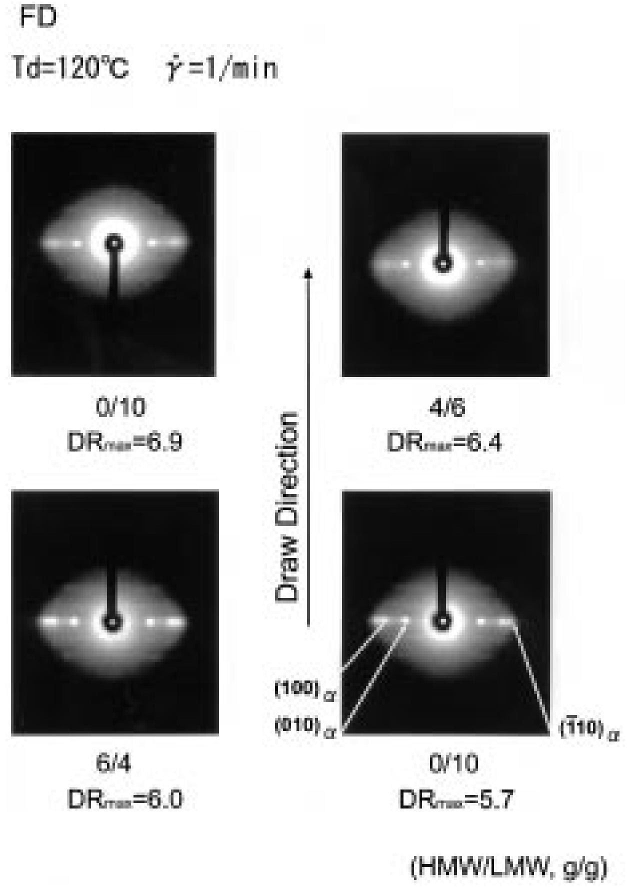

Fig. 11. WAXD photographs of drawn samples with DR_{max} from FD with different blend ratios.

4. Conclusions

(1) A series of blends of HMW and LMW, prepared by a FD method from polymer solutions, showed two T_g's, independent of the blend ratio. Each T_g corresponded to that for the HMW and the LMW. However, the blends showed a single T_g when they were annealed above the T_g of the HMW component. The blends of HMW/LMW obtained by the FD method are thermodynamically unstable. Thus, they transformed into miscible systems quite easily by the annealing above the T_g of the HMW.
(2) The deformation behavior of the blends and tensile properties of the resultant films were greatly affected by the drawing below and above the T_g of the HMW component. This was due to the immscible–miscible change which occurred around 150°C. Especially for the miscible systems (T_d = 150°C), the LMW behaved as a plasticizer of HMW. In that case, the draw efficiency evaluated from

the Young's modulus of the samples increased systematically with increasing the fraction of HMW in the blends. For the immscible systems ($T_d = 120°C$), the deformation behavior and tensile properties of the resultant drawn films were primarily governed by those for the component polymer with higher fractions in the blends.

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