

Structural Development of Poly(ethylene 2,6-naphthalene dicarboxylate) Film upon Solvent Drawing

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ABSTRACT: To investigate the effect of “chemical energy” by solvent on structural development, initially molded amorphous poly(ethylene 2,6-naphthalene dicarboxylate) (PEN) films were drawn in various solvent systems and at the optimum temperatures deliberately determined, and the resulting fine structure and properties were analyzed by using several experimental techniques. Water, 1-butanol, 1,4-dioxane/water (20 : 80 by volume), and 1,4-dioxane/1-butanol (20 : 80 by volume) were chosen for drawing solvent. For this study, in view of chemical structure and solubility parameter, though, these are nearly immiscible or partially miscible liquids against PEN, with just the plasticizing actions more or less the primary concern here. Interesting enough, the temperature range near the main endothermic peak corresponding to the depressed boiling point of liquid caused by unfavorable interaction

between PEN and solvent in mixtures of amorphous PEN film with various solvent systems, as determined by the DSC scans, was found to coincide with the optimum drawable range for each solvent system, over which several experiments, including the determination of maximum draw ratio (DR_{\max}) have been carried out throughout the study. The experimental results obtained from this study could be explained, through qualitatively, in terms of the interactions between PEN and solvents. Hence, it is expected to control the fine structure and properties of PEN films resulting from the low-temperature solvent drawing via a suitable choice of liquids and the corresponding draw temperature ranges.
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Key words: film; structure; drawing; DSC

INTRODUCTION

Poly(ethylene 2,6-naphthalene dicarboxylate) (PEN) is a relatively well-known polymer used for engineering purposes. The naphthalene ring provides rigidity to the polymer backbone, thus elevating the glass transition temperature (T_g) and enhancing mechanical properties compared to poly(ethylene terephthalate) (PET) with the benzene ring. Because of the rigidity of the polymer backbone, it can be formed into amorphous glasses by rapid quenching from melt, and crystallized by stress or thermal effects or combinations of both.

Generally, the crystallization for the polymer can be achieved from several processes. One, which is of great industrial importance and has been studied extensively, is thermal-induced crystallization. Strain-induced crystallization, also of great utility, continues to receive substantial attention. Another important process of achieving crystallization is by means of solvents, and this is termed “solvent-induced crystallization (SINC)” or “liquid-induced crystallization.”

The process by solvent may be considered as involving the following steps:¹ the solvent is first imbibed into the polymer by diffusion. The interaction between solvent and polymer causes enhanced mobility of polymeric segments by interrupting the intersegmental forces. If the interaction between polymeric segments and solvent is strong enough, then the polymeric molecules may be capable of rearranging themselves into a more thermodynamically lower energy state, generally the crystal state. It is well known that, for thermal-induced crystallization, these stable crystallites may, in turn, develop into forms of ordered superstructure such as spherulites.^{2,3} Thus, those solvents being capable of strong interaction with a given polymer may be expected to induce the crystallization. Typically, some dissolution in fact will occur at the interface between the pure solvent and polymer surface due to a large concentration gradient.⁴

Little work has been done on the morphologic changes during the SINC. Zachmann⁵ assumed the formation of spherulitic structure on the basis of its evidence in the thermal crystallization of other polymers; Sheldon⁶ ruled out the possibility of large-scale spherulitic structures from the small angle light scattering (SALS) and optical microscope observations. On the other hand, Wilkes et al.^{1,7} have reported that a spherulitic texture was obtained by immersing in the

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solvents of dioxane and dichloromethane (confirmed by SALS), which is very similar to that obtained with PET. Kim et al.^{8,9} investigated the crystalline structure of PEN crystallized by solvent and compared them with that of thermally crystallized PEN. From these studies, it has been found that the crystalline form of PEN in SINC was largely affected by the characteristics of the solvent.

The sorption of solvent into polymer has a plasticizing effect, as is well known, and accordingly, this leads to a lowering of T_g and a depressing of the melting temperature (T_m), which is less than that of T_g .^{10,11} The basic mechanism of the solvent-related process is very much the same as that of the thermal process from the glassy state because both involve, as a necessary step, the inducement of segmental mobility. However, the former achieves the goal by use of "chemical energy" arising from the interaction between the polymer and solvent, and the latter does so by use of thermal energy.¹² The advantage of using the solvent effect instead of the thermal effect may lie in the fact that the segmental mobility may be induced at temperatures much lower than those required for the dry polymer. Moreover, the interactions between the polymer and solvent may be expected to be greatly dependent on the nature of the solvent. Thus, it may be anticipated that even at a fixed temperature, the morphology and the final properties of polymer can be manipulated by the choice of solvent.

In our previous report,¹³ we had investigated fine structural changes in PEN film uniaxially drawn at various temperatures and speeds, and we had confirmed the PEN polymer has a poor thermal processability because of the high-temperature property. In this article, therefore, we carried out the solvent drawing against a glassy PEN film to get a better processability due to the backbone rigidity, and we will investigate the deformability and the fine structure on solvent-induced deformation of the PEN film. In view of that, a more improved processability than the conventional thermal process is expected, and together we will report our results on the structural development in amorphous PEN films as influenced by the drawing process at optimum temperatures much lower than that of the dry polymer in various solvent systems chosen specifically by employing several experimental techniques to investigate the effect of chemical energy on the resulting fine structure and properties of PEN films.

EXPERIMENTAL

Material and solvent drawing

PEN pellets, supplied by Teijin Co. Ltd., and with an intrinsic viscosity of 0.62 dL/g, were compression molded at 290°C followed by rapid quenching in ice

TABLE I
Solubility Parameter and Other Characteristics of Selected Solvents⁸

Name	M.F. ^a	B.P. ^b	M.W. ^c	δ (cal/cm ³) ^{1/2d}
1,4-Dioxane	C ₄ H ₈ O ₂	101.5	88.11	10.01
1-Butanol	C ₄ H ₁₀ O	117.7	74.12	11.32
Water	H ₂ O	100.0	18.00	23.40
Methanol	CH ₄ O	64.6	32.04	14.28

^a Molecular formula.

^b Normal boiling point in °C. This is the temperature at which the liquid phase is in equilibrium with the vapor at pressure of 760 mmHg.

^c Molecular weight (relative molar mass) as calculated with the 1993 IUPAC Standard Atomic Weight.

^d The solubility parameter for PEN is 11.02 (cal/cm³)^{1/2} as calculated by Hoy's method.

water to obtain amorphous samples. The film thickness was of the order of 100 μ m. The quenched PEN films were cut into rectangular shapes with a gauge length of 10 mm and a width of 5 mm. Uniaxial drawing of films was carried out in selected solvents at various temperatures using a hand-operated elongation tester. Before drawing, the samples were equilibrated at the desired temperatures for 1 min in a preheated solvent bath and were drawn to the maximum drawable ratios (DR_{max}) at a drawing rate of 100%/min. The residual solvents were leached out from the films by immersion in methanol for 2 h. In this study, 1,4-dioxane, 1-butanol, and water were chosen as drawing solvents in view of the solubility parameter (δ) and chemical structure. Actually, these are partially miscible or nearly immiscible liquids against rigid PEN molecules, so will make only plasticizing actions, more or less, depending on the solvents, which can be expected to play an important role in this study. Here we may classify 1,4-dioxane and 1-butanol as fairly interactive liquids and water as non- (or poorly) interactive liquid for PEN from the practical point of view. The solvent characteristics are represented in Table I. In addition, the determination optimum drawing temperatures were dependent upon the phenomenologic view of drawability in the chosen solvent, i.e., considering either homogeneity or noncrystallizability. The applied drawing conditions for the selected solvents are summarized in Table II.

Analyses of structural development

The density was measured at 23°C using a density gradient column, and the equatorial wide-angle X-ray diffraction (WAXD) profiles on drawn samples were obtained using a Rigaku X-ray diffractometer of D/max-III-A type with Ni filtered Cu-K α radiation and X-ray generator was operated at 30 kV and 15 mA. The differential scanning calorimetry (DSC) measurement was carried out using a TA DSC 2910 at a con-

TABLE II
Drawing Conditions for PEN Films

Solvents	Draw temperature (°C)	Draw rate (%/min)
Water	50, 60, 70, 80, 90	100
1-Butanol	60, 70, 80	100
1,4-Dioxane/water (20:80 by volume)	60, 70, 80	100
1,4-Dioxane/1-butanol (20:80 by volume)	50, 60, 70	100

stant heating rate of 10°C/min for a specimen of about 3 mg under dry nitrogen atmosphere. Visible spectroscopy analysis of drawn films was characterized using a UV/Visible Spectrometer of Perkin-Elmer Lambda 20 type, and transmittance (%) of the visible light was measured at the wavelength range of 400–800 nm. The SEM observance was performed using an Hitachi SEM S-4200, and samples were coated in the conventional manner with a thin layer (100 Å) of gold palladium to prevent charging.

RESULTS AND DISCUSSION

Interaction between pen and solvents

To estimate the interaction between PEN and solvents used in the drawing process, or suitable draw temperature ranges corresponding to each solvent system, DSC measurements were carried out from the sample pan including mixtures of initially molded amorphous

PEN film with various solvent systems. Figure 1(a) shows the DSC scans on amorphous PEN film, water, and a mixture of PEN and water, respectively. In the DSC scan for pure water, a large endothermic peak emerged at temperatures of 100–130°C. This peak seems to be due to the vaporization of water. However, in the DSC scan for the mixture of water and PEN, one wide endothermic peak appeared in the range of temperatures of 50–90°C, and another small endothermic peak was seen near 105°C. The former large peak at 50–90°C may correspond to the depressed boiling point (B.P.) of water in a water/PEN mixture caused by unfavorable mixing of PEN with nearly immiscible liquid, water. The other small peak at 105°C could be looked upon as arising from the retardation of a small amount of water contained inside the PEN molecules. On the other hand, for the DSC scan of a mixture of PEN and water shown in the insert of Figure 1(a), the cold crystallization exother-

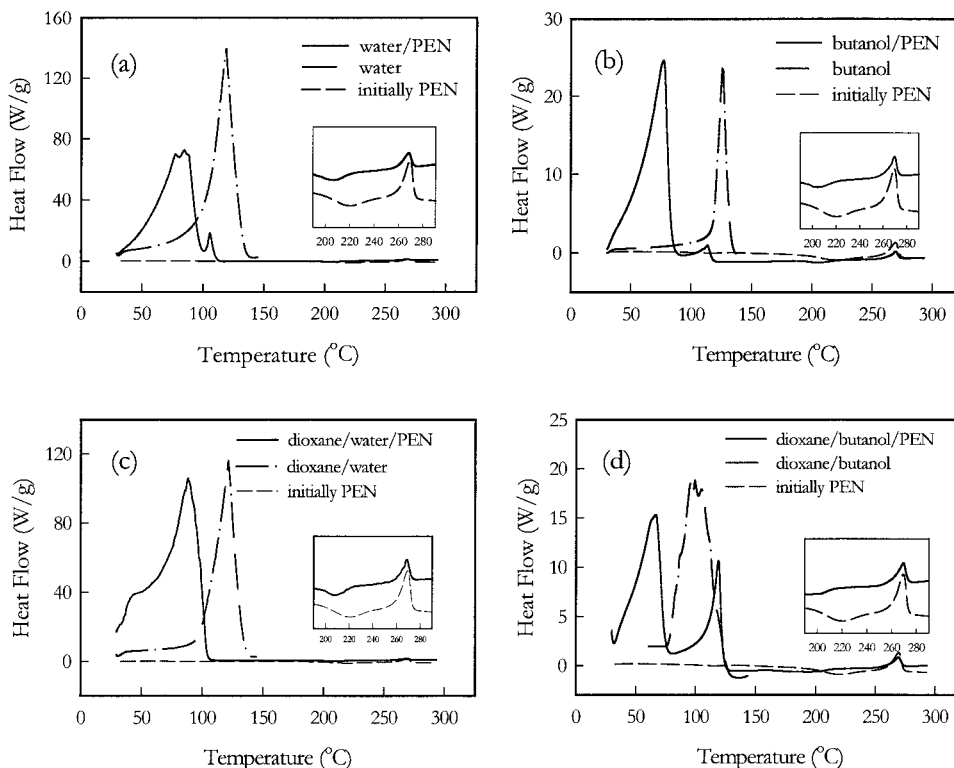


Figure 1 DSC thermograms for mixtures of undrawn PEN amorphous films with various solvent systems: (a) water/PEN; (b) 1-butanol/PEN; (c) 1,4-dioxane/1-butanol/PEN; (d) 1,4-dioxane/1-butanol/PEN.

mic peak temperature ($T_{c\text{ cold}}$) shifted to the lower one and the peak capacity decreased. The melting endothermic peak capacity also decreased compared to those of pure PEN film. Probably these are considered to be due to the plasticizing effect of water.

Figure 1(b) shows the DSC scans for amorphous PEN film, 1-butanol, and a mixture of PEN and 1-butanol to estimate the interaction between PEN and 1-butanol. In the DSC scan of 1-butanol in Figure 1(b), a large and sharp endothermic peak emerged at temperatures of 120–130°C. This peak will correspond to the vaporization of 1-butanol. However, in the DSC scan of the mixture of 1-butanol and PEN, one large endothermic peak appeared in the range of 50–80°C and another small endothermic peak was observed near 115°C. Similarly to Figure 1(a), the former peak at 50–80°C may correspond to the depressed B.P. of 1-butanol in a 1-butanol/PEN mixture caused by unfavorable mixing of PEN with a partially immiscible liquid, 1-butanol. The other small peak near 115°C seems to correspond to the retarded vaporization of 1-butanol contained inside the PEN molecules. On the other hand, comparing the DSC scan of a mixture of PEN and 1-butanol with that of the initially molded pure PEN film shown in the insert of Figure 1(b), we can see the $T_{c\text{ cold}}$ shifted to the lower temperature and the peak capacity decreased. The melting peak intensity also decreased compared to those of pure PEN. The decreasing tendencies of two peaks were found to be more obvious than those of water/PEN shown in Figure 1(a). This can be explained in terms of the solubility parameter concept, i.e., 1-butanol is considered to be more interactive liquid against PEN compared to water as judged from the values of solubility parameter given in Table I, and hence, shows a larger plasticizing effect on PEN than that of water.

Figure 1(c) shows the DSC scans on the initially molded PEN film, 1,4-dioxane/water (20 : 80 by volume) mixed solvent, and mixture of PEN/1,4-dioxane/water to estimate the interaction between PEN and the mixed solvent. For the DSC curve of the 1,4-dioxane/water mixed solvent in Figure 1(c), a large endothermic peak emerged at temperatures of 100–130°C. This peak will be due to the vaporization of the 1,4-dioxane/water mixed solvent, which has similar boiling points (see Table I). For the DSC scan of PEN/1,4-dioxane/water, however, a large broaden endothermic peak appeared in the range of temperature 90–120°C. This peak would also correspond to the depressed B.P. of mixed solvent in a mixture with PEN caused by unfavorable interaction between PEN and solvent. On the other hand, for the DSC curve of the mixture of PEN/1,4-dioxane/water shown in the insert of Figure 1(c), the $T_{c\text{ cold}}$ exothermic peak shifted to the lower temperature, and the peak intensity as well as the resulting melting endothermic peak was decreased remarkably. In fact, from the DSC experi-

ment performed on PEN/1,4-dioxane (although not reported here), the $T_{c\text{ cold}}$ was not observed, suggesting a high possibility of the occurrence of SINC by fairly interactive liquid dioxane for PEN, and hence providing ineligibility for the low-temperature (solvent) drawing because of impeded chain mobility. However, in the case of the PEN/1,4-dioxane/water system, the presence of the cold crystallization peak was confirmed as in Figure 1(c). Therefore, we may realize that the 1,4-dioxane/water mixed solvent will not make PEN crystallize, but merely the plasticizing action against PEN, thereby making the lower temperature drawing possible compared to the dry polymer.

Figure 1(d) shows the DSC scans on the initially molded amorphous PEN film, a 1,4-dioxane/1-butanol (20 : 80 by volume) mixed solvent, and a mixture of PEN/1,4-dioxane/1-butanol to estimate the interaction between PEN and the 1,4-dioxane/1-butanol mixed solvent. For the DSC curve of 1,4-dioxane/1-butanol mixed solvent in Figure 1(d), a large and broad endothermic peak emerged at temperatures of 80–120°C. This peak will be due to the vaporization of 1,4-dioxane/1-butanol mixed solvent. However, for the DSC scan of the mixture of PEN and 1,4-dioxane/1-butanol, two endothermic peaks emerged: one larger peak appeared at temperatures of 50–80°C; the other smaller peak came out at 110–125°C. In the case of the dioxane/butanol mixed solvent system, an explanation on the vaporization behavior of mixed solvent in a mixture with PEN would be a little complicated compared to the previous cases because the B.P.s for two components differ by more than 15°C (see Table I). Nevertheless, it seems reasonable to assume that the former peak at 50–80°C corresponds to the depressed B.P. of mixed solvent (mainly 1,4-dioxane) in a mixture with PEN and the latter peak near 110–125°C corresponds to the retarded vaporization of mixed solvent (mainly 1-butanol) contained inside the PEN molecules. On the other hand, for the DSC curve of the mixture of PEN and 1,4-dioxane/1-butanol shown in the insert of Figure 1(d), the $T_{c\text{ cold}}$ exothermic peak shifted to the lower temperature and was broadened, with the corresponding melting endothermic peak intensity decreased. Just as in Figure 1(c), the fact that the $T_{c\text{ cold}}$ was still observed, even though it was the fairly weakened peak capacity, may indicate that 1,4-dioxane/1-butanol consisting of both interactive liquids is also a good candidate for the low-temperature solvent drawing via the (strong) plasticizing action against PEN without making PEN crystallized easily.

Before proceeding, the temperature range around the depressed boiling points, which corresponds to the main endothermic peak of respective liquids in mixtures of initially molded amorphous PEN films with various solvents systems, should be pointed out, as determined by the DSC scans, and the temperature

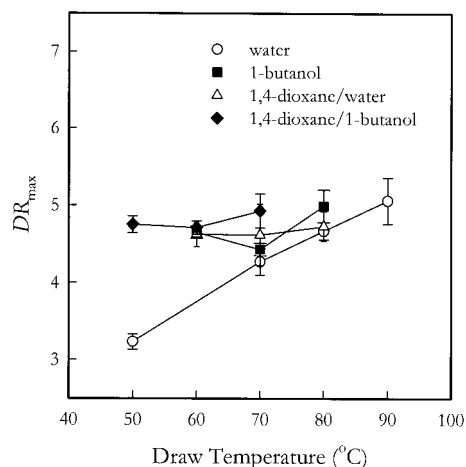


Figure 2 Draw ratios for PEN films drawn in various solvent systems.

range was considered to coincide with the optimum drawable range for each solvent system.

Drawability

The quenched amorphous PEN films were drawn up to the maximum draw ratio (DR_{max}) against each condition. The proposed draw temperatures were selected experimentally within the range of the corresponding temperatures as confirmed by DSC measurements on the undrawn PEN/solvent mixture (see Fig. 1 and Table II). Figure 2 shows the drawability of PEN films drawn up to DR_{max} under the selected conditions for each solvent system. In the first place, we will discuss the drawable temperature range for each solvent system as shown in Figure 2. For the drawing in water, the drawable temperature range of above $50^{\circ}C$ below $100^{\circ}C$ (for the normal B.P. of water is $100^{\circ}C$) has been already pointed out that the drawable temperature range seems to coincide with the endothermic (main) peak corresponding to the depressed B.P. of water in a PEN/water mixture. For the cases of the drawing in 1-butanol, 1,4-dioxane/water (20 : 80 by volume), 1,4-dioxane/water (20 : 80 by volume), the drawable temperature regions were also found to agree with the positions of the (main) endothermic peaks corresponding to the depressed B.P.s of respective liquids in PEN/solvent mixtures caused by the unfavorable interaction between PEN polymer and solvents as shown in Figure 1(b)–(d). Above these temperatures the drawing was actually impossible because the SINC could be developed as a result of enhanced plasticizing action of interactive liquids on PEN.

In the next place, we will discuss on changes of DR_{max} with draw temperature for each solvent system. The DR_{max} of PEN films drawn in water were shown to increase linearly with temperature. At the

draw temperature of as high as $90^{\circ}C$, the DR_{max} was fairly high—as much as 5. This may probably be because the plasticizing action is enhanced by water, although water is a poorly interactive liquid against PEN. On the other hand, the changes of DR_{max} with the draw temperature for the PEN films drawn in 1-butanol, 1,4-dioxane/water, and 1,4-dioxane/1-butanol systems exhibited about the same tendency, i.e., up to the intermediate temperature studied the DR_{max} remained nearly uniform or decreased slightly, and then it increased remarkably with increasing draw temperature. The possible reasons for the fact that the values of DR_{max} at the respective intermediate temperatures covered for the above three solvent systems are as low as 4.5–5 would be as follows. First, the uniform drawing to the DR_{max} was impossible, owing to the excess segmental mobility by drawing near the main endothermic peak corresponding to the (depressed) B.P.s of liquid components in PEN solvent mixtures. Next, structural inhomogeneities such as cohesive bodies and/or cavities as observed by SEM [see Fig. 6(b)–(d)] arising from a kind of imperfect crystals with the M.P. around $150^{\circ}C$ (as observed by DSC scans, see Figs. 5(b)–(d)) have been formed sporadically over the entire film surface probably due to the enhanced plasticizing action by fairly interactive liquids such as 1-butanol or 1,4-dioxane against PEN at these temperature ranges.

Density

The densities of the PEN films drawn at selected temperatures in the each solvent were shown in Figure 3. For the drawing in water the density decreased until $70^{\circ}C$ and then increased with increasing draw temperature. It seems reasonable to assume that at $70^{\circ}C$ the fibrillation within PEN films was developed and then interfibrillar voids among microfibrils occurred be-

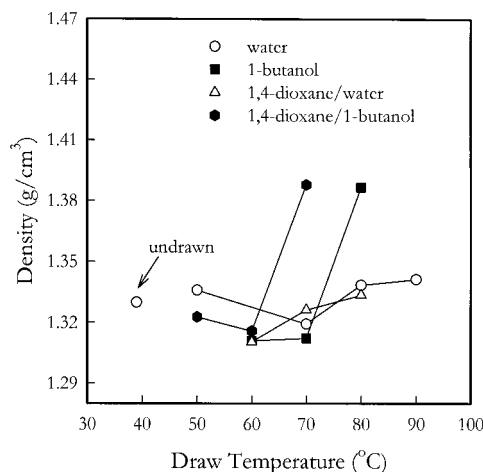


Figure 3 Densities for PEN films drawn in various solvent systems.

cause of the low mobility of the chain segment, like the behavior in cold drawing at lower temperature than T_g of PEN film discussed on our previous article.¹³ However, for the drawing at 50°C, the density increased slightly compared with that for the amorphous film. This may suggest that the fibrillation was not so propagated yet because the DR_{max} at 50°C has a value of about 3 lower than the others. At the temperatures above 80°C, the density increased gradually with the draw temperature. This is considered to be due to the increase in chain orientation, and hence crystallinity, arising from higher drawability caused by the enhanced plasticizing action of water at this temperature range. For the drawing in 1,4-dioxane/water, the densities exhibited a tendency to increase with draw temperature and the increase tendency of densities is similar with that of films drawn in water; but the densities of films drawn at 60 and 70°C were lower than that of the undrawn amorphous PEN. This tendency was probably attributed to the reason that the 1,4-dioxane/water is a mixed solvent consisting of a crystallizable interactive solvent and an immiscible solvent. The decrease phenomenon of density at 60 and 70°C compared to that of undrawn film might be ascribed to the existence of microvoid caused by the removal of noninteractive solvent (water). For the drawing at as high a temperature as 80°C, however, the density was slightly increased compared to that of undrawn PEN film probably because the crystallization by solvent (dioxane) and the chain orientation by higher drawing have been accelerated.

On the other hand, in the 1-butanol and 1,4-dioxane/1-butanol solvent systems, the densities were nearly uniformed or decreased slightly up to the intermediate temperatures and then increased rapidly. Moreover, up to the intermediate temperatures in the each solvent, the densities were lower than that of undrawn PEN film, and the films drawn above these temperatures had much higher densities for both solvent systems. This might be expected to result from the fact that up to the intermediate temperatures the close-packed structure by drawing was not formed yet, but above the intermediate temperatures the crystallinity, and hence density, increased remarkably because the crystallization effect by interactive solvents as well as the orientation effect by drawing was abruptly increased.

Crystalline structure

The changes of crystalline structure on drawing of PEN films in various solvent systems were characterized using X-ray diffraction and DSC. Figure 4(a)–(d) show the equatorial X-ray diffraction profiles for PEN films drawn in water, 1-butanol, 1,4-dioxane/water, and 1,4-dioxane/butanol at each selected temperature, respectively, together with that for undrawn amor-

phous PEN film. They exhibit the (010), (100), and (110) planes X-ray reflections of α -crystal at $2\theta = 15.6$, 23.3 , and 27.1° , respectively. For the films drawn in water [see Fig. 4(a)], the intensities of crystalline reflections increased gradually with the draw temperature until 80°C, above which the intensities become much stronger. For the drawing in the nearly immiscible liquid, water, a reliance on the draw temperature was fairly increased, and the relationship between draw temperature and drawability or its crystallinity was more or less linear. For the X-ray diffraction profile of PEN films drawn in 1-butanol at draw temperatures of 60, 70, and 80°C (see Fig. 4(b)), the intensities of crystalline reflection increased slightly with the draw temperature. The development of the α -crystalline planes seems to be markedly increased at 70°C and above with much stronger intensity. Moreover, it was confirmed that the development of crystalline planes has been attained over the entire draw temperature region. For the cases of drawing in 1,4-dioxane/water and 1,4-dioxane/1-butanol at the temperatures of 60–80 and 50–70°C, respectively, the development of α -crystalline planes of the former was prominent at 70°C and above, while for the latter, over the entire draw temperature range, the reflections of α -crystalline planes were developed.

Figure 5(a)–(d) show the DSC thermograms of PEN films drawn in various solvent systems at each selected temperatures. For those of the PEN films drawn at 50–90°C in water together with that of undrawn amorphous PEN film [see Fig. 5(a)], after the drawing process, the $T_{c\ cold}$ exothermic peaks and T_g slopes as observed in Figure 1(a) disappeared, and the T_m endothermic peaks were sharpened with increasing draw temperature. Figure 5(b) shows the DSC thermograms of PEN films drawn at 60, 70, and 80°C in 1-butanol, in drawing at 60°C, an increase of crystalline melting peak near 270°C and a disappearance of the cold crystallization peak near 220°C. This may reflect that the orientation-induced crystallization and an increase of crystalline perfection have been brought about upon drawing in 1-butanol. But in drawings at 70 and 80°C, the intensity of melting endothermic peaks decreased; instead, the broad another endothermic peak was observed around 150°C, probably due to the enhanced segmental mobility caused by the increase in draw temperature. Accordingly, it is believed that the PEN films drawn in 1-butanol had a kind of imperfect crystalline portions. The DSC thermograms of PEN films drawn at 60, 70, and 80°C in 1,4-dioxane/water (20 : 80 by volume) were shown in Figure 5(c). After the drawing process, the cold crystallization exothermic peak disappeared and the intensities of melting endothermic peak increased gradually and were sharpened with increasing draw temperature. Accordingly, it is thought that an occurrence of the orientation-induced crystallization and an in-

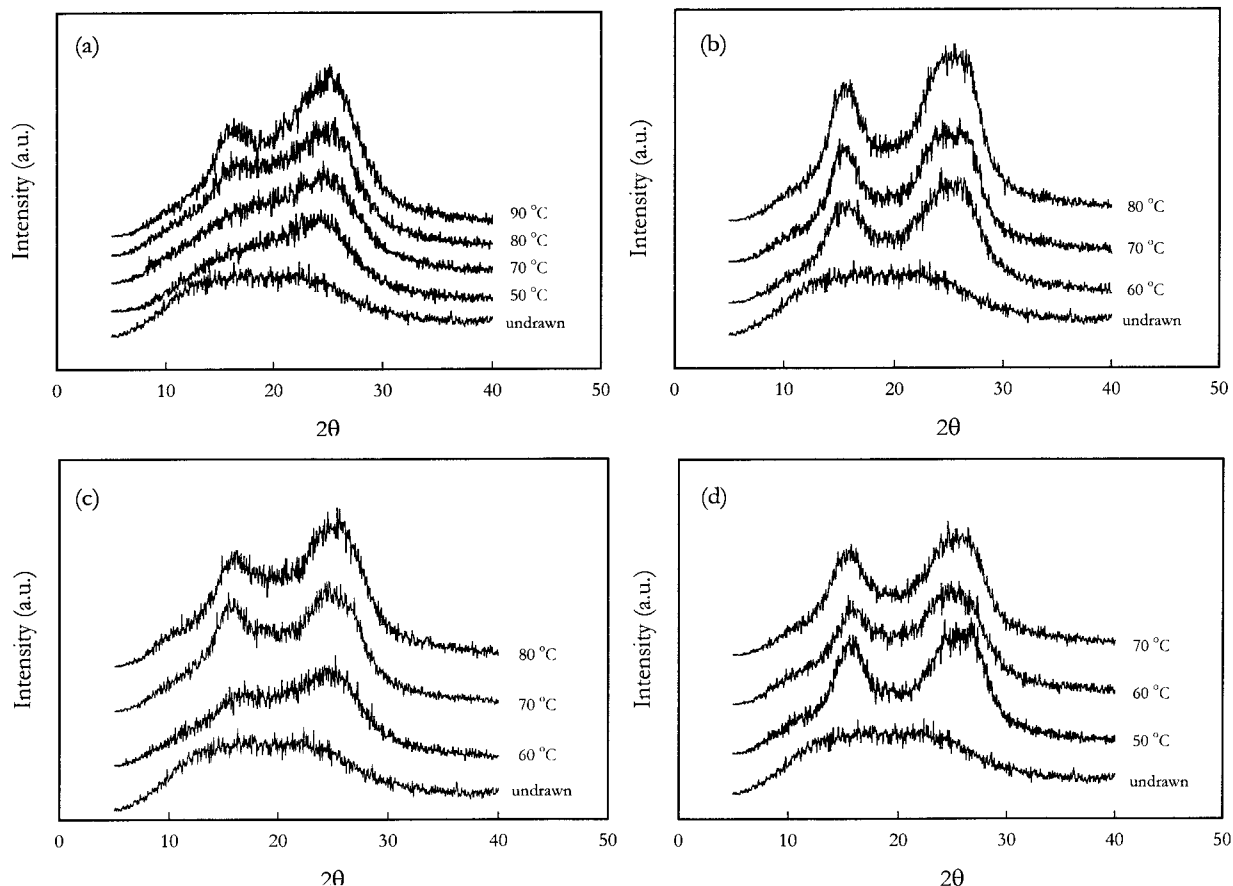


Figure 4 Equatorial WAXD profiles for PEN films drawn in various solvent systems at different temperatures: (a) water; (b) 1-butanol; (c) 1,4-dioxane/water; (d) 1,4-dioxane/1-butanol.

crease of the crystalline perfection have been developed upon drawing amorphous PEN film in 1,4-dioxane/water mixed solvent at 60–80°C. The DSC thermograms of PEN films drawn at 50, 60, and 70°C in 1,4-dioxane/1-butanol were shown in Figure 5(d). Up to 60°C, an increase of melting endothermic peak intensity and a disappearance of cold crystallization peak were observed, and hence, the orientation-induced crystallization and an increase of crystalline perfection were confirmed again. But for the drawing at 70°C, the intensity of melting endothermic peaks near 270°C decreased. Instead, the broad endothermic peak near 150°C was observed Figure 5(b). Similarly, it is believed that a kind of imperfect crystalline portions was formed within PEN films upon drawing in 1,4-dioxane/1-butanol mixed solvent at 70°C.

Surface morphology

Figure 6(a) shows the surface textures of the PEN films drawn at 50 and 90°C in water using the scanning electron microscope. The films drawn in water were found to keep a uniform surface condition. But it was confirmed that the shear zone inclined at 45° to the stretching axis was formed on the surface of the drawn

film. It has been known that the shear zone is usually formed just before yielding. Accordingly, the above shear zone is believed to result from the necking phenomenon during the drawing of PEN in water.

Figure 6(b) shows the surface SEM photographs of the films drawn at 60 and 80°C in 1-butanol. The drawn films were seen to have many small “cohesive bodies” on the surface and the vivid shear zone. It is thought that the existence of small cohesive bodies on the surface of the PEN film was due to the sporadically plasticizing action by the interactive solvent, 1-butanol, over the entire film surface. Presumably, the existence of the broad endothermic peaks around 150°C as shown in Figure 5(b) can be interpreted as the melting of the cohesive bodies denoting an imperfect crystal. From the appearance of the vivid shear zone, the occurrence of necking during drawing in 1-butanol has also been confirmed.

Figure 6(c) shows the surface SEM photographs of the films drawn at 60 and 80°C in 1,4-dioxane/water. A kind of “cavitated texture” was formed over the surface of the film, and the texture looked like an internal void. The cavitated texture by internal voids may be caused by water, which may exhibit a relatively poor interaction against PEN but a good perme-

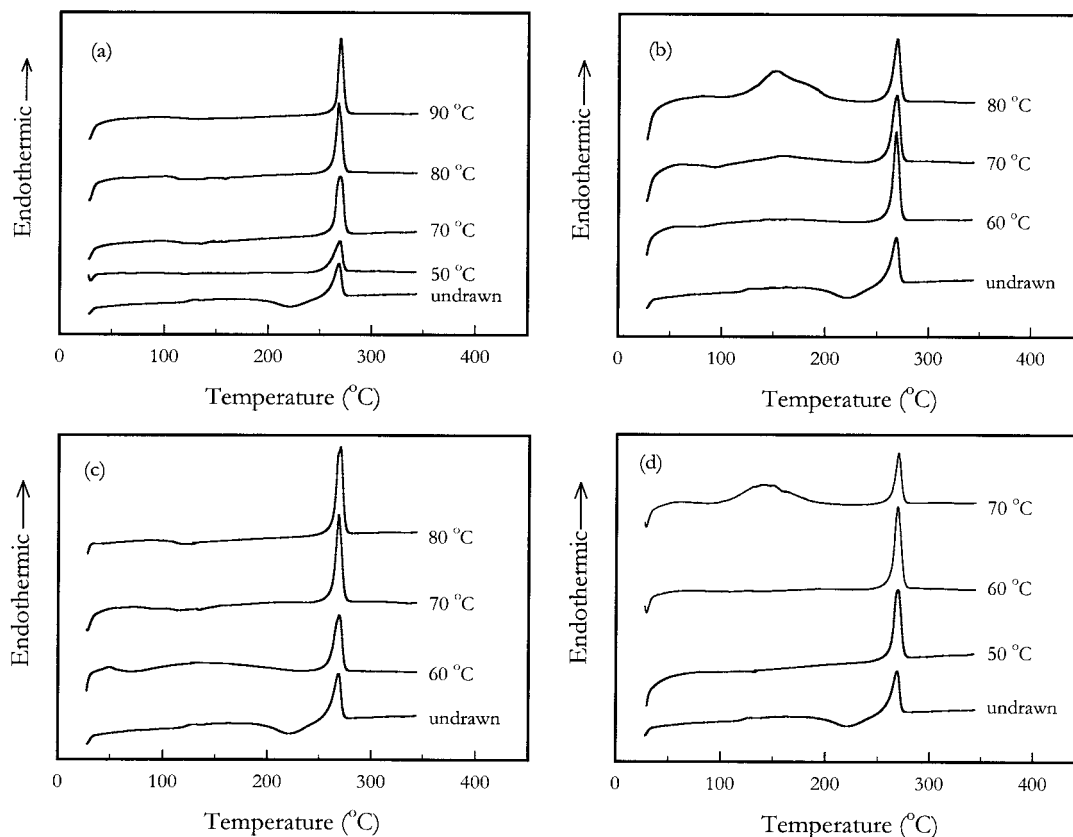


Figure 5 DSC thermograms of PEN films drawn in various systems at different temperatures: (a) water; (b) 1-butanol; (c) 1,4-dioxane/water; (d) 1,4-dioxane/1-butanol.

ability associated with low molecular weight. As can be seen from this figure, the cavitation on film surface became more crowded with increasing draw temperature.

Figure 6(d) shows the surface SEM photographs of the PEN films drawn at 50 and 70°C in 1,4-dioxane/1-butanol. The films drawn at 50°C were also seen to have many small cohesive bodies over the surface, but

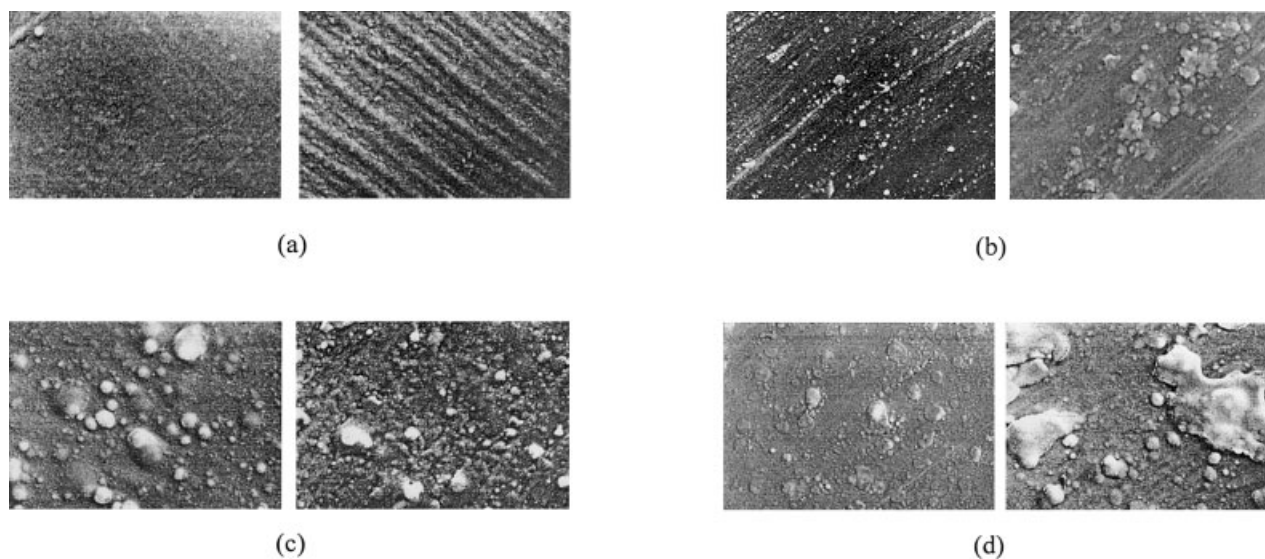


Figure 6 SEM photographs of PEN films drawn in various solvent systems at different temperatures: (a) water at 50 and 90°C; (b) 1-butanol at 60 and 80°C; (c) 1,4-dioxane/water at 60 and 80°C; (d) 1,4-dioxane/1-butanol at 50 and 70°C.

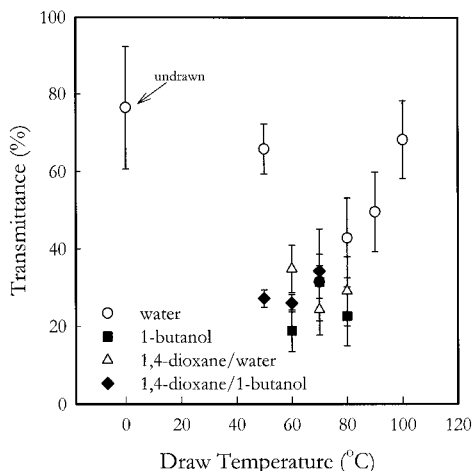


Figure 7 The transparency of PEN films drawn under selected conditions for various solvent systems.

for 70°C, the big cohesive bodies emerged sporadically on film surface. It seems reasonable to speculate that the existence of these big cohesive bodies was caused by the partial imperfect crystallization effect owing to the enhanced plasticizing action of 1-butanol/1,4-dioxane mixed solvent, both interactive liquids, against PEN molecules, in agreement with the existence of the broad endothermic peak around 150°C shown in Figure 5(d).

Transparency

Figure 7 shows the transmittance of visible light at wavelengths of 400–800 nm to estimate the transparency of PEN films drawn under selected conditions for various solvent systems. For the PEN films drawn in water, the film drawn at 50°C had a similar transparency to that of the undrawn amorphous PEN film. But for the cases drawn at 70, 80, and 90°C in water, the turbidity increased remarkably. It is considered that this tendency of turbidity was due to the scattered reflection of visible light by an occurrence of the resultant interfibrillar void caused by fibrillation within PEN film when drawing in poorly interactive liquid, water. On the other hand, the increases in turbidity for the films drawn in 1-butanol, 1,4-dioxane/water, and 1,4-dioxane/1-butanol might be attributed to the combined effects of the cohesive bodies and the cavitated textures formed on the film surface by the solvent actions of fairly interactive liquids (dioxane and butanol) and poorly interactive liquid (water), respectively, against PEN molecules.

CONCLUSIONS

From the investigation on the structural development during the solvent-drawing process of unoriented amorphous PEN films in various solvent systems specifically chosen using DSC, WAXD, SEM, etc., the following results were obtained.

It was revealed from the DSC scans that the B.P. of each liquid in mixtures of amorphous PEN films with various solvents was appreciably depressed compared to that of pure liquid without PEN probably because of unfavorable interaction between PEN and liquids. In addition, the temperature range around the (main) peak corresponding to the depressed B.P. was found to coincide with the drawable range where all the experiments involved were for each solvent system.

When drawing in 1-butanol and 1,4-dioxane/1-butanol, a kind of imperfect crystalline portion caused by the (strong) plasticizing action of solvents, as confirmed by the presence of cohesive bodies sporadically scattered on the film structure. In the case of the drawing in 1,4-dioxane/water, with increasing draw temperature as a result of the complementary effect between fairly interactive liquid, dioxane, and poorly interactive liquid, water, against PEN. In addition, on the surface of the PEN films drawn in both water and 1-butanol the shear zone indicated at 45° to the stretching axis was observed, reflecting on the occurrence of necking during solvent drawing.

The experimental results thus obtained could be explained, though qualitative, in terms of the interactions between PEN and solvents. Therefore, it is expected to control the fine structure and properties of PEN films resulting from the (low-temperature) solvent drawing via a suitable choice of liquids and the corresponding draw temperature range.

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