

Structural, Mechanical, and Thermal Properties of Extruded Sheets of a Liquid Crystalline Copolyester

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SYNOPSIS

Structural, mechanical, and thermal properties of extruded sheets of a liquid crystalline copolyester containing *p*-hydroxybenzoic acid and 2-hydroxynaphthoic acid were investigated using X-ray diffraction measurements, differential scanning calorimetry, rheovibron measurements, and scanning electron microscopic observation. The extruded sheets of the thermotropic copolyester are composed of layered structures containing skin and core layers. A skin layer comprises fine fibrils oriented almost parallel to the extrusion direction. A core layer contains poorly oriented thicker fibrils or platelike structures. The orientation function of sheets and their tensile dynamic modulus parallel to the extrusion direction increase with increasing draw-down ratio of the sheet. Annealing of the sheet caused the increases in the temperature and the heat of crystal-mesophase transition, the heat-resistance to the mechanical tensiles properties, and the inherent viscosity of the polymer. The effect of annealing on the structural properties of the extruded sheet was discussed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Rigid chain molecules of thermotropic liquid crystalline polymers (LCP) are apt to be oriented parallel to the direction of flow in the liquid crystalline melt. The state of well-oriented chain molecules obtained by flowing is almost maintained after solidification of the LCP. The high degree of orientation of the chain molecules yields superior mechanical properties such as tensile modulus and strength.¹ In processing such as extrusion and injection molding, however, one can hardly obtain a unique velocity of flow of the liquid crystalline melt. In most cases, the flow of the melt has a gradient of velocity and shows a shear flow that has an effect on the orientation of rigid chain molecules or domain textures believed to exist in mesophase states. The degree of orientation of the LCP processed under a shear flow is frequently dependent upon the location of the molded parts. A typical example showing this orientational property is the skin/core structure.² In

general, the solid-state structures of the LCP depend very strongly on the flow and the thermal histories made in the mesophase state.

Weng et al. investigated in detail the solid-state structure of injection-molded plaques of a thermotropic copolyester consisting of 58 mol % *p*-hydroxybenzoic acid (HBA) and 42 mol % 2,6-hydroxynaphthoic acid (HNA).² They found a gradient solid-state structure of layers described by a hierarchical structure with several levels of structural organization for the molded thermotropic copolyester.² Fibrous structures composed of the copolyester molecules are arranged in the layered structures. A skin macrolayer consists of several more or less oriented sublayers and a core one has no oriented structures. The structural hierarchy has been also found in a broad range of oriented fibers, extrudates, and injection-molded parts from a thermotropic HBA/HNA copolyester by Sawyer and Jaffe.³ They observed three distinct fibrillar species: 5 μ m macrofibrils, 500 nm fibrils, and 50 nm microfibrils in the thermotropic copolyester fibers.³ The change in thickness and orientation of the layered structure has also been examined for injection-molded articles of thermotropic copolyesters.^{4,5}

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Annealing of the LCP causes improvements of the temperature of the crystal-mesophase transition and the degree of crystallinity and has little effect on the orientation of the LCP molecules.⁶ Lin and Winter reported that small crystals grow with annealing at temperatures above the crystal-mesophase transition one and that the heat-resistance to mechanical properties becomes higher for a thermotropic HBA/HNA copolyester.⁷

Many studies on thermotropic HBA/HNA copolyesters have been made for fibers and injection-molded articles, but very few for extrusion-molded sheets. We have investigated the properties of extrusion-molded sheets of a thermotropic HBA/HNA copolyester. The orientation profiles in the sheets have been examined by polarized reflection spectroscopy. The orientation behavior at the surface of sheets has been shown to be equivalent to that in the bulk of thinner sheets.⁸ Effects of annealing on the structure formation of the same thermotropic copolyester as used in a previous paper⁸ have been studied by wide-angle X-ray diffraction.⁹ The lateral packing of the chain molecules of the copolyester is transformed from a hexagonal packing to an orthorhombic one in the course of annealing.⁹ The purpose of this research is to investigate the structural, mechanical, and thermal properties of extrusion-molded sheets of the thermotropic copolyester and to examine the effects of annealing on the properties of the sheets.

EXPERIMENTAL

The liquid crystalline polymer used in this work is a commercial copolyester containing 73 mol % HBA and 27 mol % HNA (Polyplastics Co.). The polymer exhibits the crystal-mesophase transition at about 278°C. Sheets of the polymer were extrusion-molded using a single-screw extruder equipped with a coat-hanger die, after pellets of the polymer were dried at 90°C for 12 h and then at 150°C for 3 h. The coat-hanger die was composed of a crosshead with a diameter of 15 mm, manifold, damming zone, and die lip area, as shown in Figure 1. The die lip area was 20 mm long in the flow direction and 120 mm wide. The gap of the die lip was adjusted at 0.75 mm. The die temperature was controlled at $290 \pm 2^\circ\text{C}$. The extrusion molding was carried out at an extrusion pressure of about 35 kg/cm². The extruded sheets were drawn down in the molten state after leaving the die outlet and were slowly cooled to ambient temperature. The draw-down ratio was con-

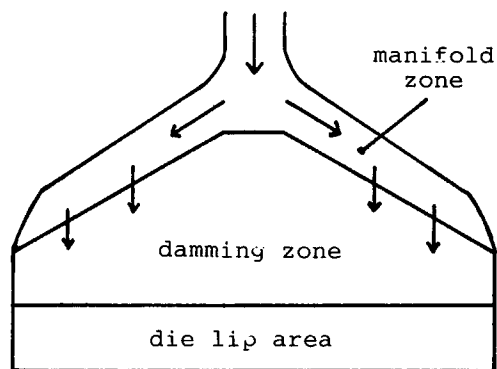


Figure 1 Diagram of the coat hanger die. Arrows show the direction of flow of the polymer.

trolled by changing the take up speed. Annealing of the sheets was carried out at temperatures from 180 to 270°C for 6 h *in vacuo*. The sheet used in this annealing experiment was a draw-down ratio of 4. Dimensions of the sheets did not change significantly in the course of annealing.

Inherent viscosities of the polymer were measured at 60°C in a 6 : 4 mixture (by volume) of pentafluorophenol and *p*-chlorophenol at a polymer concentration of 0.1 g/100 mL. The inherent viscosity of the polymer pellet was 5.37 dL/g.

Wide-angle X-ray diffraction (WAXD) diagrams were taken with a flat-film camera. Ni-filtered CuK α radiation generated by a Geiger Flex XGC-20 (Rigaku Denki Co.) was used as an X-ray beam. The crystal orientation function in the extruded sheets was determined from the azimuthal intensity distribution of WAXD. The WAXD intensity was measured by using a scintillation counter and a pulse height analyzer.

Dynamic tensile modulus of the sheets was investigated at a frequency of 110 Hz by using a Rheovibron DDV-III-EP (Orientec Co.). Density was measured with a carbon tetrachloride-*n*-heptane density gradient column at 25°C. The precision for the density measurement was in the range of $\pm 0.001 \text{ g/cm}^3$.

Thermal behavior was investigated with a Perkin-Elmer differential scanning calorimeter (DSC) Model 2 at a heating rate of 20°C/min. Temperature calibration was based on tin and lead.

To examine the interior structures of the extruded sheets by scanning electron microscopy (SEM), the sheets were fractured parallel or perpendicular to the direction of extrusion at room temperature or at liquid-nitrogen temperature. Surface replicas of the fractured surface were studied by transmission electron microscopy.

RESULTS AND DISCUSSION

Mechanical Properties of Extruded Sheets

Fracturing the sheets obtained in this work perpendicular to the direction of extrusion by hand at room temperature was very difficult, while the sheets were easily ruptured parallel to the extrusion direction. This anisotropic mechanical properties of the sheets are exhibited by a dynamic tensile modulus, shown in Figure 2. The dynamic tensile modulus perpendicular to the extrusion direction is much smaller than that parallel to the direction and gives almost a constant value independently of the draw-down ratio of the sheets. On the other hand, the dynamic modulus parallel to the extrusion direction increases rapidly with increasing draw-down ratio up to a value of 8 and then levels off. The variation of dynamic tensile modulus parallel to the extrusion direction with draw-down ratio corresponds very well to the orientation function of sheets, shown in Figure 3. Therefore, an increase in the modulus parallel to the extrusion direction can be attributed to higher molecular orientation in the sheets. The anisotropy of mechanical properties is characteristic of well-oriented molded articles of liquid crystalline rigid-chain polymers.^{10,11} In the case of extruded sheets, the anisotropy becomes more conspicuous with decreasing thickness of the sheets.

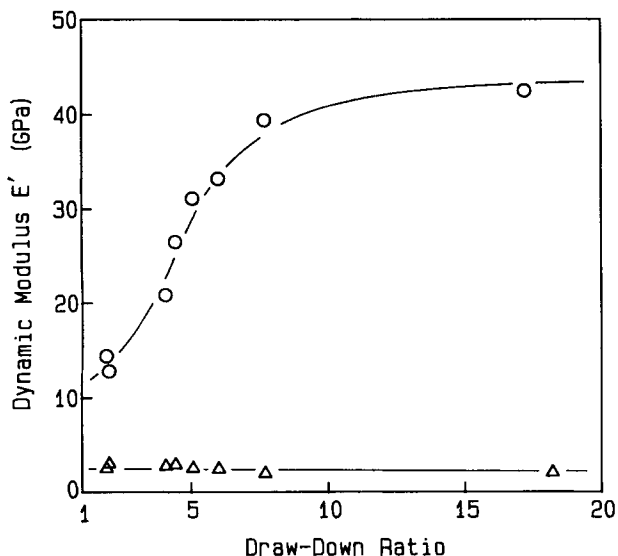


Figure 2 Dynamic tensile modulus of extruded sheets at a frequency of 110 Hz as a function of draw-down ratio. Circles and triangles represent the modulus parallel and perpendicular to the extrusion direction, respectively.

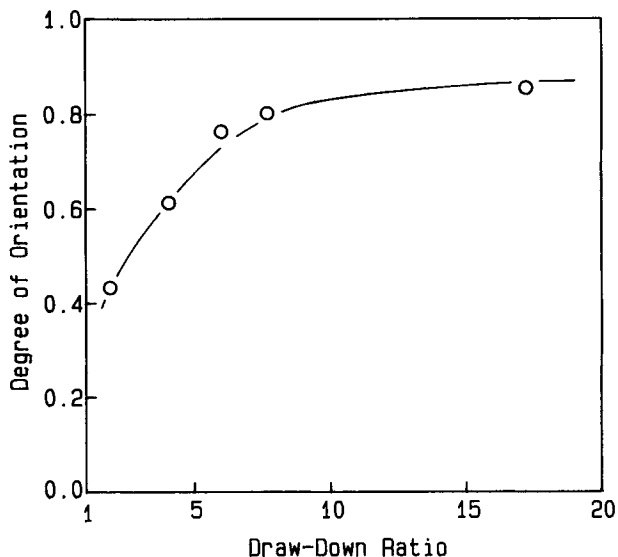


Figure 3 Orientation function of extruded sheets as a function of draw-down ratio.

Structural Properties of Extruded Sheets

Figure 4 displays fractured lateral surfaces of an extruded sheet. Multilayered structures about 10 μm in thickness of each layer can be seen in the vicinity of a surface of the sheet in Figure 4(a). The layered structure has also been obtained by tearing off the extruded sheet by hand at room temperature as several thin layers including a skin one (top layer from a sheet surface). Therefore, the sheet is believed to be composed of multilayered structures containing skin and core layers, as shown in Figure 5. A core layer tended to become thicker with increasing thickness of the sheet. The result of X-ray diffraction measurements revealed that a skin layer has a higher orientation of rigid chain molecules parallel to the extrusion direction and that a core layer has a poorer one. The layered structures observed in the extruded sheet obtained in this work are similar to those in the injection-molded plate of thermotropic copolyesters.^{2,3}

A lot of fibrous structures oriented parallel to the extrusion direction is observed, as shown in Figure 4(b). A small difference in density of the fibrous structures between the parts in the vicinity of the sheet surface and the inner parts of the sheet can be seen in Figure 4(b). There are more concentrated fibrous structures in the vicinity of the sheet surface than those in the inner parts. The density of sheets increases a little with increasing draw-down ratio, as shown in Figure 6. As an increase in draw-down ratio corresponds to a decrease in the thickness of

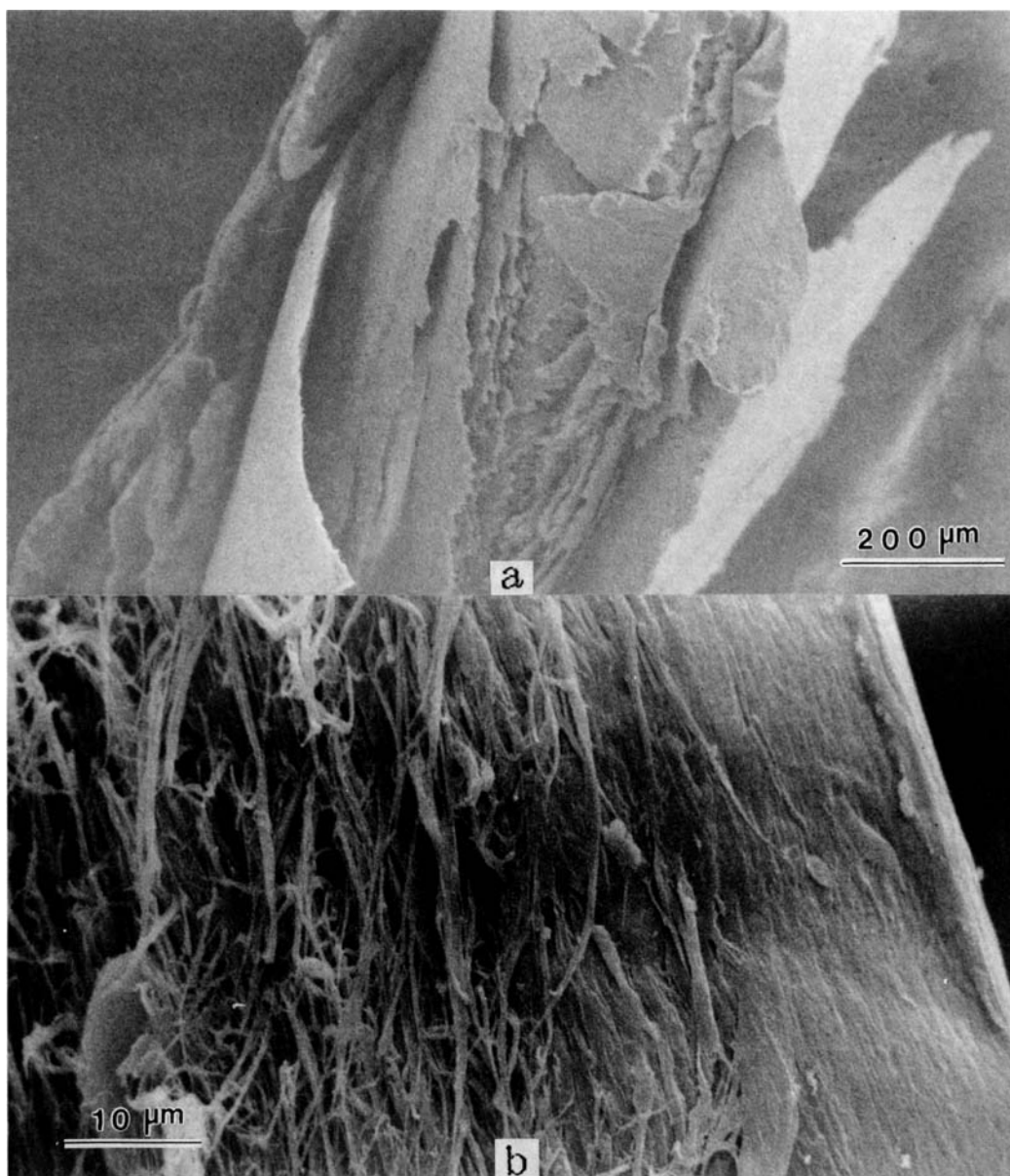


Figure 4 SEM of a lateral surface of a extruded sheet fractured (a) perpendicular and (b) parallel to the extrusion direction. This sheet has a draw-down ratio of 3.

the sheet, it means a decrease in thickness of the core layer of the sheets. In the case of extruded strands of the HBA/HNA copolyester used in this work, the degree of orientation of the central region (core part) of the strands increased with increasing draw-down ratio, in other words, with decreasing the strand's diameter, and finally attained to almost the same value as that of the surface region (skin part), as reported in a previous paper.¹² Well-oriented fibrous structures were developed with increasing draw-down ratio. The effect of thickness

on the degree of orientation for the extruded sheet is believed to be very similar to that of the diameter for the extruded strand. Therefore, Figures 4(b) and 6 indicate that the skin layer of sheets is composed of dense and well-oriented fibrous structures. A difference in density of fibrous structures between a skin layer and a core one has been observed for a thermotropic copolyester injection-molded plate.¹³

A layered structure in the sheets consists of numerous fibrous structures. Figures 7 and 8 illustrate the surface of skin and core layers, respectively, ob-

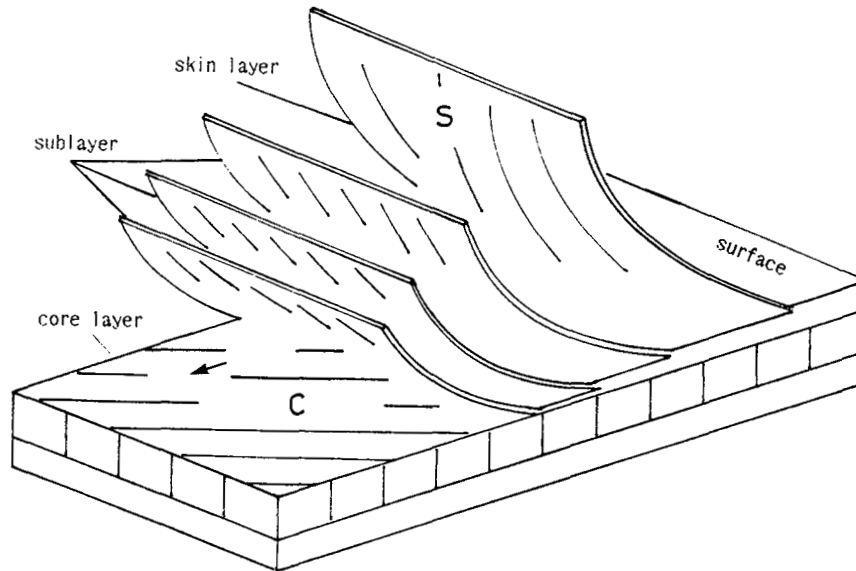


Figure 5 Schematic representation of a layered structure of an extruded sheet.

tained by tearing off a sheet parallel to the extrusion direction at room temperature by hand. The surfaces shown in Figures 7 and 8 correspond to the surfaces (s) and (c) indicated in Figure 5, respectively. The surface (s) is a back one of a skin layer. Thin fibrous structures oriented almost parallel to the extrusion direction are observed in the skin layer in Figure 7. A fibrous structure shows a ribbonlike shape characteristic of the morphology of a fibril observed in the molded parts of thermotropic rigid-chain polyesters.^{14,15} Microfibrils 20–30 nm in thickness were

observed in a replica surface of the skin layers by a transmission electron microscope. On the other hand, platelike structures wider than the ribbonlike fibrils are often seen in a core layer, as shown in Figure 8. Fibrillation occurs to some extent in the extremities of the platelike structure; however, the direction of fibrillation is not necessarily parallel to that of extrusion. Probably, the fibrillation in a core layer does not happen as remarkably as that in a skin layer.

Considering a size of the platelike structure observed in Figure 8, it seems to relate to a domain texture that exists in liquid crystalline states. The domain texture in a fluid of liquid crystalline rigid-chain polymers is believed to orient parallel to the flowing direction and then to deform and fractionalize during a flow under a shear stress. Possibly, the fibrillation of a domain texture follows the deformation and the fractionalization. Marrucci proposed that a disclination in a liquid crystalline state plays an important role in the orientation and deformation of the domain textures during a flow.¹⁶ In this work, the deformation and fractionalization processes of domain textures during a flow of the polymer melt in the extrusion machine and the hanger-type die could not be elucidated. However, the observation of skin and core structures in the sheets suggests that numerous fine fibrils oriented parallel to the extrusion direction are developed by the orientation and the fractionalization of domain textures in a skin layer applied the largest shear stress and that the orientation and the fibrillation of do-

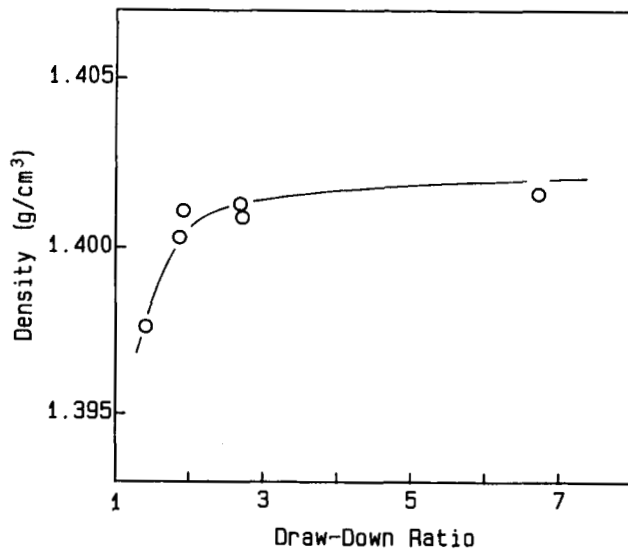


Figure 6 Variation of density of extruded sheets with draw-down ratio.

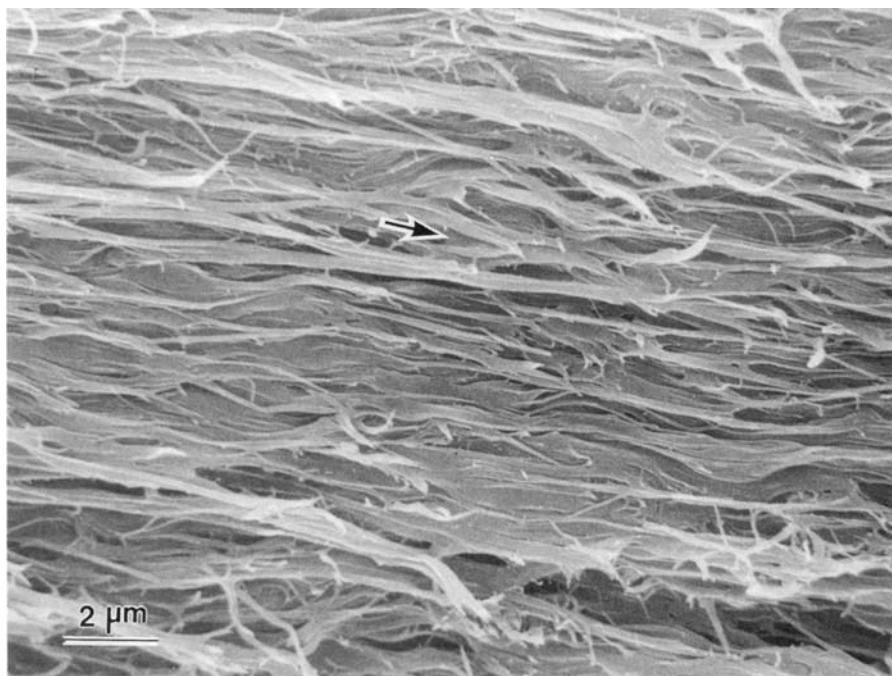


Figure 7 SEM of a back surface of a skin layer corresponding to the surface (s) shown in Figure 4. An arrow in the figure indicates the direction of extrusion.

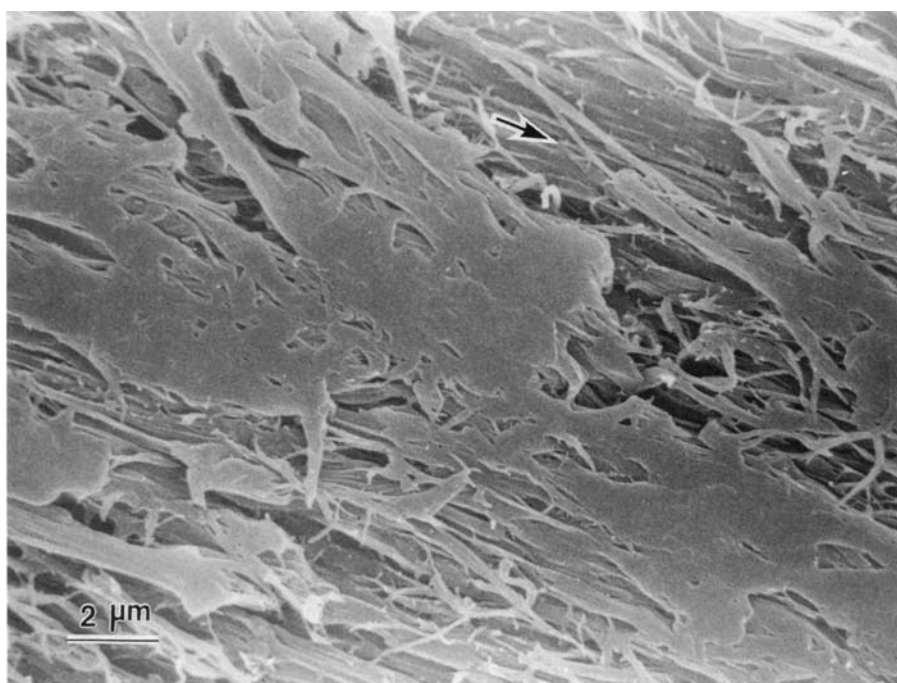


Figure 8 SEM of a surface of a core layer corresponding to the surface (c) shown in Figure 4. An arrow in the figure indicates the direction of extrusion.

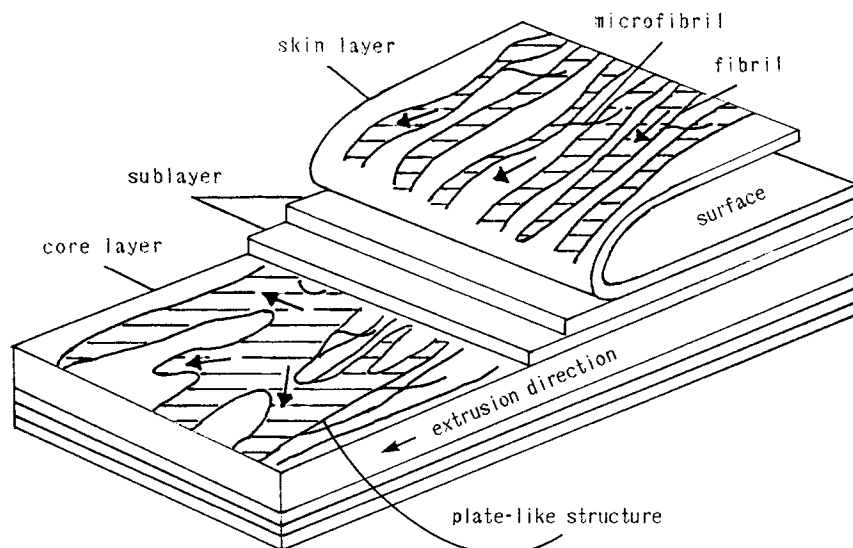


Figure 9 Schematic representation of a skin/core structure of an extruded sheet. The core layer contains platelike textures in which fibrillation is imperfect, whereas a skin layer is composed of fibrous structures. Arrows in the skin and core layer surfaces indicate the direction of molecular orientation.

main textures are very poor in a core layer applied the smallest or zero shear stress. Figure 9 illustrates schematically the structure of the extruded sheet, based on the results obtained in this study.

Effects of Annealing on the Thermal Properties of Extruded Sheets

Figure 10 exhibits DSC heating curves for as-extruded and annealed sheets. A single endothermic peak (T_{m1}) attributed to the crystal-mesophase (nematic melt) transition of the polymer appears in the DSC curves for the as-extruded sheet and those annealed at temperatures above 230°C. However, the sheets annealed at temperatures in the range of 180–220°C have a broader endothermic peak (T_{m2}) at temperatures of 218–240°C than does the endothermic peak of the crystal-mesophase transition.

Endothermic peak temperatures and their peak areas (heats of phase transitions) obtained from the DSC curves shown in Figure 9 are plotted against annealing temperature in Figures 11 and 12, respectively. The broader endothermic peak temperature (T_{m2}) tends to become higher with increasing annealing temperature (Fig. 11). The sheets annealed at temperatures up to 220°C have almost the same temperature (T_{m1}) of the crystal-nematic melt transition as that of the original one. The T_{m1} of

the sheets annealed at temperatures above 230°C, however, becomes higher with increasing annealing temperature, as shown in Figure 11. The heat of the crystal-nematic melt transition (ΔH_{m1}) increases very slowly with increasing annealing temperature up to 220°C. At the same time, the heat for the broader endothermic peak (ΔH_{m2}) becomes larger with annealing temperature, as shown in Figure 12. It should be noted that ΔH_{m1} increases suddenly and reaches a maximum value at an annealing temperature of 230°C. The value of H_{m1} for the sheets annealed at temperatures in the range of 230–270°C is seven to nine times higher than that for the original one, though it tends to become slightly lower with increasing annealing temperature.

Both the values of T_{m2} and ΔH_{m2} are dependent upon annealing temperature (Figs. 11 and 12). Butzbach et al. investigated in detail the effect of annealing on thermal and structural properties of a thermotropic 58 mol % HBA/42 mol % HNA copolyester and have concluded that crystallization of the copolyester occurs in two steps: first, rapid crystallization and, second, a slow one that corresponds apparently to postcrystallization.⁶ Consequently, multiendothermic peaks often appear in DSC curves for the annealed samples. The phase ordered by the slow crystallization is thermally unstable and its melting temperature and heat tend to vary with annealing temperature. The thermal behavior of annealed samples obtained in this work is similar to

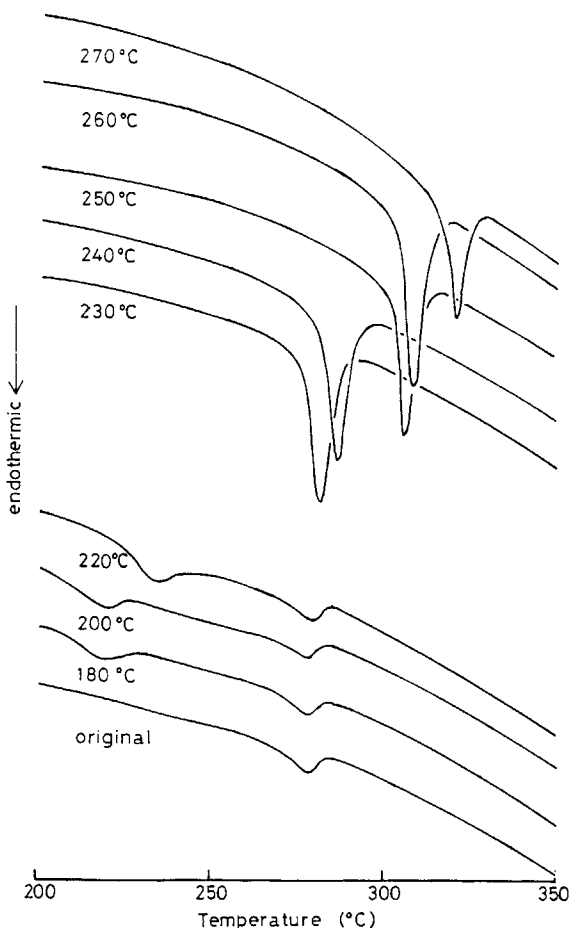


Figure 10 DSC heating curves of the extruded sheet before and after annealing at a temperature indicated in the figure for 6 h *in vacuo*.

that of annealed ones reported by Butzbach et al.⁶ Therefore, the phase melted at T_{m2} is believed to correspond to that crystallized slowly in the course of annealing at temperatures from 180 to 220°C in this work.

The ΔH_{m1} for the samples annealed at temperatures above 230°C decreases slightly with increasing annealing temperature, as shown in Figure 12. The heat of crystal-nematic melt transition is dependent not only upon annealing temperature, but also upon annealing time. Longer annealing periods are necessary for crystalline polymers to form enough ordered structures at higher annealing temperatures. Therefore, a slight decrease in ΔH_{m1} with increasing annealing temperature above 230°C may be attributed to a constant annealing period, 6 h, used in this work.

As illustrated in Figures 10–12, the thermal properties of the sheets annealed at temperatures below

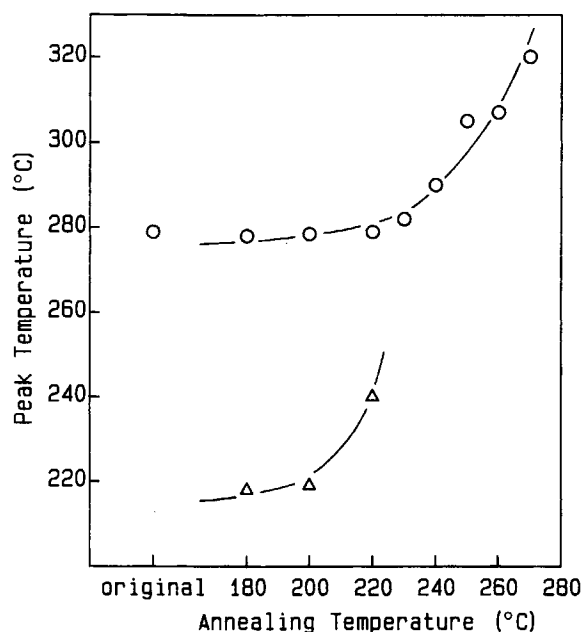


Figure 11 Endothermic peak temperatures of the annealed sheets as a function of annealing temperature. Circles and triangles represent T_{m1} and T_{m2} , respectively.

220°C are remarkably different from those of the sheets annealed at temperatures above 230°C. Figure 13 shows densities of the original and annealed sheets. As the density of all samples is in the range

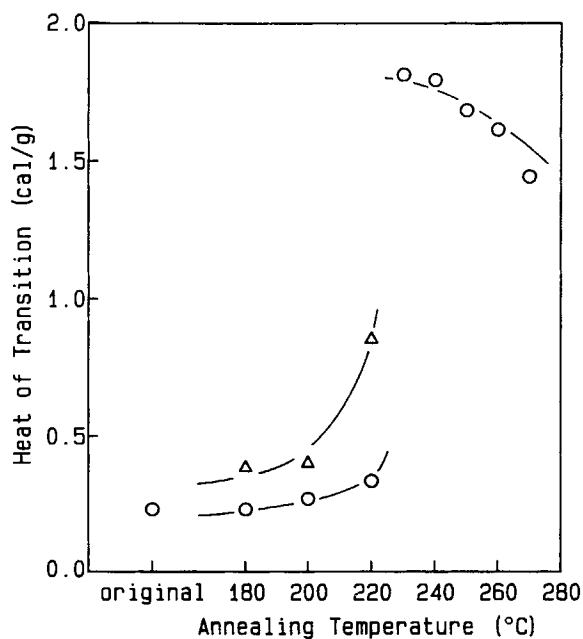


Figure 12 Heats of phase transitions of the annealed sheets as a function of annealing temperature. Circles and triangles represent ΔH_{m1} and ΔH_{m2} , respectively.

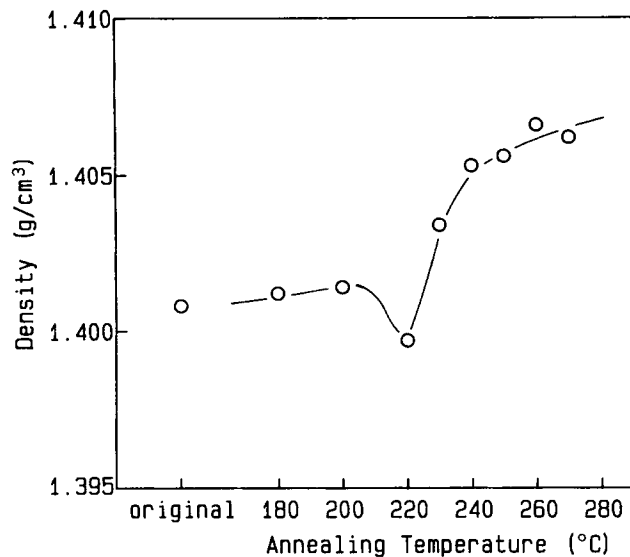


Figure 13 Variation of density of original and annealed sheets with annealing temperature.

of 1.399–1.407 g/cm³, the change in density with annealing temperature is very small. However, it should be noted that the density decreases slightly once for all at an annealing temperature of 220°C and then increases again at 230°C. As the ΔH_{m1} and ΔH_{m2} do not decrease at an annealing temperature of 220°C, the decrease in density does not mean a decrease in the degree of crystallinity of the annealed sheet. Probably, a structural change in an ordered phase begins at 220°C and then a new ordered phase is formed at 230°C, as described in Figure 8 in a previous paper.⁹ The wide-angle X-ray studies for the same annealed sheets as the ones used in this work have shown that the lateral packing of molecular chains of the HBA/HNA copolyester is transformed from a hexagonal packing to an orthorhombic one in the course of annealing above 230°C.

Mechanical and Structural Properties of Annealed Sheets

Dynamic viscoelastic behavior of the sheets before and after annealing is shown in Figure 14. As far as the dynamic viscoelastic properties of thermotropic HBA/HNA copolyesters have been reported up to now, the copolyesters have three relaxation peaks at least: a γ transition (the lowest temperature one) due to rotational motion of *p*-phenylene rings, a β transition due to rotation of 2,6-naphthylene rings, and an α transition (the highest temperature one) due to rotation of a large portion of rigid chains,

analogous to the glass transition of amorphous polymers.^{17,18} In this work, the γ , β , and α peaks are observed at about -50, 50, and 120°C, respectively (Fig. 14). The dynamic tensile modulus is retained to a certain extent at higher temperatures for the sheets annealed at temperatures above 230°C than that for the original sheet, whereas the value of the modulus does not increase strikingly with annealing. This result indicates that the heat resistance to mechanical properties of the sheet becomes higher with increasing annealing temperature.

The annealed sheets are also composed essentially of layered structures, exhibited in Figure 5, and the orientation of the sheets hardly alters before and after annealing. The bonds of layers, however, become faster with increasing annealing temperature because it is harder for skin and intermediate layers to tear off the annealed sheets by hand. Figure 15 shows a back surface of a skin layer of sheets before and after annealing. Ends of fibrils, caused by tearing the skin layer off the sheet, are observed. The ends of fibrils mentioned above were seen in the back surfaces of layered structures of annealed sheets more than in those of original sheets. The back surface of a skin layer of the annealed sheets appears to be more ductile than that of the original sheets, as shown in Figure 15. This result implies that fibrous structures in a sheet become longer with annealing. Inherent viscosities of the polymer are plotted against annealing temperature in Figure 16.

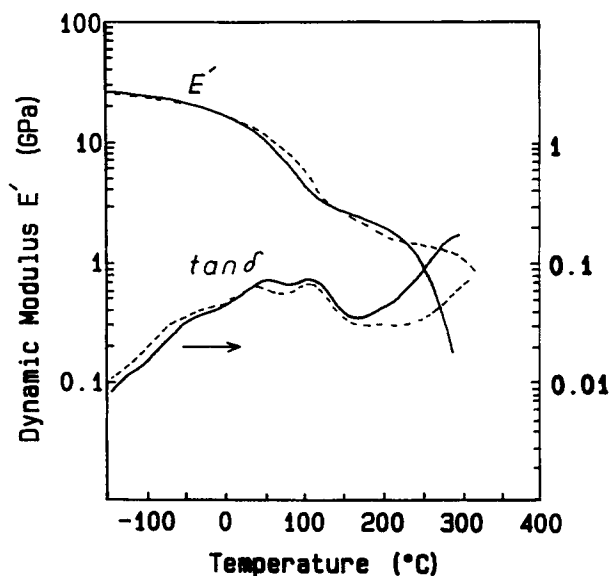


Figure 14 Viscoelastic curves of the extruded sheet (solid line) before and (dotted line) after annealing at 260°C for 6 h *in vacuo*.

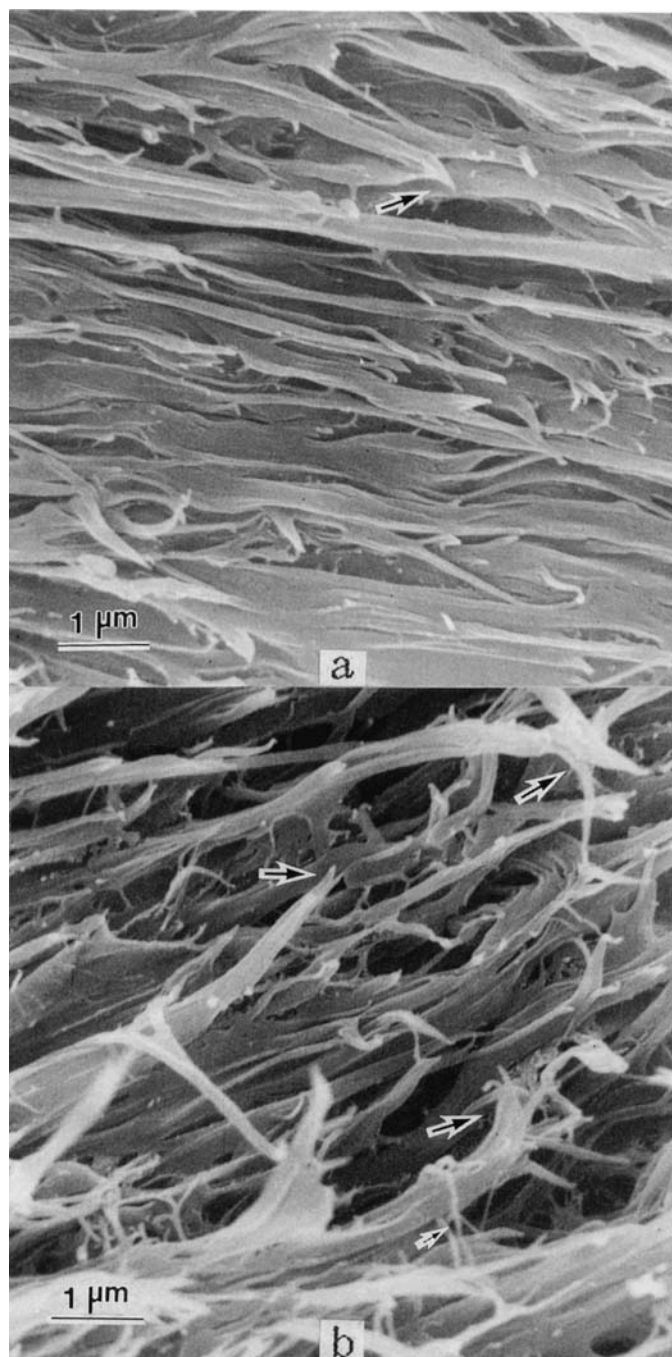


Figure 15 SEM of a back surface of a skin layer of the extruded sheet (a) before and (b) after annealing at 260°C for 6 h *in vacuo*. Arrows in the figure indicate the ends of fibrils.

The inherent viscosity increases with increasing annealing temperature. The sheets annealed at above 230°C were insoluble in a solvent used in this work. Probably, the results shown in Figures 15 and 16 suggest that annealing contributes to an increase

in the average molecular weight of the copolyester and that the average length of fibrous structures becomes longer with annealing. Consequently, the bonds of layered structures may be reinforced by annealing. A remarkable effect of annealing on the

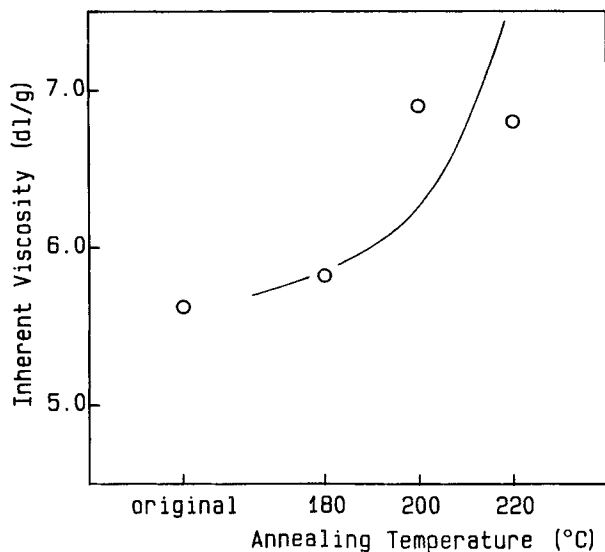


Figure 16 Inherent viscosity of annealed sheets of the thermotropic HBA/HNA copolyester as a function of annealing temperature.

tensile modulus has not been observed yet for molded parts of thermotropic copolyesters, but the tensile strength has often increased considerably with annealing.^{19,20} It is inferred from the results exhibited in Figures 15 and 16 that the tensile strength of the sheets obtained in this work is improved fairly by annealing.

CONCLUSIONS

Extruded sheets of a thermotropic HBA/HNA copolyester are composed of layered structures containing skin and core layers. A skin layer comprises fine fibrils oriented almost parallel to the extrusion direction. On the other hand, a core layer contains poorly oriented thicker fibrils or platelike structures in which fibrillation is not enough. The orientation function of sheets and their dynamic tensile modulus parallel to the extrusion direction increase with increasing draw-down ratio of the sheet. Annealing of the sheet caused the increases in the temperature and the heat of crystal-mesophase transition, the heat-resistance to the mechanical tensile properties, and the inherent viscosity of the polymer. Thermal behavior of the sheets annealed at above 230°C is different from that of the sheets annealed at below 220°C. A different ordered phase is believed to form

at annealing temperatures above 230°C. The layered structure and the orientation of sheets were hardly influenced by annealing. The bonds of layered structures in sheets are reinforced by annealing, though the dynamic tensile modulus parallel to the extrusion direction does not increase remarkably.

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