The Reversible Plasticization of the Aromatic Copolyester of Poly(ethylene Terephthalate) And 60 Mol % p-Acetoxybenzoic Acid with 1,1,1,3,3,3-Hexafluoro-2-Propanol*

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Synopsis

In recent mechanooptical studies with solution cast films of the aromatic copolyester of poly(ethylene terephthalate) and 60 mol % p-acetoxybenzoic acid from 1,1,1,3,3,3-hexafluoro-2-propanol, a volatile solvent with bp 59°C, we observed that the solvent plasticizes and affects considerably the stress–strain behavior of the copolyester at ambient temperature. Whereas a dry copolyester film is typically brittle failing at $\leq 10\%$ strain, a film containing 12% w/w 1,1,1,3,3,3-hexafluoro-2-propanol can be stretched readily to $\geq 300\%$ strain. When the solvent is removed by evaporation or by heating at an elevated temperature ($\geq 120°C$), the films lose their ductility, indicating that the plasticization is reversible.

INTRODUCTION

Semiflexible crystalline polymers is a class of polymers which has been developed in recent years by the conscious efforts of polymer scientists to overcome the intractability of rigid-rod polymers and obtain processable polymer compositions with high thermal and mechanical stability. In comparison to the rigid rod polymers, the semiflexible polymers have added flexibility which can be engineered by varying the fraction and the sequence distribution of the rigid or mesogenic segments and the flexible segments in their chain backbone. Such polymer compositions exhibit a liquid crystalline state on heating (thermotropic) and/or in solution (lyotropic) and have unusual rheological properties in comparison to the conventional flexible polymers.[1]

In our efforts to understand the structure of liquid crystalline polymers for establishing processing–structure and property relationships, we investigated the thermotropic copolyesters of poly(ethylene terephthalate) with 60 and 80 mol % p-acetoxybenzoic acid and the lyotropic solutions of cellulose der-

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ivatives in polar solvents.[2] In the studies with the aromatic copolyesters of poly(ethylene terephthalate) and 60 mol % p-acetoxybenzoic acid (PET/PHBA 40/60) we have examined also the rheooptical properties of concentrated solutions of this copolyester in 1,1,1,3,3,3-hexafluoro-2-propanol and the mechanooptical properties of its solution cast films. The latter exhibited some remarkable structural changes and mechanical properties when they were treated thermally and deformed by tensile drawing which associated with the plasticizing effect of the solvent on the polymer. Since the solvent could be removed completely by evaporation, the plasticization was temporary. In this report we discuss the plasticizing effect of hexafluoro-2-propanol on the optical, thermal, and mechanical properties of the aromatic copolyester of 40/60 PET/PHBA.

EXPERIMENTAL

Method of Preparation

The aromatic copolyester of poly(ethylene terephthalate) and 60 mol % p-acetoxybenzoic acid was provided kindly by Tennessee Eastman. The copolyester was dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol (Eastman Kodak) (~ 4% w/w) and was cast in the form of thin films (10–100 μm) on glass plates under a saturated hexafluoropropanol atmosphere.

CHARACTERIZATION

Optical observations were conducted with a Zeiss photo microscope using polarizing light. Thermal analysis data were obtained with a DuPont thermal analyzer (Model 1900). The amount of solvent retained in the cast films after solvent evaporation was determined from the weight loss of the films using a DuPont 951 thermogravimetric analysis balance. Infrared spectra were obtained with a Perkin-Elmer spectrophotometer, Model 283. Wide angle X-ray photographs of the variously treated samples of the aromatic copolyester were obtained with a flat plate camera using Ni-filtered CuK_α radiation. The tensile properties were determined with ribbon specimens 4 in. long × 0.2 in. wide at a strain rate of 8.3×10^{-3} s^{-1} using an Instron tensile testing machine. The surface morphology of the as cast films before and after tensile drawing was studied by scanning electron microscopy (SEM) using a Phillips electron microscope (SEM 505).

RESULTS

When the as received copolyester is viewed in the optical microscope with cross-polarized light at ambient temperature, it appears as a uniform phase [Fig. 1(a)], which on heating to 260°C transforms to a nematic mesophase [Fig. 1(b)]. Upon further heating to 290°C or higher, small spherical domains (~ 10 μm in diameter) appear in the nematic meshophase which remain visible up to 330°C [Fig. 1(c)]. The as cast films from the hexafluoropropanol solvent were transparent (Fig. 2) and became weakly birefringent on heating at 80°C. Upon heating to 130°C, the films showed stronger birefringence and
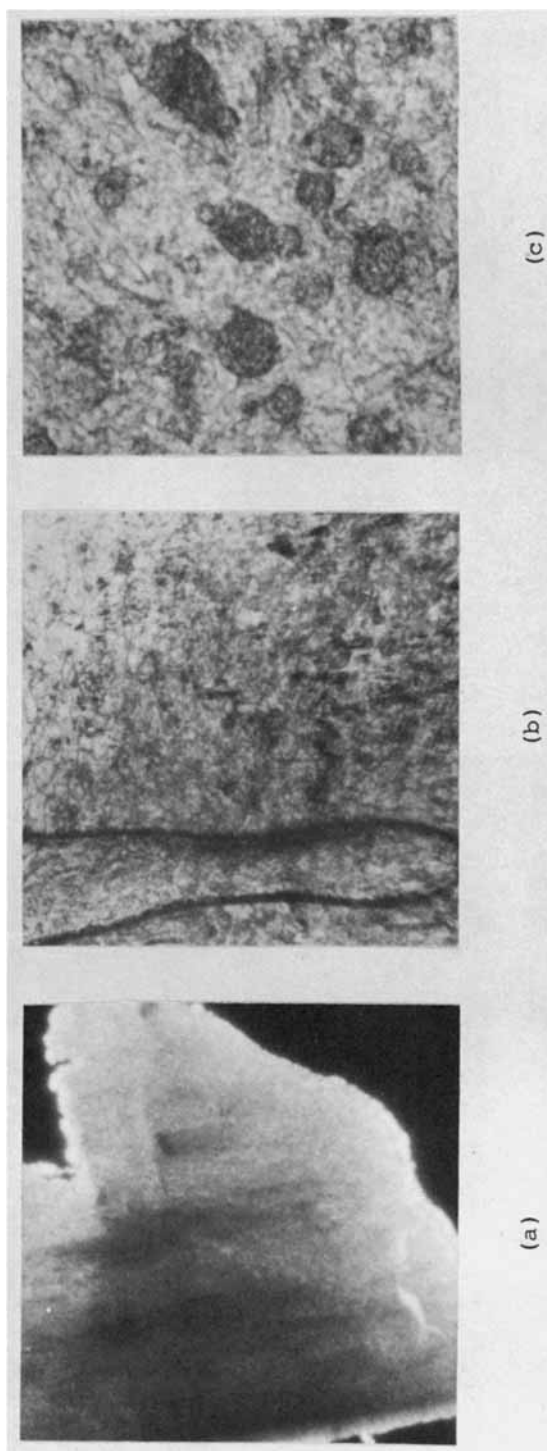
Fig. 1. Optical micrographs of the as received 40/60 copolyester at: (a) ambient temperature (50 ×), (b) 260°C (150 ×) (c) at 330°C (500 ×).

(b)

(a)

Fig. 2. Optical micrographs (125 ×) of the cast films of the 40/60 copolyester from hexafluoro-propanol at: (a) ambient; (b) 80°C.

Fig. 3.   Scanning electron micrographs of randomly distributed p-acetoxybenzoic and crystals in the cast films of 40/60 copolyester.

on further heating above 140°C exhibited liquid crystallinity until at ~ 330°C they began decomposing.

Randomly distributed crystals which appeared as bright spots (a few μm in size) were discernable in both the originally clear films and when the latter became opaque on heating. Scanning electron microscopy (Figure 3) showed that the bright spots were p-acetoxybenzoic lamellar crystals similar in size and structure with the observed crystals in microtomed specimens of the as received pellets.[3] Thermal analysis indicates that the as received copolyester shows three transitions: one at 63°C, another at 196°C, and yet another at 245°C, which is eliminated on second heating. The as cast film shows on first heating a transition at 48°C and a transition at 205°C. On second heating the lower transition is observed at 51°C, the higher transition is eliminated, and a new transition is observed at ~ 180°C [Fig. 4(a)]. As shown in Figure 4(b), a similar cast film after annealing at 130°C for 15 min showed in addition to the lower (~ 45°C) and the higher (~ 218°C) transitions, a transition at 148°C. On second heating the lower transition was observed at 53°C, the higher transition disappeared and an intermediate transition at ~ 190°C was observed as with the as cast film. When a cast film was drawn at ambient temperature, e.g., to 108% elongation, it showed no transition at 218°C; on second heating it showed the same behavior as the cast film after annealing [Fig. 4(c)]. A cast film after vacuum drying showed the same thermal behavior as the cast film after drawing; however, its lowest transition (53°C) was ~ 10°C higher. All samples showed on cooling a transition at ~ 150°C. The thermal analysis data are summarized in Table I.
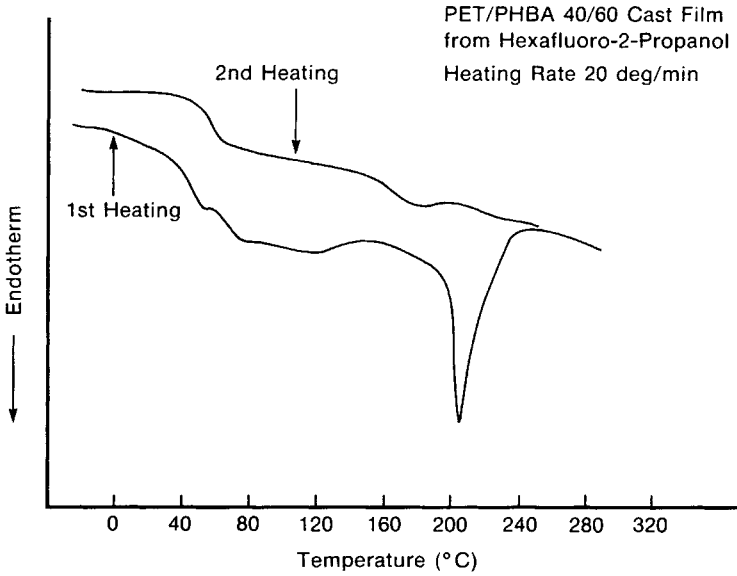
(a)
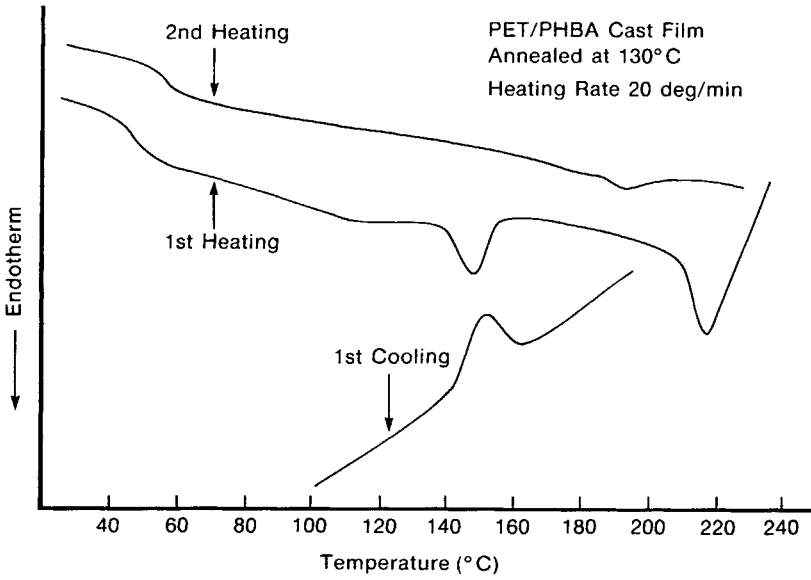
(b)

Fig. 4.   Differential thermal analysis curves on first and second heating of the cast PET/PHBA 40/60 copolyester from hexafluoro-2-propanol at 20°C/min heating rate: (a) cast film; (b) cast film after annealing at 130°C; (c) after tensile drawing at ambient temperature to 108% elongation.
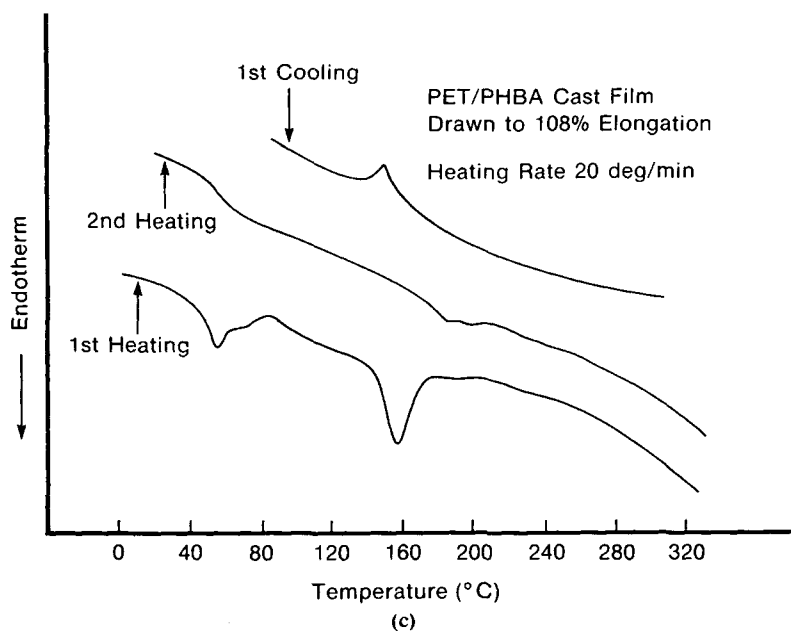
Fig. 4. (*Continued*).

Thermogravimetric analysis (TGA) shows that the as cast films lose ~ 12% of their weight on heating to ~ 210°C and ~ 65% when they decompose at 450–520°C (Fig. 5). A cast film after vacuum drying shows no weight loss prior to its decomposition, ~ 1% weight loss after tensile drawing set ambient temperature, and ~ 5% weight loss upon annealing at 130°C for 15 min. These TGA data are shown in Figure 6.

Infrared spectroscopy indicates that the as cast film of the 40/60 copolyester exhibits a broad absorption at 3600 cm^{-1}, which is significantly reduced when the film is annealed at 130°C for 15 min. (Fig. 7). This absorption is diminished further when the film was vacuum dried or drawn at ambient temperature. The effect of thermal treatment on the stress–strain behavior of a cast 40/60 copolyester film is shown in Figure 8. The cast film was ductile and could be drawn at ambient temperature to ~ 400% elongation. The film

TABLE I
Thermal Analysis Data with PET/PHBA 40/60 Copolyester after Different Treatments

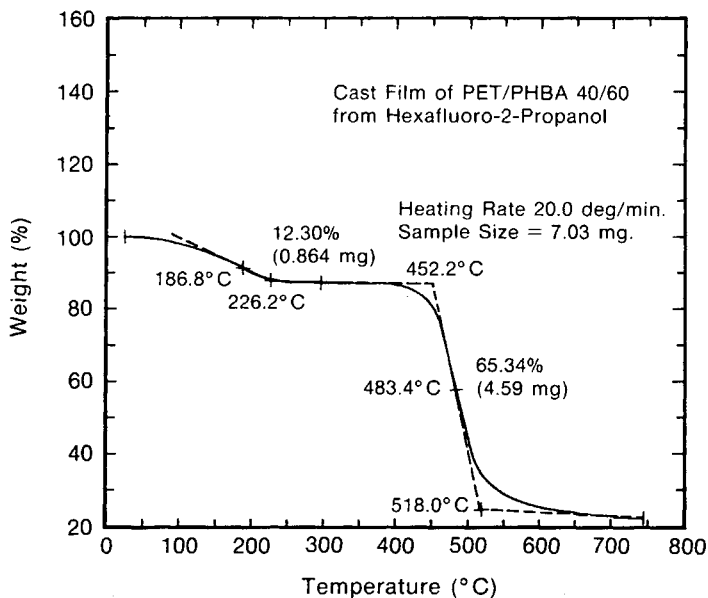| Sample	Temperature transitions (°C)		
	1st Heating	1st Cooling	2nd Heating
As received pellets	63,196,245	148	59,192
As cast film	48,205	151	51,175–180
Cast film annealed at 130°C for 0.5 h	45,148,218	151	53,191
Cast film drawn at RT to 108% elongation	41,155,192	155	52,185–190
Cast film after vacuum drying	53,151,193	151	53,196

Fig. 5. Thermogravimetric analysis of the cast film of PET/PHBA 40/60 copolyester from hexafluoro-2-propanol.

deformation in the early, draw stage, i.e., before necking, was nonuniform as was assessed by the development of randomly distributed transparent and opaque regions. After necking, the film became completely opaque. The film remained ductile when the tensile testing was performed at 80°C. However, the ductility was lost when the polymer was heated at 110°C and became very brittle when it was annealed at 130°C for 15 min. The X-ray diffraction
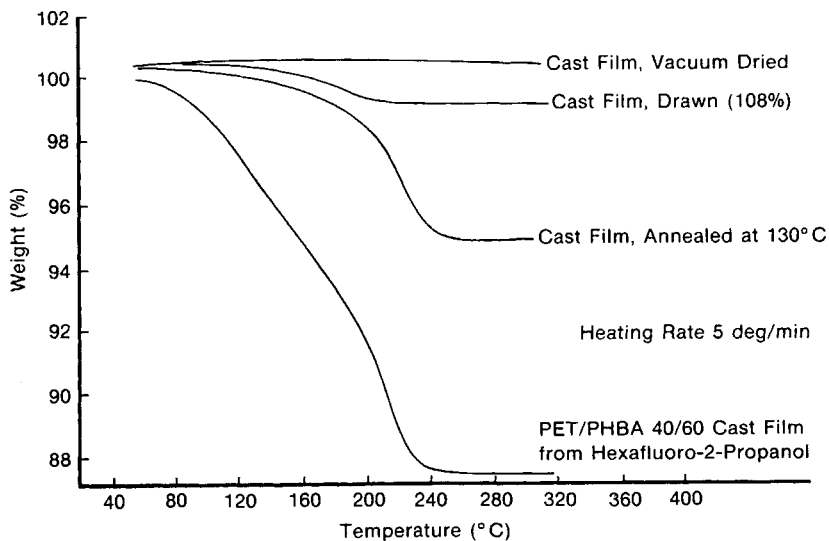

Fig. 6. Thermogravimetric analysis of the cast 40/60 copolyester after different processing conditions.
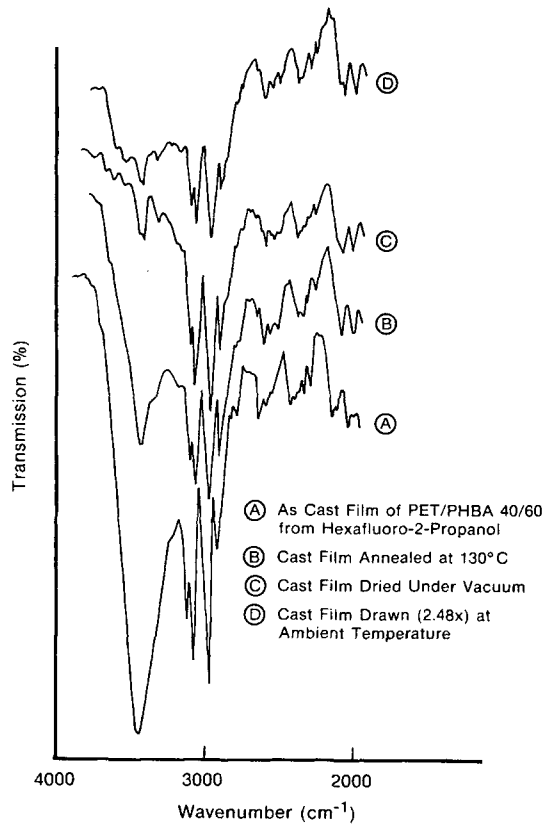
Fig. 7.   Infrared spectrogram of the cast film of PET/PHBA 40/60 copolyester from hexafluoro-2-propanol after different processing conditions: (a) as cast; (b) cast film annealed at 130°C; (c) cast film dried under vacuum; (d) cast film drawn (2.48 ×) at ambient temperature.
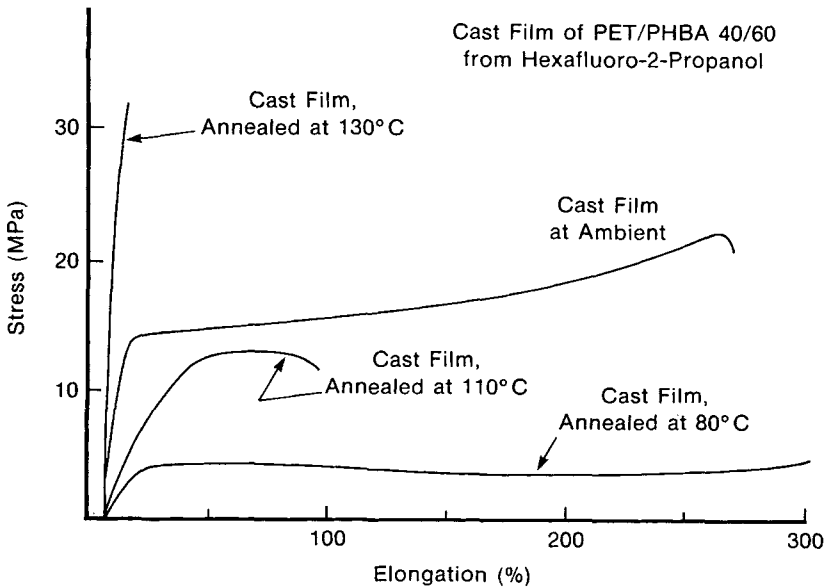

Fig. 8.   The effect of thermal treatment on the stress-strain behavior of the cast film of PET/PHBA 40/60 copolyester from hexafluoro-2-propanol.

As Cast Film   Cast Film, Annealed   Cast film, Vacuum Dried
                          at 130°C

As Cast Film, Drawn (2.7x)   As Cast Film, Drawn (2.7x)
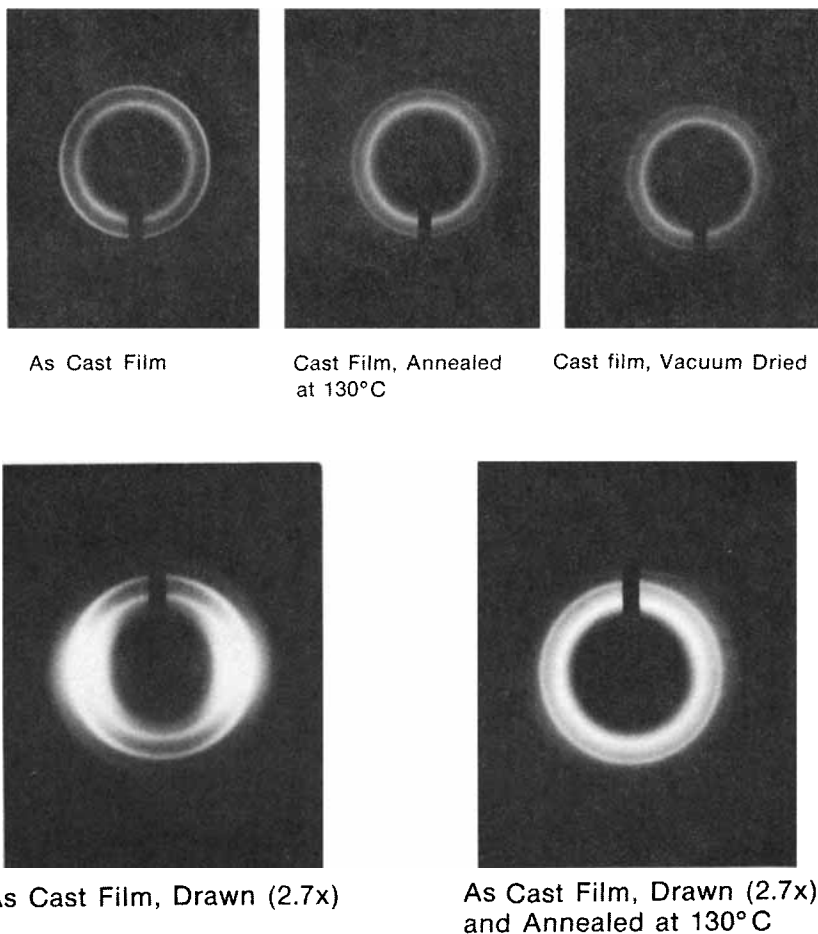   and Annealed at 130°C

Fig. 9. X-ray diffraction patterns of cast 40/60 copolyester after different treatments and processing conditions.

patterns in Figure 9 indicate that the cast films are crystalline and independent of the sample treatment. It is interesting that: (a) even the transparent films are partially crystalline and (b) the drawn samples show amorphous but no crystalline orientation which is lost after annealing.

DISCUSSION

Two issues must be addressed in the discussion of these experimental results. The transparency of the as cast films and the remarkable change of their optical and mechanical properties upon heating. The as received aromatic copolyester 40/60 is opaque and, as shown in Figure 1, exhibits a thermotropic behavior on heating. The thermotropic melt forms an opaque supercooled phase on cooling to ambient temperature and exhibits a small degree of crystallinity. Rheo-optical and electron microscopy studies with both this copolyester (40/60) and the (20/80) composition indicate that the observed crystallinity associates with rich in PHBA domains[3,4]; the amount of these

domains must be appreciable as suggested by the observation of the two glass transition temperatures with samples of both the cast films and the as received 40/60 copolyester.[5] The fraction of the adventitious PHBA lamellar crystals in the cast films of the 40/60 copolyester (Fig. 3), which have been observed also with the 20/80 copolyester up to ~ 500°C,[6] is too small to affect their optical and thermal properties. The depression of the lower T_g and the presence of the nonreversible endotherm at 205–215°C, which associates with the release of the solvent as documented also by the TGA data, indicate that the cast films were plasticized. At present, we believe that the plasticization occurs via a hydrogen bonding interaction between the carbonyl groups on the chain backbone with the hydroxyl hydrogen of the solvent. This type of interaction is suggested by the pronounced IR absorption band at 3600 cm^{-1} of the —OH group of the solvent which diminished as the solvent was removed from the film by annealing or vacuum drying. Although, some solvent (~ 6% w/w/) is released from the film during annealing, it requires drying under vacuum or some significant molecular motion, as in tensile drawing, to remove all the solvent from the polymer. From the X-ray results, it appears that the solvent plasticizes selectively domains which are nonrich in PHBA and which become transparent as they lose their liquid crystalline character. This selective plasticizing process is documented by the fact that only amorphous orientation is observed during the drawing process which is lost after annealing. The PHBA crystals and the PHBA-rich domains apparently were not plasticized and remained undeformed upon drawing, as shown in the SEM photomicrograph in Figure 10.

Fig. 10.   Scanning electron micrograph of a cast film of PET/PHBA 40/60 copolyester after tensile drawing to 108% elongation.

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In addition to the T_g depression and the remarkable change in the optical and thermal properties, the plasticization effect is documented further by the stress–strain behavior of the as cast films at different temperatures. The remarkable ductility of the cast films at room temperature associates with the presence of the solvent ($\sim$ 12% w/w/) which interacts with the polymer by a stable hydrogen bonding at this temperature. As the tensile testing temperature was raised, the solvent evaporated more readily during the drawing process, and the film showed reduced ductility. The ductility decreased further above 80°C, i.e, when the films became weakly birefringent. As shown in Figure 8, the film became brittle when it was annealed at 130°C, a process which involved the removal of $\sim$ 6% w/w/ of solvent from the polymer. The change from the ductile to the brittle behavior with increasing temperature is in contrast to the well-known dependence of the stress–strain behavior of polymers on temperature and demonstrates clearly the reversibility of the plasticization process.

The possibility of plasticizing a polymer with a volatile solvent which may interact temporarily with the polymer and be removed either during or after its solid state processing is advantageous because it allows the plasticization of the polymer to occur through a process in which the final product is freed from the plasticizer. The process demonstrated originally with the plasticization of polyamides using anhydrous ammonia,[7] which plasticized reversibly only the amorphous component, has been explored more recently using iodine to plasticize both the crystalline and amorphous phases in this class of polymers.[8] The present study represents the first reversible plasticization in a polymer which is known to exhibit liquid crystalline behavior and lose its liquid crystalline character when plasticized.

CONCLUSION

We have investigated the plasticization of the aromatic copolyester PET/PHBA 40/60 with 1,1,1,3,3,3-hexafluoro-2-propanol. We observed that this solvent plasticizes reversibly the polymer by temporary hydrogen bonding interaction with the carbonyl groups of adjacent molecular chains. The plasticizing effect on the aromatic copolyester is documented by the depression of its physical and mechanical properties, X-ray analysis, and the loss of its liquid crystalline character.

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