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Mechanical properties of as-extruded and heat-treated poly-(*p*-phenylene benzobisthiazole) films

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The stress–strain behaviour and morphological features of PBT films before and after heat treatment are reported. PBT films possess extraordinary mechanical properties comparable to those of the fibres. A non-uniform residual stress distribution is proposed to account for the elastic–plastic behaviour of as-extruded films and the subsequent extensive fibrillization during tensile testing or tension heat treatment. Tension heat treatment results in significant axial modulus and tensile strength increase by improving overall sample orientation and lateral crystallite size with concomitant straightening of buckled regions in the film.

1. Introduction

Poly-(*p*-phenylene benzobisthiazole) (PBT) belongs to a new class of rigid rod, extended chain, aromatic heterocyclic polymers. The interest in these types of materials is rapidly increasing as they have become important in the field of reinforced composites as a high-strength, high-modulus, environmentally resistant structural material.

The best samples of PBT fibres currently exhibit tensile strength and moduli as high as 3.3 and 330 GPa, respectively, and specific moduli and strength – 8.7 and 5.8 times that of steel. PBT fibres are found to be very thermostable (up to 375° C in air and up to 550 to 600° C in N_2 atmosphere) [1]. They are resistant to harsh environments and retain over 50% of their modulus and strength after three days in nitric and sulphuric acids [2].

The structure and mechanical properties of PBT fibres have been recently discussed in several papers [1–4]. It is expected that PBT films will exhibit mechanical properties comparable to those of conventional unidirectional fibre composites but with much higher thermo-oxidative resistance and without the need for fibre reinforcement. The stress–strain behaviour and the structure of PBT films, as-extruded and after heat treatment, are the topics of this paper.

2. Experimental details

The films used in this study were produced by Dr E. Chenevey of the Celanese Research Corporation. The technique involves extrusion of a polyphosphoric acid (PPA)–PBT solution into a water coagulation bath using a flat die with a variable air gap length. Samples were 4 to 9 mm wide with thickness ranging from 5 to 10 μm. The polymer had an intrinsic viscosity of 14 dl g^{-1} in methane sulphonic acid at 25° C.

After coagulation in water, the films were further washed in water and dried without constraint at various temperatures. Heat treatment was done under tension at 525° C with 2 to 3.5% applied stretch in order to increase the level of mechanical properties. The fine structure of PBT film was recently studied and discussed in terms of the molecular orientation and lattice order which is sensitive to the conditions of heat treatment [5, 6].

Tensile tests of the as-extruded and heat-treated films were performed on a Toyo Tensilon model UTM-11 machine at a strain rate of 0.8% min^{-1} and on an Instron testing machine at a strain rate of 4.0% min^{-1}. The system compliances were determined experimentally for both machines and grip systems. The average data for Young's modulus,

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stress at break and elongation at break were found to be in very good agreement for samples tested on the Toyo or Instron. Mounting and testing of these films is difficult as they split easily, especially after heat treatment. Typically, the gauge length was 25 mm, but different lengths were used to determine the influence of gauge length on the mechanical properties. All specimens were centre-line mounted on special slotted tabs using an epoxy glue. The tabs were gripped so that the test specimens were aligned axially in the jaws of the constant speed movable-crosshead test machines.

The morphological features of the films were determined by light optical and electron optical microscopy and wide-angle X-ray diffraction. Polarized light microscopy was carried out on a Leitz microscope. Scanning electron microscopy (SEM) was done using an ETEC Autoscan operated at 20 kV. Film samples for SEM observation were first sputter-coated with a 35 nm layer of gold in a Polaron E5100 coating unit to minimize charging problems. PBT materials exhibit good electron beam radiation resistance [7]. Flat film X-ray photographs of stacks of ten films were recorded on a Statton camera.

3. Results and discussion

3.1. Stress–strain properties

A small increase in modulus (15 to 30%) accompanied by lower elongation without significant change in strength occurs for films dried in the absence of tension at 167 and 305° C when compared to lower (117° C) temperature drying. Moreover, a dramatic improvement of mechanical properties was achieved by tension heat treatment at 525° C of previously dried films.

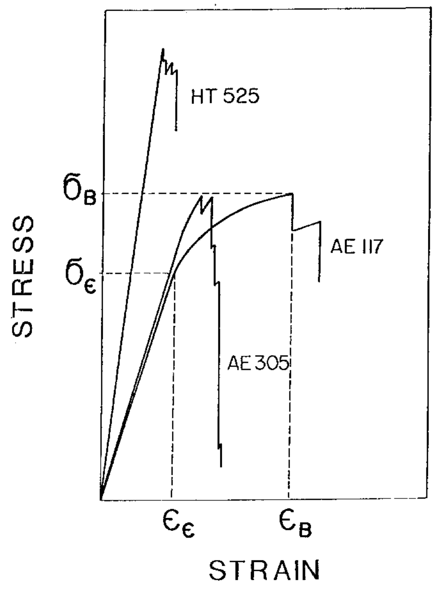

Figure 1 Stress–strain behaviour of as-extruded (AE) and heat-treated (HT) PBT films.

As in the case of fibres, the as-extruded (AE) PBT film samples exhibit non-linear stress–strain behaviour (Fig. 1). The amount of apparent "plastic" deformation decreases with higher temperatures of drying. All tension heat-treated samples exhibited linear stress–strain behaviour without any region of "plastic" deformation, i.e. the elastic stress limit and stress at break were essentially equal. The multigraded shape of the stress–strain curves is due to non-cooperative failure of the elements of the film during fracture. The data reported in Table I for stress and elongation at failure (σ_B and ϵ_B) correspond to the highest value of the breaking force. Applied strains above 2% during heat treatment did not further improve the properties of films (Fig. 2). Although the average values of modulus and strength of PBT films are impressive, considerable property variability is present due to macro-imperfections in the material such as bubble-like depressions on the surface and cavities in the films (see arrowed regions in Figs. 3a and b). The elastic limits (σ_ϵ and ϵ_ϵ) are more reproducible and hence more reliable characteristics of material properties.

TABLE I Mechanical properties of PBT film

Temperature (° C)		Young's modulus	Stress at break	Elongation at break	Elastic limits	
Drying	Heat treatment	E (GPa)	σ_B (GPa)	ϵ_B (%)	σ_ϵ (GPa)	ϵ_ϵ (%)
117	–	132 ± 13	1.23 ± 0.2	2.5 ± 0.5	0.83 ± 0.1	0.63 ± 0.03
167	–	155 ± 4	1.23 ± 0.2	1.5 ± 0.4	0.87 ± 0.1	0.56 ± 0.07
305	–	171 ± 23	1.27 ± 0.3	1.0 ± 0.2	0.72 ± 0.1	0.42 ± 0.04
117	525	238 ± 6	1.50 ± 0.2	1.0 ± 0.2	1.50 ± 0.2	0.64 ± 0.06
305	525	238 ± 18	1.51 ± 0.2	1.0 ± 0.2	1.51 ± 0.2	0.63 ± 0.14

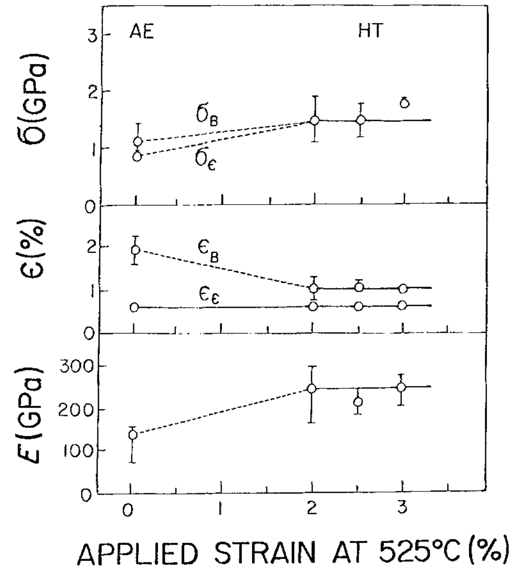

Figure 2 Variation of room-temperature mechanical properties for PBT films heat treated at 525° C with various levels of applied strain.

3.2. Cyclic loading

Loading–unloading experiments with increasing levels of strain on the as-extruded films demonstrate that the first part of the deformation is completely elastic and that increasing plastic deformation results in appreciable work hardening (see Fig. 4). As can also be seen from Fig. 4, the as-extruded films possess permanent memory and can exhibit linear elastic behaviour after sufficient work hardening. Cyclic loading–unloading at constant maximum force reveals that the initial material hysteresis decreases with number of cycles and eventually reaches zero, i.e. after considerable cyclic conditioning, the as-extruded films behave elastically (see Fig. 5). During this conditioning the modulus can increase by up to 1.5 times that of the initial sample. Consequently, the as-extruded film can be stiffened by stretching even at room temperature.

These observations suggest that the as-extruded films contain some irregularities of structure which can be changed by the application of stress and/or high temperature. Previous work on PBT fibres demonstrated that residual stress and buckled fibre elements accounted for rather similar elastic–plastic behaviour in the as-spun fibres [3].

The residual stress and resultant buckling of portions of the fibre were caused by the high shrinkage forces developed during fibre coagulation and drying. The internal stress model attributes the departure from linear elastic behaviour to the fracture of the fibrillar elements which experience the highest tensile stress as a result of the applied plus initial internal (residual) stress. The plastic part of the stress–strain curve results from the consecutive fracture of overstressed elements in the fibre. In addition, because the structural elements do not act cooperatively, the overall fibre strength is less than that of an identical fibre without residual stress. Work hardening occurs during plastic deformation as initially

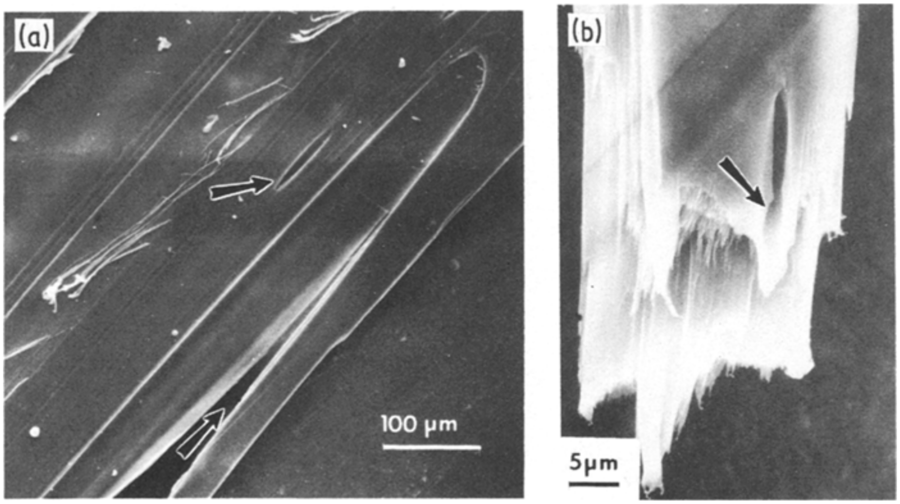

Figure 3 Scanning electron micrographs of PBT film. (a) Low magnification micrograph of film surface showing longitudinal splits and aligned bubble-like depressions on film surface; (b) higher magnification of tensile fracture. Arrows point to voids.

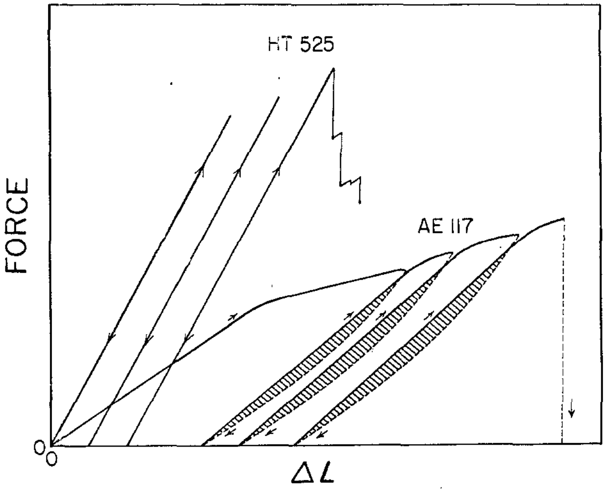

Figure 4 Loading–unloading force–elongation curves for as-extruded and tension heat-treated PBT films. Successive loading curves for the HT525 sample have been horizontally shifted for clarity.

buckled elements are straightened. During unloading the friction forces between elements are sufficient to prevent sliding between them. The elastic modulus of unloading and reloading will then correspond to the effective modulus of a structure with (more) continuous elements.

The existence of structural irregularities in PBT films is indicated by transmitted polarized light optical and scanning electron microscopy. Fig. 6 is a pair of optical micrographs of an as-extruded film. Well aligned, elliptical voids are evident when the film is oriented at 45° to the polarizer. When the film is oriented at 0° to the polarizer, the regions of misorientation around the voids are apparent. SEM shows the as-extruded film to have a rough, wavy surface texture when viewed at a grazing angle to the surface (see Figs. 3 and 7a). When PBT film is plastically deformed it becomes noticeably more shiny to the eye and SEM micrographs of tensioned heat-treated or cyclically deformed as-extruded films have a much smoother appearing surface (see Fig. 7b).

3.3. Tensile fracture

While the high axial orientation of PBT films leads to very good axial mechanical properties, this same high orientation leads to poor properties in the transverse direction. During tensile testing, longitudinal splits grow in number and in size with increasing stress. Cracks initiate from the elongated voids (see arrow Fig. 3a) splitting the film into smaller ribbons or strips. This splitting effect may be caused by the non-uniform stress distribution in the initially wavy film. Successive fracture of individual strips occurs as reflected in the multigraded shape of the stress–strain curve (recall Fig. 1).

Testing of the tension heat-treated specimens reveals a large number of finer cross-section strips (see Figs. 8c and d). Apparently strong fibrilliza-

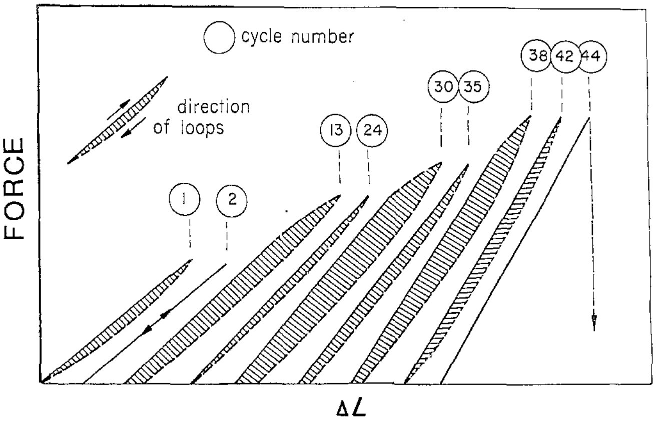

Figure 5 Force–elongation curves for an as-extruded film dried at 117° C. The numbers within each circle indicate that loading cycle. Successive curves are horizontally shifted for clarity.

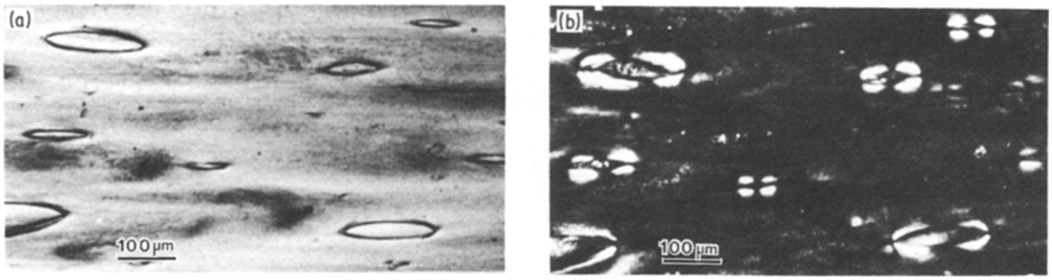

Figure 6 Polarized light micrographs of as-extruded PBT film. (a) Voids elongated along extrusion direction evident in film in transmitted light 45° to polarizer; (b) Regions of misorientation revealed about voids for film orientation at 0° to polarizer.

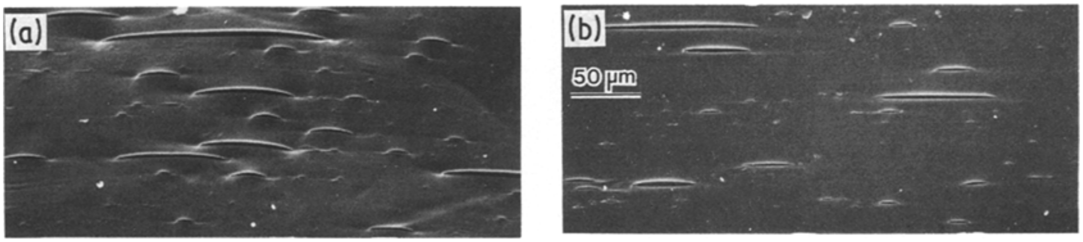

Figure 7 Scanning electron micrographs of PBT films viewed at grazing angle to film surface. (a) As-extruded film with wavy textured surface; (b) film surface after cyclic deformation (35 cycles) appears smoother.

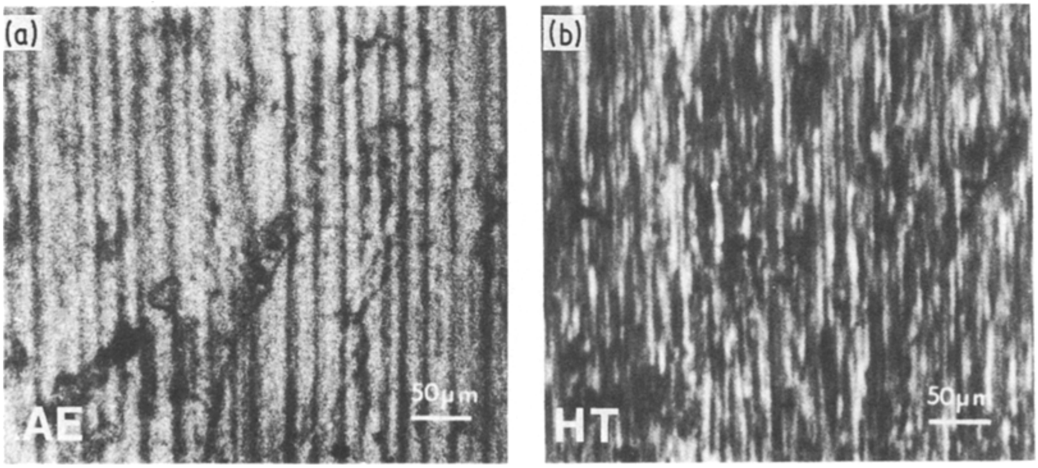

Figure 8 Optical micrographs of PBT films. (a) and (b) Acid etched AE and HT films; (c) and (d) tensile fractured AE and HT specimens.

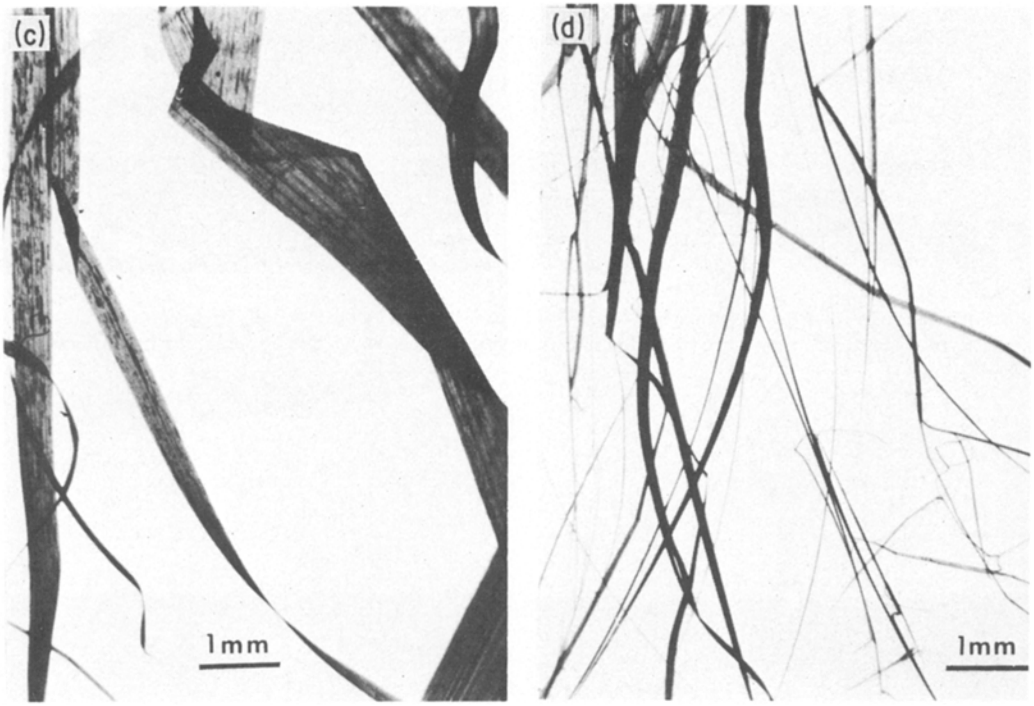

Figure 8 Continued.

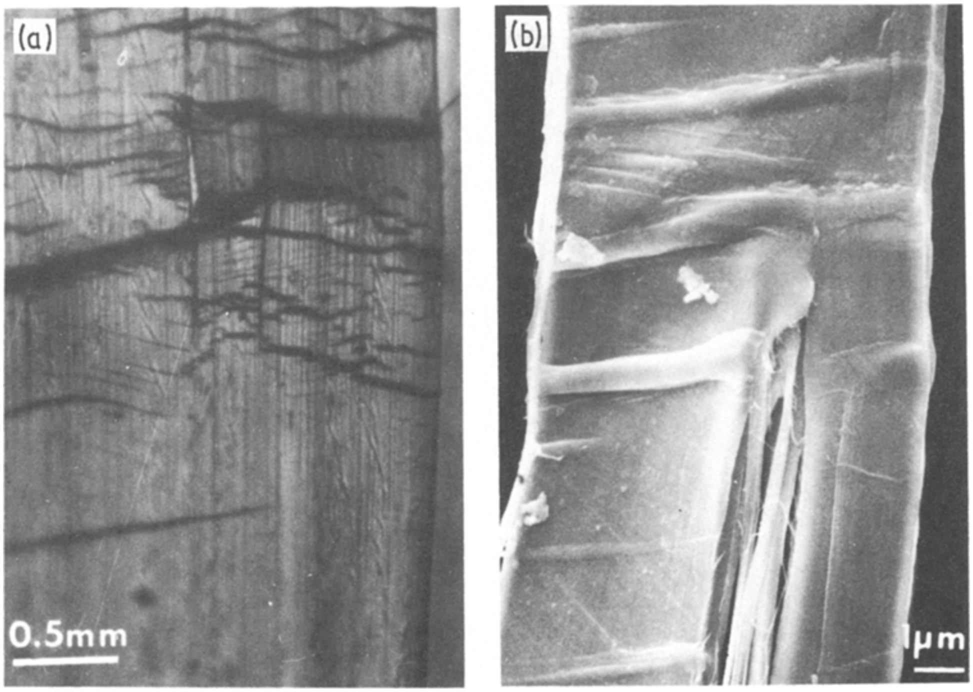

Figure 9 Morphology of fractured PBT films. (a) Optical micrograph showing transverse bands; (b) SEM micrograph showing transverse bands and axial splitting.

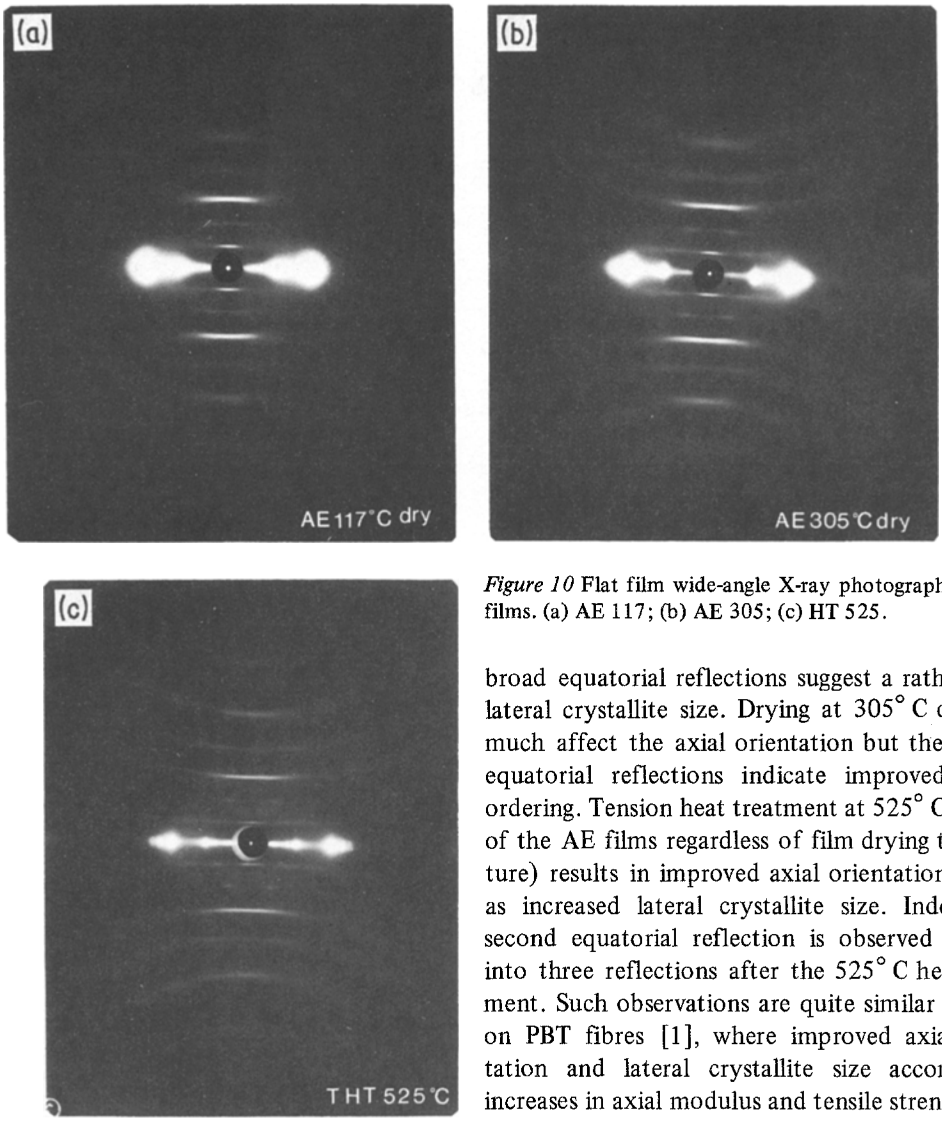

Figure 10 Flat film wide-angle X-ray photographs of PBT films. (a) AE 117; (b) AE 305; (c) HT 525.

tion of the film structure must occur during the heat-treatment process. This is suggested by the observation of the PPA–H_2O etched surfaces of AE and HT ribbons (see Figs. 8a and b). A high shock force is generated during sample rupture and causes gross buckling of the individual ribbons after failure. These features appear as transverse dark bands in transmitted polarized light micrographs (Fig. 9a) and as transverse surface pleats in SEM micrographs (Fig. 9b).

3.4. Microstructural changes during heat treatment

Fig. 10 displays flat film X-ray patterns of as-extruded and tensioned heat-treated films. The AE-117 film displays high axial orientation but the broad equatorial reflections suggest a rather small lateral crystallite size. Drying at 305° C does not much affect the axial orientation but the sharper equatorial reflections indicate improved lateral ordering. Tension heat treatment at 525° C (of any of the AE films regardless of film drying temperature) results in improved axial orientation as well as increased lateral crystallite size. Indeed, the second equatorial reflection is observed to split into three reflections after the 525° C heat treatment. Such observations are quite similar to those on PBT fibres [1], where improved axial orientation and lateral crystallite size accompanied increases in axial modulus and tensile strength.

The AE and HT films were also compared with respect to solubility in phosphoric acid/water solution. After immersion for 15 min at 25° C in a 2.5/1 by volume mixture of H_3PO_4 and H_2O, the AE117 film was considerably swollen while the HT film was not noticeably changed. After 2 h, the AE film was completely dissolved and the HT525 film was swollen about 500% in thickness while shrinking about 30% in length. No further changes occur for the heat-treated film for immersion of up to 2 weeks. The resistance to dissolution caused by the heat-treatment process may be attributable to the development of local regions of highly-ordered chains and/or possible development of chemical cross-links between chains due to reaction involving residual acid or N_2 during the high-temperature heat treatment.

4. Conclusions

Tension heat-treated PBT films feature extraordinary mechanical properties. They possess high modulus (240 GPa) and high strength (1.5 GPa) comparable to values of tension heat-treated PBT fibres. A non-uniform residual stress distribution is due to shrinkage forces during film coagulation and drying and is proposed to account for the elastic–plastic behaviour of as-extruded films and the subsequent extensive fibrillization during tensile testing or tensioned heat treatment. A higher temperature of drying increases axial modulus without any change in strength by relief of residual stress. Plastic deformation at room temperature can also increase axial modulus by a work-hardening mechanism related to the straightening of buckled elements. Tension heat treatment results in significant improvement of both axial modulus and tensile strength by improving overall sample orientation and lateral crystallite size with concomitant straightening of buckled regions in the film. On the basis of swelling/dissolution studies in H_3PO_4/H_2O mixtures, it is suggested that chemical cross-linking of PBT may occur during high temperature heat treatment.

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