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Temperature and strain rate dependence of the deformation behaviour of poly(*para*phenylene benzobisthiazole)

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The mechanical properties of PBT films feature an interesting temperature and strain-rate dependence. The elastic modulus and yield behaviour have been studied over a wide temperature range from 30 to 650° C. The onset of a structural reorganization is observed at about 300° C. The dependence of yield stress on strain rate at different temperatures was examined in terms of the Eyring theory of an activated rate process. It was found that the stress activation volume varies with temperature. The overall elastic–plastic behaviour as a function of temperature and strain rate was interpreted in terms of a previously suggested model that incorporates residual stresses in a rigid rod-like polymer. Enhancement of modulus was also observed due to deformation of the films under elevated temperatures, where better molecular orientation and lateral ordering are achieved.

1. Introduction

Poly(p-phenylene benzobisthiazole) (PBT) is a wholly aromatic, extended chain, rigid rod-like polymer. It can be processed into fibres and thin films of high modulus, high strength and good thermal stability [1–4]. The structure of PBT has been reported as well-aligned rods packed in a two-dimensional net with translational displacements along the chain axis [5]. The morphological features and mechanical properties of PBT films before and after heat treatment are discussed in a recent communication [6], where the elastic–plastic behaviour of the material is accounted for by a nonuniform residual stress-distribution. The tension heat treatment enhances greatly the axial modulus and strength. Straightening of buckled macrostructure regions was observed by scanning electron microscopy. A more detailed model incorporating the residual stresses introduced during coagulation of a rod-like structure has been developed to interpret the effectiveness of tension heat treatment in case of PBT fibres [4]. The overall sample orientation improvement and lateral crystallite size increase from tensioned heat treatment has been detected by means of WAXS in both fibres and films [6–9].

The primary emphasis of previous studies was focused on the deformation behaviour and morphological aspects evaluated before and after heat treatment. Limited data are available on the mechanical properties of PBT fibres, measured at high temperatures. An interest arose to follow the mechanical properties and failure mechanism as a function of temperature and strain rate. Tensile deformation as a material response to temperature and loading rate is of great theoretical and technical interest.

The experimental part of the work reported below includes the following: determination of the temperature dependence of tensile modulus, yield stress and ultimate properties of PBT film by means of short-term isothermal test evaluation of the effect of annealing on the modulus changes on the return cycle (cooling); measurements of the yield stress as a function of strain rate at different temperatures and thermal stress analysis for the samples subjected to successive heating. The data obtained indicate that as-extruded PBT films undergo a structural transition in the temperature range close to 300° C which changes the character of the tensile and stress-relaxation behaviour.

2. Experimental details

2.1. Material

The PBT films used in this study were obtained from Celanese Research Company, Summit, New Jersey. Films were extruded through a dry-jet wet spin apparatus from PBT solution in polyphosphoric acid (9.2% solids) into a water coagulation bath. Deionized water was used as a washing bath. The measured denier was 416 and final width of the air dried (without tension applied) samples was 4.5 mm.

2.2. Tensile tests

The tensile tests were performed on a Instron Testing Machine with strain rates from 0.04×10^{-3} to $8.33 \times 10^{-3}\,\text{sec}^{-1}$ and over a range of temperature from 30 to 675° C in nitrogen atmosphere. Test samples of gauge length 200 mm were aligned inside a tubular oven parallel to the axis of the jaws of an Instron machine. Free ends of the samples mounted on the paper tabs

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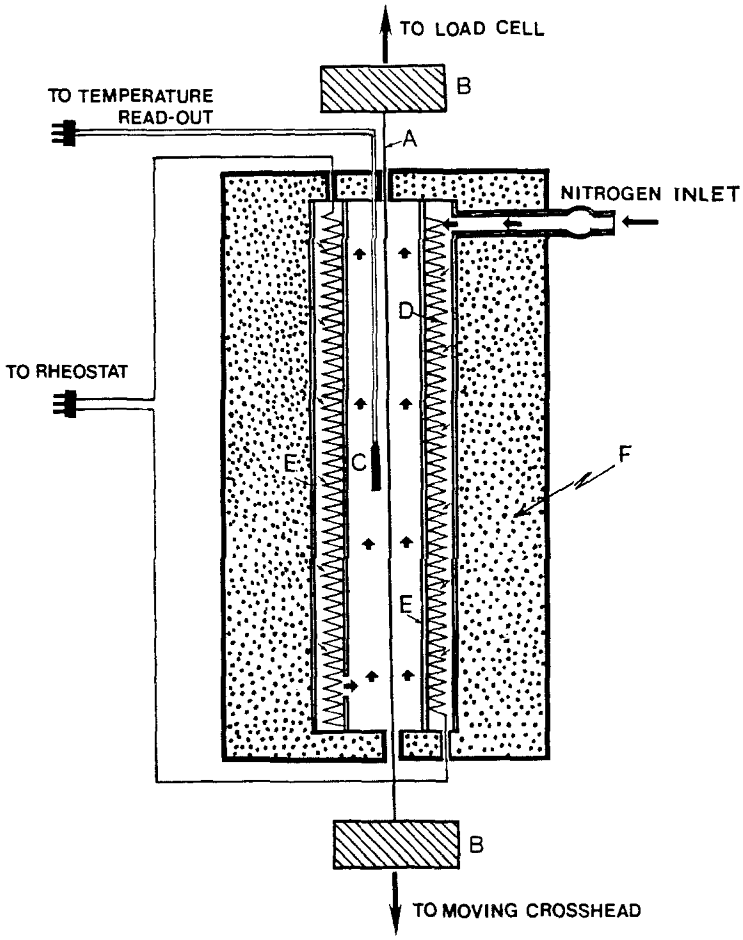

Figure 1 Schematic illustration of the test arrangement; (A) sample; (B) clamps of the testing machine; (C) thermocouple; (D) heating wire; (E) thermoresistant glass; (F) insulation.

were gripped outside of the oven. Room temperature air was blown on to the jaws in order to minimize the machine compliance due to heating. Samples were conditioned for 5 min at each temperature prior to each test.

2.3. Oven construction

Fig. 1 shows a schematic diagram of the oven used as environmental chamber. It consists of two coaxial silica cylinders. Heating wires were wrapped on the surface of the inner cylinder. The outer cylinder was insulated with asbestos and covered with a metal jacket. The oven was provided with two gas inlets. Nitrogen gas was purged into the upper inlet at a rate of 4 litre min^{-1} during the heating and 20 litre min^{-1} when cooling was required. The gas circulates around the wiring in the space between two tubes and enters the specimen chamber through the lower inlet in the inner cylinder.

Nitrogen gas circulation surpresses the oxidation process of the polymer and regulates the heating and cooling of specimen chamber. The upper and lower ends of the oven were sealed with asbestos covers such that only two small ports were left to allow sample insertion. A removable flattened metal tube was used to avoid sample damage during this insertion. A platinum RTD thermocouple was placed near the sample surface in the middle of the oven. Temperature control and regulation was provided by means of a rheostat. The temperature gradient along the oven, from the middle to the ends, was measured as $-0.34°$ C mm^{-1} at 100° C and $-1.1°$ C mm^{-1} at 700° C.

2.4. Force–temperature experiment

Using the previously described equipment, the stress changes in the sample could be followed over a temperature range of 30 to 650° C. A heating rate of 11° C min^{-1} was controlled manually.

3. Results and discussion

3.1. Stress–strain behaviour

The PBT films possess an elastic–plastic type of deformation at test temperatures from 30 and up to 550° C. The departure from linear elastic behaviour and influence of tension heat treatment on the deformation behaviour has been previously discussed in terms of structural irregularities and internal stresses introduced during processing. The plasticizing effect of any residual solvent also has to be taken into consideration [10]. More careful examination of this matter is in progress and will be reported in a future communication [11].

Representative stress–strain curves, for different temperatures, obtained at the same strain rate (0.08×10^{-3} sec^{-1}) are shown in Fig. 2. It was observed that the portion of the apparent plastic deformation gradually increased at the expense of an elastic one in the 30 to 300° C region. The reverse was observed when the temperature was further increased. The material became stiffer again and showed a dominant elastic behaviour. The stress–strain dependence at 580 °C and above appeared to be completely linear.

The dependence of ultimate stress and strain, yield stress and elastic modulus on the temperature was derived from the stress–strain curves. The value of the

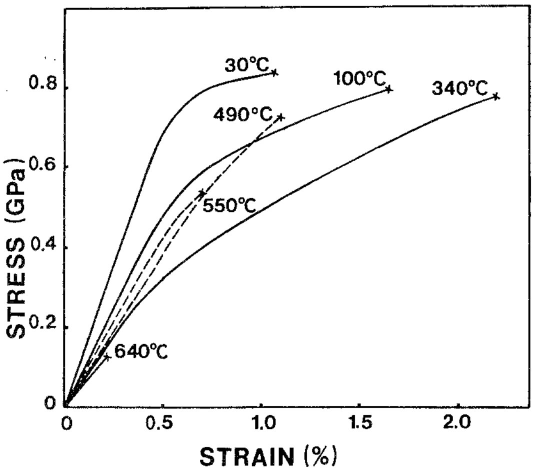

Figure 2 Stress–strain curves at various temperatures for PBT film at a strain rate $0.08 \times 10^{-3} \text{sec}^{-1}$.

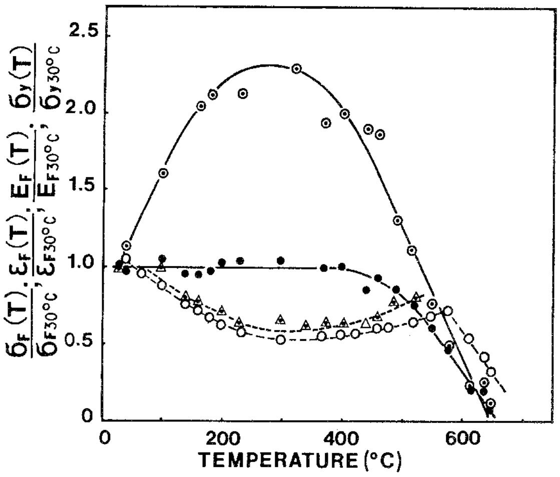

Figure 3 Effects of test temperature on the relative changes of the mean values of: (1) ultimate strength (●); (2) Young's modulus (○); (3) yield stress (△); (4) elongation of PBT film (⊙).

highest stress was taken as the ultimate strength σ_F. The ultimate strain ε_F corresponds to the elongation at the breaking point with the Young's modulus E calculated from the slope of the initial linear region of the stress–strain curve. The yield point was estimated from the intersection of two tangent lines [12].

The mean values of $\varepsilon_F(T)$, $\sigma_F(T)$, $\sigma_y(T)$ and $E(T)$ are plotted in Fig. 3 as ratios of the characteristic values obtained at room temperature. According to these data, PBT can be regarded as an interesting thermally stable polymer, whose strength hardly changes up to 450° C. The fact that ultimate strength does not decrease in this region may indicate a more efficient straightening of the buckled elements during the testing at higher temperatures, causing an internal stress redistribution with resulting changes in the spectrum of the defects responsible for the specimen failure. The observation of the sample surface changes seems to confirm this suggestion. The surface appeared to be smooth and glossy after the testing in contrast to that of the manufactured film.

The lowering of strength starting from 450° C was accompanied by a colour change from yellowish to metallic blue which progressively increases, until decomposition (above 650° C) where the material became black and lost most of its mechanical properties. The considerably lower temperature of degradation than observed by DSC and DTA [11] is very likely due to thermo-oxidation because of the presence of oxygen in the testing environment.

On the basis of the strain prior to fracture [13] two transitions can be identified: a "brittle–ductile" transition taking place at temperature range up to 200° C and reverse "ductile–brittle" transition occurring above 300° C. The best drawing properties were observed in the temperature region of 180 to 350° C where a nice smooth surface finish was developed during the test. This is consistent with the behaviour during the loading–unloading cycles (see following discussion in corresponding section). Above 500° C the typical brittle fracture resulted in a uniform breakage in the middle of the specimen (e.g. samples H and I in Fig. 4). In this region the polymer behaviour is noticeably affected by the degradation process as can be clearly seen on the curve corresponding to the temperature dependence of elastic modulus. These data suggest that the temperature range studied can be divided into three regions. In the first region (30 to 300° C) the modulus of PBT decays with the temperature similar to that of other polymers. Since lateral interactions decrease with temperature the deformation process is facilitated at higher temperature and larger material compliance is observed. The modulus reaches its minimum value (50% of that at ambient temperature) at 300° C. The second region is characterized by steady enhancement until the modulus reaches a new maximum (about 75% of the initial value) at 575° C. The following deterioration of the mechanical properties is most likely due to thermal degradation.

According to a previous model for PBT fibres and films based on the existence of overstressed buckled elements in the structure, the modulus of such a material will be governed by the degree of straightening of these elements. It is logical to assume that unbuckling requires a smaller applied force when the temperature is raised. The yield stress varies in this manner over the region of 30 to 300° C and passes through a minimum in the region of 250 to 400° C. Higher stresses are required for plastic deformation at temperatures above 400° C, since the material becomes stiffer. This suggests that the motion of the structural units becomes more restricted due to changes in the internal structure. Apparently the 5 min thermal conditioning employed (essentially a short-term non-tensioned heat treatment) is sufficient to produce these changes. At higher temperatures these structural changes dominate over the softening effect of temperature. The ratio of the yield stress to modulus, which is essentially the strain at yield, also changes with the temperature. The value of 0.005 calculated at room temperature is much smaller than that for typical polymers (0.025 [14–16]) most likely due to the perfection of the chain alignment.

3.2. Heating–cooling experiment

Fig. 5 shows the variation of the modulus as a

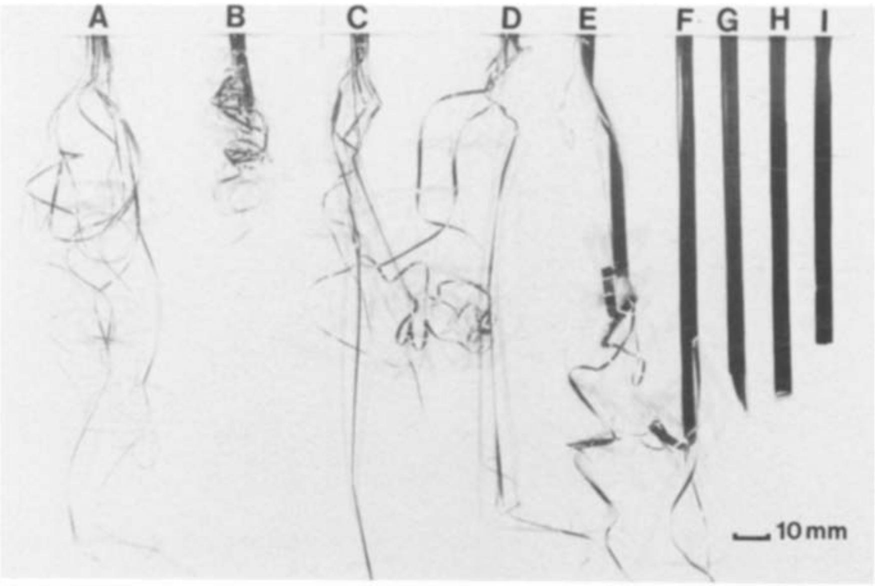

Figure 4 Photograph of PBT film samples after fracture at evaluated temperatures: (A) 60° C, (B) 144° C; (C) 185° C; (D) 370° C; (E) 440° C; (F) 490° C; (G) 550° C; (H) 613° C; (I) 650° C.

function of temperature upon cooling. In this experiment samples were annealed for 5 min at 190° C (curve B) and 575° C (curves C and D) then the temperature was lowered and tensile tests were carried out (after conditioning for an additional 5 min at each test temperature). The lowest curve (A) is the same as in Fig. 3 for comparison. The path of return cooling curves is different to that of the heating. The modulus steadily increases upon cooling. After tensioned annealing at 575° C the performance of PBT can be improved in such a way that at 350° C the modulus is equal to over 80% of that of initial sample at 30° C, and exceeds the initial value by 20% when completely cooled (data on curve C).

The difference between the three cooling curves is due to different measuring procedures employed. While curve C was constructed according to the mean values obtained at each temperature for a number of samples, curves B and D represent the measurements done on a single specimen throughout the entire temperature range. Much higher values of modulus are achieved upon cooling due to strain cycling (work hardening) effect for these multiply tested specimens as reflected in curve D. Curve B (cooling) is likely to be analogous to the first part of curve A (heating to 190° C). The deviation in modulus values observed can be accounted for by the same effect of work hardening. These observations suggest structural changes are initiated in the vicinity of 300° C.

It is also interesting to compare the elastic modulus changes upon heating and cooling for different types of polymers. The experimental data for three selected polymers are combined in Fig. 6. Curve A shows the behaviour of PBT, while curves B and C represent methyl cellulose (MC) and polymethylmethacrylate (PMMA), respectively [17]. The rate of the modulus decrease with temperature is highly dependent on molecular backbone stiffness. In the case of flexible chains (PMMA) the transition is considered as a glass-rubbery state transition and overall deformation achieved during the tensile test is fully recoverable. In contrast plastic deformation accumulates upon heating for MC and PBT. The noticeable irreversible increase in the modulus of MC measured above 200° C is accounted for by the development of crystallinity in a previously amorphous polymer. PBT is characterized as a single-phased material [9], it seems that the changes in its structure follow a similar path, overall general perfection of molecular order.

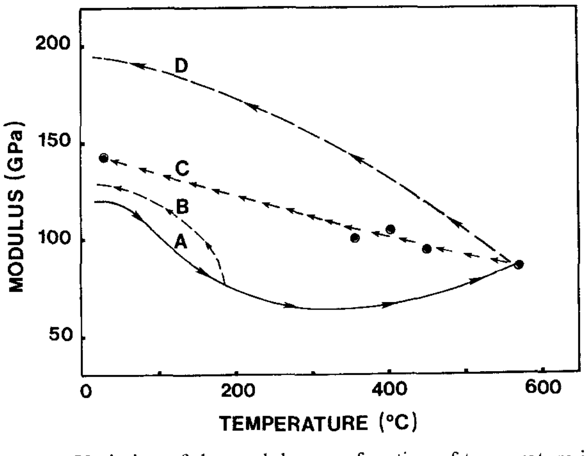

Figure 5 Variation of the modulus as a function of temperature in heating–cooling experiment. Notation explained in the text.

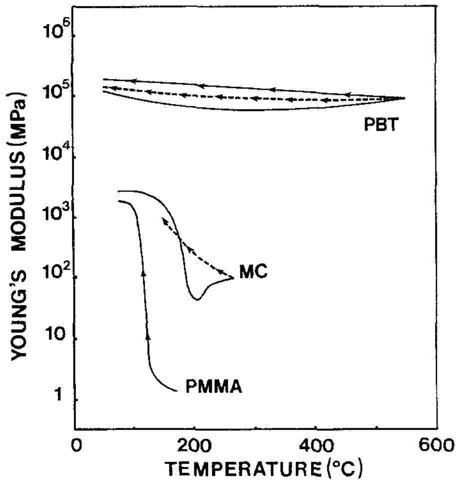

Figure 6 Modulus against test temperature for various polymers: PBT, methylcellulose and poly(methylmethacrylate).

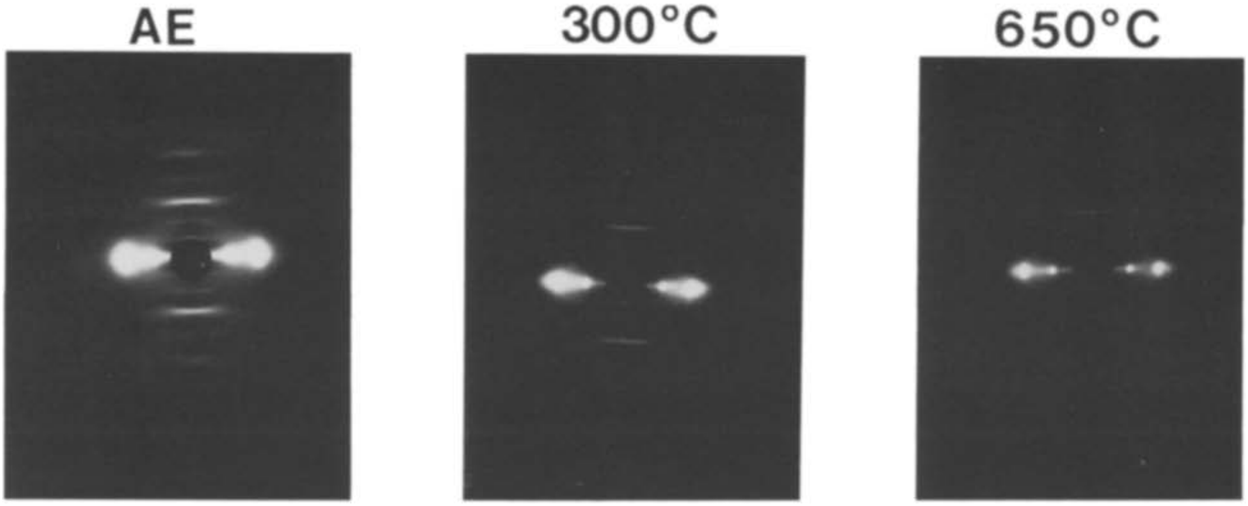

Figure 7 The WAXS flat film patterns of (1) the as-extruded sample. and (2) the tensioned at 300 and 650° C samples.

3.3. X-ray data

The irreversible changes of structure with heat treatment of PBT could be detected by means of X-ray diffraction. WAXS flat film patterns for PBT films tensioned (during the tensile test) at different temperatures (30, 300 and 650° C) are compared in Fig. 7. It is evident that for higher temperature a lower azimuthal spread of the major equatorial reflections is observed. This is associated with significant increase in the axial orientation. There is also an increase in extent and perfection of the lateral molecular order as observed from the decreased radial breadth of the same reflections. Increase in the lateral "crystallite" size accompanied by a simultaneous overall orientation improvement has been previously suggested on the basis of study of the heat treatment on PBT fibres and films [4, 7, 9]. These morphological changes are substantially enhanced when tension is applied during heat treatment and results in greater improvement of mechanical properties of PBT as shown in Allen's work [9]. Accumulation of plastic deformation during the multiple tests on the same sample leads to higher modulus value achieved upon the cooling in our experiment (compare curves C and D in Fig. 5).

3.4. Work-hardening effect

A separate series of experiments consisted of tensioning PBT films for a number of cycles at various temperatures. Typical data are represented in Fig. 8. The ratio of modulus after cycling to the initial modulus (E_c/E_0) is strongly dependent on the temperature and tension applied. The most efficient work hardening effect was observed in the temperature region corresponding to the extremum of the dependence $E(T)$, $\varepsilon_F(T)$ and $\sigma_y(T)$. The modulus may increase 100% or higher with the number of cycles required relatively small [3–7] and dependent on the temperature and the load amplitude.

4. Activation volume

It would be interesting to know whether appreciable changes in activation volume occur as the polymer changes its state. Different experimental methods for estimating the activation volume have been recently reviewed [18]. A method which employs a series of constant strain-rate tests is most appropriate for our investigation.

Stress–strain characteristics of PBT were obtained at different strain rates and different temperatures (30, 160, 305 and 450° C). The experimental curves for 30 and 160° C are given in Fig. 9. The yield stress is plotted as a function of logarithmic strain rate in Fig. 10.

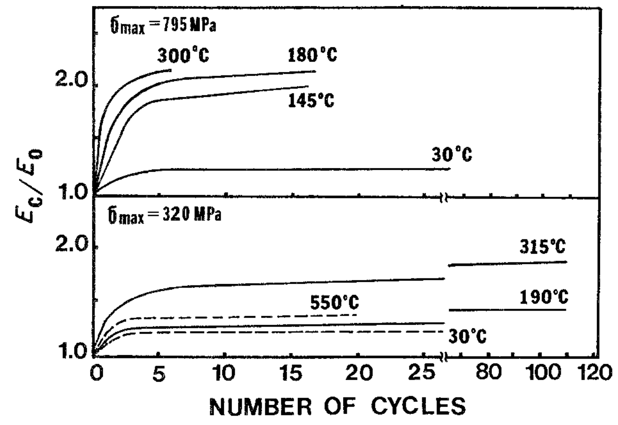

Figure 8 The dependence of modulus increase measured at different temperatures on the number of cycles (A) for a load amplitude 320 MPa; (B) for a load amplitude 795 MPa.

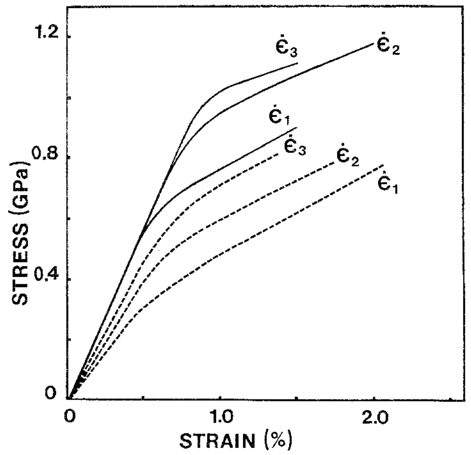

Figure 9 Deformation curves obtained at 30° C (solid lines) and 160° C (dashed lines) and various strain-rates: $\dot{\varepsilon}_1 = 0.04 \times 10^{-3}\,\text{sec}^{-1}$; $\dot{\varepsilon}_2 = 0.42 \times 10^{-3}\,\text{sec}^{-1}$; $\dot{\varepsilon}_3 = 4.17 \times 10^{-3}\,\text{sec}^{-1}$.

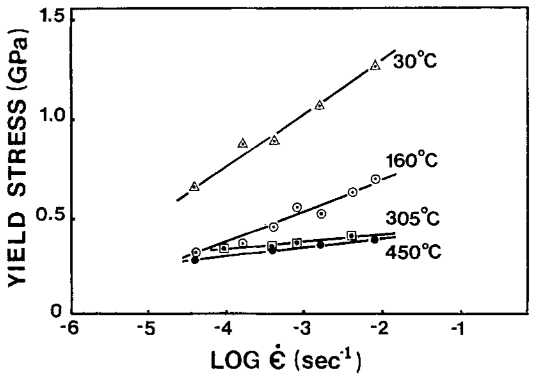

Figure 10 The yield stress of PBT as a function of temperature and strain rate.

The data show that the yield stress depends strongly on the strain rate at room temperature whereas the dependence is very small at 305 and 450° C. At these temperatures the material is seen to pass into a state where the yield process becomes almost time independent.

The observed linearity of the dependence of the yield stress on the strain rate (or time) at constant temperature can be described by the Eyring theory which deals with an activated rate process [19]. The Eyring equation for an activated rate process can be written in terms of strain rate and temperature as

$$\dot{\varepsilon} = \dot{\varepsilon}_0 \exp - \left(\frac{\Delta U - \sigma_y V^*}{kT}\right) \qquad (1)$$

where $\dot{\varepsilon}_0$ is a constant, ΔU is the activation energy for an activated-rate process, σ_y is the yield stress, V^* is the stress activation volume, k is the Boltzmann constant and T is the absolute temperature. This equation implies that stress at yield and the logarithm of strain rate have a linear relationship with a slope given by

$$\frac{\partial \sigma_y}{(\partial \ln \varepsilon)_T} = \frac{kT}{V^*} \qquad (2)$$

Fig. 11 shows the calculated values of the stress activation volume, V^*, plotted as a function of test temperature.

A relatively small increase of the activation volume with test temperature is observed in the lower temperature range. There is, however, a rapid increase in V^* for test temperature at 300° C and above. Above approximately 300° C the activation volume is nearly independent of temperature. The activation volume estimated for temperatures above 300° C is approximately an order of magnitude higher than that estimated for temperatures below 150° C.

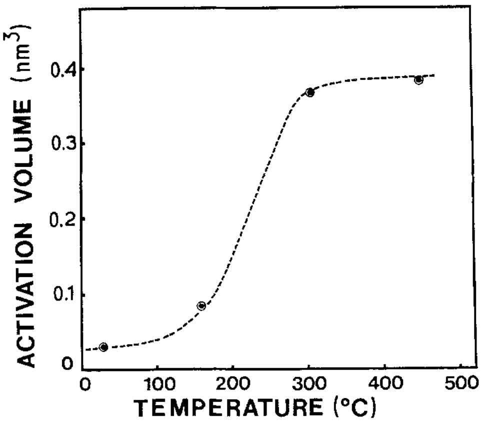

Figure 11 The dependence of the activation volume on the temperature.

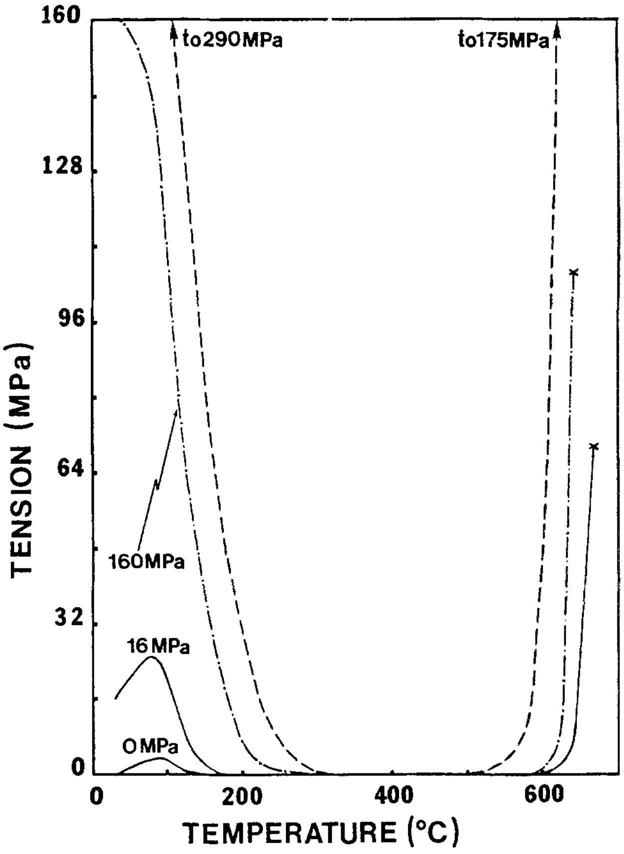

Figure 12 Force-temperature dependence for PBT film: without external constraint and with an applied stress of 16, 160 and 290 MPa.

4.1. Extension–contraction

In this experiment, axial stress was constantly monitored as the temperature was raised from ambient to 650° C, while the length of the specimen was held constant. It was found that a measurable shrinkage force is developed at a very early stage of heating even with no initial constraint (Fig. 12). The force reaches a maximum at approximately 80° C and decays to zero at about 150° C. In this region, a continuous elongation of the film occurs. With increased temperature a very rapid increase in the retractive force occurs at about 600° C. Results obtained on the preloaded samples follow a similar trend except that the initial shrinkage force has been over-balanced by a higher applied stress on the sample. The temperature of the recovery (full release of the applied stress), the temperature where new contraction starts and the temperature for the maximum of the shrinkage force are strongly dependent on the preloading regime (see Fig. 13). The rate of contraction at high temperatures indicates the intensity of the structural reorganization, the latter can be manipulated by the applied temperature and/or tension within the limits of material strength and thermal stability. A combination of 150–200 MPa tension at 630 to 670° C was found

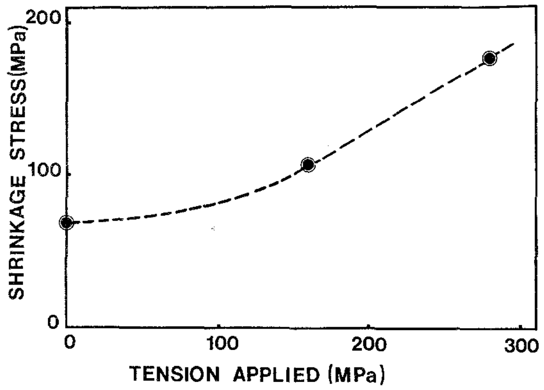

Figure 13 The shrinkage force as a function of applied tension prior to annealing.

optimal on the basis of systematic study for PBT fibre heat treatment [9].

Although the interrelationship between applied force, temperature and sample shrinkage is evident, the mechanism of the sample extension–retraction behaviour with heat treatment remains unclear. Generally the changes in the material properties under the influence of heating and tension are certainly related to straightening of the buckled segments of the microfibrils and further perfecting of structure. The observed modulus increase with the higher test temperature also may suggest a densification mechanism (loss of microvoids) in analogy with plastically deformed carbon fibres [20]. More advanced discussion is difficult because it is hard to separate all the effects including the influence of residual solvent found in the starting material [10].

5. Conclusion

The deformation behaviour of poly(*p*-phenylene benzobisthiazole) films which consist of a fibrillar structure composed of highly oriented rod-like molecular bundles was studied as a function of temperature and strain rate. Both the tensile modulus and yield stress show a similar temperature dependence. They decrease slowly under the influence of increasing temperature to minimum values around 300° C; and after then they start to increase with the test temperature. Upon cooling, the elastic modulus of PBT films, annealed at 600° C, increases with decreasing test temperature. The considerable enhancement of modulus is similar to that produced by tensioned heat treatment.

Cyclic deformation and tensioned heat treatment of PBT films improve the overall orientation and the lateral ordering of the structure which consequently enhances the strength and modulus. The interrelationship between tension and temperature is such that similar results may be achieved by either variable within the limits of the material strength and thermal stability.

The yield stress of PBT increases linearly with the strain rate at a chosen test temperature. This behaviour can be modelled in terms of a single activated rate process. The stress activation volume for the deformational processes calculated from the Erying rate theory showed a rapid ten-fold increase in the region of 150 to 300° C to a constant activation volume at higher temperatures. The stress at break of the PBT films remained nearly unchanged over a considerable temperature range (up to 500° C), which indicates good strength at high temperatures. The strain at break showed a temperature dependence with a maximum, around 300° C, which may be considered as an optimum temperature for ductile behaviour.

Tensioned PBT films showed an expansion–contraction behaviour upon successive heating, associated with mobility changes of structural elements in the polymer system which leads to an irreversible change in thermomechanical properties.

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