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Constrained annealing of biaxially oriented SAN copolymer films

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Biaxially oriented styrene–acrylonitrile (SAN) copolymer films with a draw ratio of 6.9 in the machine direction (MD) and 2.9 in the transverse direction (TD) were annealed under constraint in both directions. The films fractured during annealing developed cracks along the TD. The temperature dependence of the time to fracture showed an Arrhenius plot with an activation energy of 114 k cal mol^{-1}. When annealing was terminated before fracture, the work to fracture on tensile deformation of the annealed film increased with annealing time, with a maximum increase of about 53% in the MD and 40% in the TD. The annealed films showed fewer bands or more fine shear bands as compared with unannealed films. These observations suggest a toughening effect in oriented films when annealed under dimensional constraint.

1. Introduction

It is known that the mechanical properties of glassy polymers can be enhanced by preferential orientation. The effect on tensile modulus and toughness, and the microstructural changes upon deformation in oriented glassy polymers, have been reported in a number of studies [1–3]. More recently, a study [4] on the thermal recovery of biaxially oriented films showed that the recovery process involved large dimensional changes. Such changes followed second-order kinetics for a portion of the process and could be attributed to the stored energy resulting from biaxial orientation.

In this paper, the thermal and mechanical behaviour of biaxially oriented films annealed under dimensional constraint is described. Annealing of plastically deformed polystyrene under dimensional constraint has been reported [5] to reveal the separability of molecular processes involved in the recovery. Since molecular motions do occur during annealing, it is likely that the mechanical response could also be altered due to a possible change in the degree of chain alignment. For biaxially oriented films, annealing with dimensional constraint can be achieved by capitalizing on the two-dimensional nature of the thin film. The properties of the annealed films can then be examined using conventional mechanical testing methods.

2. Experimental procedures

2.1. Materials and specimen preparation

The styrene–acrylonitrile (SAN) random copolymer used in this study was made by the Dow Chemical Company. It contained 70% styrene and 30% acrylonitrile with a glass transition temperature of 102° C. The average molecular weight determined by gel permeation chromatography was 185 000. Biaxially oriented films about 28 μm thick were made from the resin through a biaxial orientation process. Materials, received in pellet form, were extruded at 216° C in a Killion extruder and subsequently oriented at 171° C using a conventional blown-film bubble process [6]. The degree of orientation along the machine direction (MD) and the transverse direction (TD) was varied by the extent of drawing and blowing along the respective directions. The degree of orientation along the MD was made higher than that of the TD: 6.9 in the MD and 2.9 in the TD as determined by a thermal annealing technique [4]. The optically clear films were air cooled to room temperature and packed in rolls 11″ wide with the length direction being the MD, and the width, the TD. Pieces of specimen films of 6 × 6″ were razor-cut from the roll with the edges parallel to the MD and TD. The films were cleaned by using an anti-static master brush. Printed ruled papers were placed underneath the film to help guide the directions during cutting.

2.2. Thermal annealing with dimensional constraint

The constrained annealing experiment was carried out as follows: a pair of square stainless steel frames, 6 × 6″ and $\frac{1}{4}$″ thick, with a 4 × 4″ centre opening, was machined and finished. The film was sandwiched between the frames and taped to the frame surface by using double-sided Scotch tape. To ensure the flatness of the film, and a perfect contact between the film and frame, a frame was first taped around the four sides, and the taped surface was then pressed on the film surface. Another pretaped frame was subsequently pressed onto the other side of the film. The film and frame assembly was held together with eight c-clamps distributed evenly around the frame. The clamped assembly was then annealed in a VWR 1410 oven with the use of a motor-driven fan to increase the convection. The oven temperature was displayed by using an

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Omega model 199 digital thermometer. To minimize the temperature fluctuation when the annealing was started, the c-clamps were preheated in another oven at 95° C before the samples were attached. Samples were annealed at temperatures near to or higher than the glass transition temperature, until observable cracks were developed on the film surface as observed through the glass window in the oven. The time to fracture of the films was recorded. Some samples were annealed under the same clamped condition but removed from the oven before fracture. Duplicate tests were performed throughout the study.

2.3. Instron tensile tests

The films annealed under the clamped condition without fracture were razor-cut into stripes 3 × 0.25″ along both directions following the method described previously [3]. They were subjected to uniaxial tension in an Instron testing machine. Samples were precisely aligned and gripped in a pair of air jaws with a gauge length of 1″. The air jaws were operated by using compressed air so that little or no distortion was introduced in the samples during loading. The surface of the jaws was coated with a thin layer of rubber to assure excellent contact between the grip and film surfaces.

2.4. Optical microscopy

Observations were made on the tested samples using a Nikon Optiphot reflection light microscope. Surface details were examined with Nomarski contrast. Pictures were taken by using a Nikon UFX-II photographic system.

3. Results and discussion

3.1. Fracture of films upon annealing under constraint

When the biaxially oriented films were annealed with mechanical clamping for a specified time period, cracks started to develop in the film leading to eventual film fracture. The surface of the cracks was oriented along the TD, the direction that had the smaller degree of orientation. The incipiency of crack formation was observed directly on the film as indicated by the change of surface reflectance under illumination. Sometimes several cracks developed at the same time along the boundary of the metal frame; the test was then repeated to verify the edge effect at the boundary. The annealing time for the initial crack formation was recorded.

Since the biaxially oriented films are known to recover toward the unoriented state when annealed without constraint [4], the driving force for the fracture of films annealed under constraint is likely to be the stored energy introduced in the oriented structure. During annealing the stored energy is released so that the oriented structure tends to relax and minimize the amount of energy stored; this is accompanied by apparent dimensional changes as shown in the previous study. Namely, the dimensions along the MD and TD decreased while the thickness increased with annealing time. In a constrained state, where the dimensions along the MD and TD are fixed, the original recovery process is hindered during annealing. The stored energy is probably released by deforming the material against the constraining force which ultimately results in a localized crack. The time to formation of an incipient crack is indicative of the rate of recovery for the strain-controlled fracture process. The temperature dependence of the rate constant could yield an activation energy comparable to that observed for dimensional recovery.

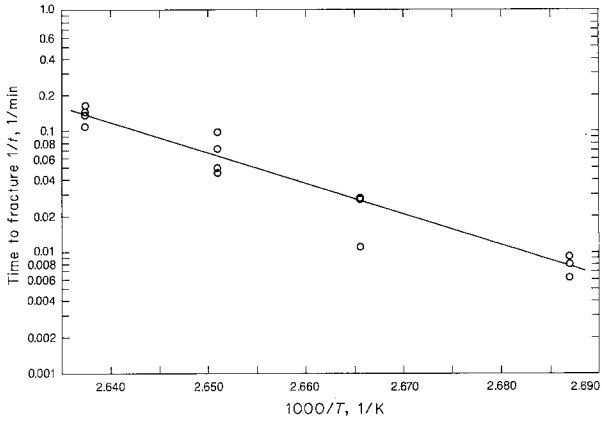

Figure 1 Temperature dependence of the reciprocal time to fracture of SAN films when annealed under dimensional constraint. $\Delta H = 114\,k\,cal\,mol^{-1}$.

Since the rate is proportional to the reciprocal of the time to fracture, the temperature dependence of the reciprocal time to fracture was plotted as shown in Fig. 1. Each data point plotted represents an individual test without the edge effect, as indicated earlier. The plot shows an Arrhenius relationship within limited data scatters. The activation energy as measured from the slope is $114\,k\,cal\,mol^{-1}$. This value is lower than that of the later stages of the dimensional recovery, 120 to $127\,kcal\,mol^{-1}$ [4] based on second-order recovery kinetics. Since cracking of films occurred at short annealing times, the result implies the possibility of lower activation energy processes which could have occurred at earlier stages of recovery.

3.2. Tensile test of films annealed under constraint

To see how the mechanical behaviour varies after being annealed under constraint, the films were annealed at 102° C for different time periods before fracture. Films were air-cooled to room temperature and removed from the frame for tensile tests. The thickness of the film before and after annealing, as measured by using a Brown & Sharpe No. 1 micrometer, was found to be unchanged within measurement accuracy, indicating that no apparent dimensional recovery occurred during annealing. The stress–strain curves of specimens cut along the MD and annealed for four different time periods are shown in Fig. 2. While the yield stress seems to be unchanged, the total elongation increases with annealing time. The results on the TD stretching are shown in Fig. 3. The yield stress does not appear to vary at the beginning but increases at longer annealing times. The total elongation, like that of the MD, increases with annealing time. The results show that toughness increased as

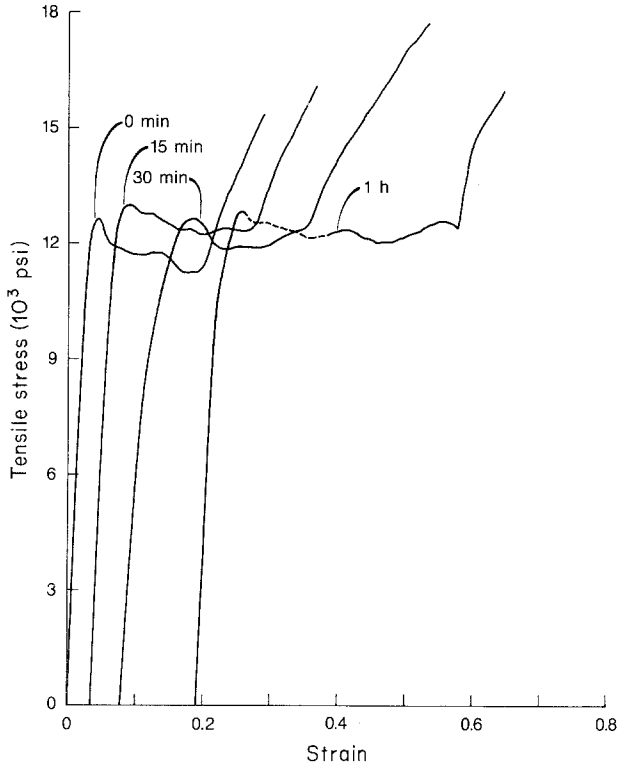

Figure 2 Stress–strain curves of films deformed along the MD after annealing under constraint at 102° C for different time periods (curves displaced for clarity). Gauge length = 1″; crosshead speed = 0.2″ min^{-1}.

annealing times were increased from 15 min to 1 h. Annealing longer than 1 h caused fracture of the film, as reported earlier. A plot of the apparent work to fracture against annealing time is shown in Fig. 4. It is clear that the work to fracture increases systematically with annealing time. Each data point shown represents an individual test. The maximum increase of work to fracture in the MD is about 53% and that in the TD is about 40%, as compared with unannealed films.

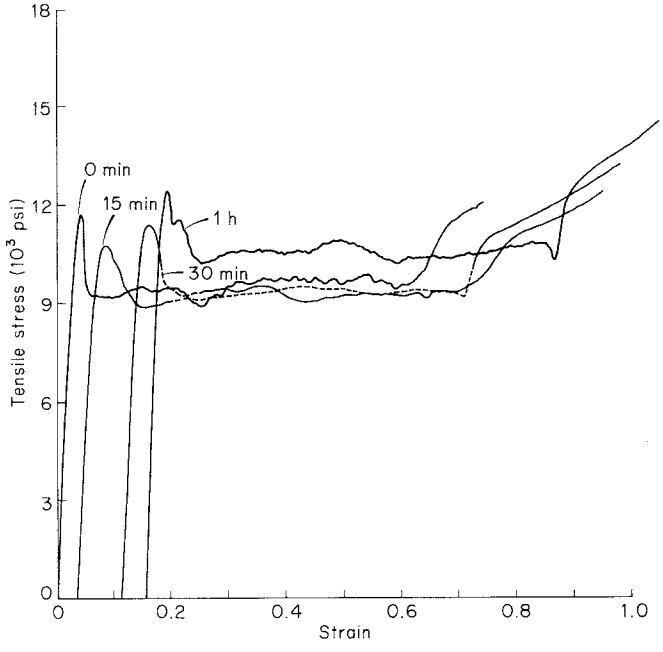

Figure 3 Stress–strain curves of films deformed along the TD after annealing under constraint at 102° C for different time periods (curves displaced for clarity). Gauge length = 1″; crosshead speed = 0.2″ min^{-1}.

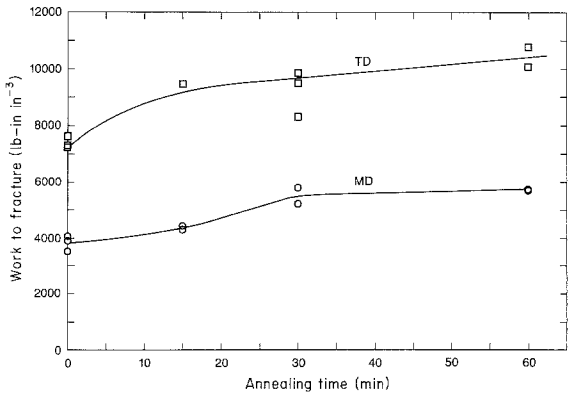

Figure 4 Variation of work to fracture with annealing time of films before deformation along the MD and TD. Temperature, 102° C.

The increase of toughness can be viewed as an effect resulting from further deformation in the existing oriented film along the two major directions. Since the dimensions along the two directions were fixed, deformation could be achieved by stretching the films along the two mutually perpendicular directions so that further orientation processes could take place at temperatures close to T_g. Since little or no change in film thickness was observed, the process could involve chain slippage or conformational rearrangement along the oriented directions. In contrast, films annealed without dimensional constraint showed an embrittlement effect. For a specimen annealed at 106° C for 5 min, the tensile behaviour was typical of a brittle mode of fracture, with little or no elongation observed. Since the rate of dimensional change was very fast at the early stages of the recovery process [4], such a transition in the deformation mode may require only a slight change in dimension or degree of chain alignment, and may occur at early stages of the recovery process.

3.3. Morphology of shear bands

Previous studies [3] have shown that shear bands formed by stretching along the two mutually perpendicular directions exhibit two different morphologies. When deformation occurred along the MD, diffuse fine shear bands with an intersection angle of about 119.2° were produced. When deformation occurred along the TD, shear bands with definitions of fine, coarse and thick bands [7, 8] were seen with distinctively different morphologies. The intersection angle was about 123.6° before necking. These bands seemed to merge into thick deformation zones when necking started. During the necking process, further shear deformation was seen inside the thick deformation zones, producing new sets of shear bands with an intersection angle of about 81°.

For films annealed under constraint, some variations in the morphology of shear bands were observed. First, when the annealing time was 30 min or less, fine shear bands which were generated from the MD deformation appeared to show the same morphology and intersection angles as compared with that of the unannealed films. For the 1 h annealing test, however, specimen surfaces were mostly featureless after deformation, and fine bands were observed only at certain

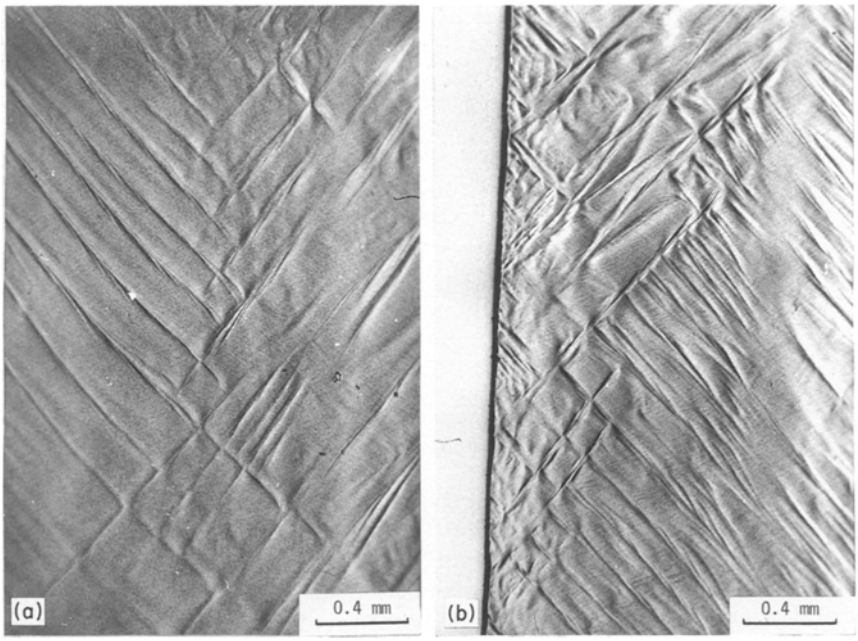

Figure 5 (a) Morphology of shear bands inside the neck of a specimen stretched 50% along the TD after annealing at 102° C for 1 h under constraint. (b) Morphology of shear bands inside the neck of a specimen stretched 50% along the TD without annealing.

edge defects or surface irregularities. This observation could indicate that more extensive and smaller scale shear motions were produced during the deformation. The bands generated were probably diffusive. For deformation along the TD, the band morphology again showed similarities to that of the nonannealed films for an annealing time of 30 min or less. For the 1 h annealed films, the bands inside the neck were not so abundant and tended to be localized as shown in Fig. 5a for a specimen stretched by 50%, as compared with that of the unannealed film stretched to the same elongation as shown in Fig. 5b. The intersection angle, however, was about the same. The fact that the highly annealed films showed fewer observable bands or less definition in band morphology under the optical microscope suggests that annealing favours the formation of fine shear bands, and this could contribute to the increase in tensile toughness.

4. Conclusions

1. Biaxially oriented SAN films fractured during annealing under dimensional constraint, with cracks developed along the transverse direction. The temperature dependence of the time to fracture showed an Arrhenius relationship with an activation energy of 114 k cal mol^{-1}, which is slightly lower than that observed for the later stages of the dimensional recovery.

2. The films annealed under constraint before fracture showed a toughening effect upon stretching. The toughness increased with annealing time, with a maximum increase of about 53% in the machine direction and 40% in the transverse direction.

3. The highly annealed films showed fewer shear bands or less definition of band morphology in the neck under the optical microscope, suggesting that annealing under constraint favours the formation of fine shear bands.

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References

1. K. J. CLEEREMAN, H. J. KARAM and J. C. WILLIAMS, *Mod. Plast.* **30** (1953) 119.
2. M. C. SLONE and F. W. REINHART, *ibid.* **31** (1954) 203.
3. C. C. CHAU and L. C. RUBENS, *Polym. Engng. Sci.* **27** (1987) 1095.
4. C. C. CHAU, L. C. RUBENS and J. K. RIEKE, *Polymer* **29** (1988) 99.
5. T. M. KUNG and J. C. M. LI, *J. Appl. Phys.* **60** (1986) 2659.
6. J. B. MAURO and J. J. LEVITZKY in "The Science and Technology of Polymer Films", Vol. 1, edited by O. J. Sweeting (Interscience, New York, 1968) p. 459.
7. J. B. C. WU and J. C. M. LI, *J. Mater. Sci.* **11** (1976) 434.
8. C. C. CHAU and J. C. M. LI, *ibid.* **17** (1982) 652.

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