Kinetics of recovery of biaxially oriented styrene–acrylonitrile copolymer films

C. C. Chau, L. C. Rubens and J. K. Rieke
Materials Science and Engineered Products Laboratory, Central Research, Dow Chemical Company, Midland, MI 48674, USA

(Received 30 April 1987; revised 27 August 1987; accepted 1 September 1987)

Styrene–acrylonitrile copolymers were biaxially oriented to obtain a draw ratio of about 6.9 in the machine direction (length) and 2.9 in the transverse direction (width). The prepared films, 28 μm thick, were annealed at elevated temperatures for different time periods. The length and width of the film gradually decreased, accompanied by an increase of the film thickness during recovery. The variations of the film length, width and area with time were all found to follow second-order kinetics for the later part of the recovery process. The second-order rate constant for area recovery, k_a, was found to be related to k_l and k_w, the rate constants for length and width recovery, as $1/k_a = l_\infty/k_w + w_\infty/k_l$. The fitted final area A_∞ was equal to $l_\infty w_\infty$, obtained individually from the fitting of second-order kinetics. The Arrhenius plots of the rate constants showed activation enthalpies in the range from 120 to 127 kcal mol^{-1}. Based on these observations, the kinetics of volume recovery were also shown to be second-order at long recovery times.

(Keywords: recovery; biaxial orientation; glassy polymers; kinetics)

INTRODUCTION

Polymeric products are often oriented or plastically deformed during the fabrication process. The state of stress and the recovery process of stretched or oriented polymers upon thermal annealing are of practical importance and have been studied extensively for many years. Examples reported include annealing of oriented nylon fibres[1,2], morphological changes of cold-drawn and annealed polypropylene[3], uniaxially stretched poly(ethylene terephthalate)[4–6] and polystyrene[7].

The mechanism of a recovery process can sometimes be revealed by its kinetics. However, few studies of the kinetics have been reported. Benbow[8] studied recovery of twisted polyethylene rods by following the change of twist angles. Park and Uhlmann[9–11] assumed parallel processes for the recovery of deformed polymers and obtained activation energy spectra from them. More recently, Li[12] reported the shear strain recovery in thick shear bands in polystyrene; the recovery was found to follow second-order kinetics in the later part of the process. Similar observations were also obtained in the indentation recovery of polystyrene[13]. The recovery data of volume change in polystyrene obtained by Kovacs[14] as analysed by Li[12] was also found to obey second-order kinetics. These observations suggested that the defect mechanism resulted from plastic deformation and that the recovery process is caused by the same type of mechanism.

Biaxial orientation is known to influence significantly the macroscopic properties of polymers. Both tensile strength and modulus[15,16] showed dramatic increases over non-oriented materials. In oriented styrene–acrylonitrile copolymer films, localized shear banding rather than crazing was seen to occur throughout the tensile yielding process[17]. Evidently, biaxial deformation greatly changed the physical structure. Like the case of linear deformation, glassy polymers deformed by biaxial stretching may recover upon annealing at temperatures higher than the glass transition temperature. The recovery processes should show dimensional changes along the two stretched directions. A study of the recovery kinetics would help in the understanding of the physical state of biaxially oriented polymers. In this work, biaxially oriented styrene–acrylonitrile copolymer films were prepared for the recovery study. The changes of length, width and area of specimen films during thermal annealing were measured. The relationship between the recovery processes was investigated.

EXPERIMENTAL

Materials and specimen preparation

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 weight-average molecular weight determined by gel permeation chromatography was 185000. Biaxially oriented films about 28 μm thick were made from the resin through a controlled biaxial orientation process. Materials, received in pellet form, were extruded at 216°C in a Killion extruder and subsequently oriented at 171°C via a conventional blown film bubble process[18]. The degree of orientation along the machine direction (MD) and the transverse direction (TD) was controlled by the extent of drawing and blowing along the respective directions. The degree of orientation along MD was made higher than that of TD. The optically clear films were air-cooled to room temperature and packed in rolls 11 inch (~28 cm) wide with the length direction being the MD, and the width direction being the TD. Pieces of specimen films 80 mm × 80 mm were razor-cut from the roll with the edges parallel to the MD and the TD; they were cleaned by using an antistatic master brush. Printed ruled papers

0032-3861/88/010099-07$03.00

were placed underneath the film to help guide the directions during cutting. The cut specimens were then ready for annealing tests.

Thermal annealing and dimensional measurements

Specimen films were laid flat on 'Kim-Wipe' papers which were put on a glass plate preheated in a Fisher Isotemp Series 200 forced convection oven at the set temperature before starting the annealing experiments. The oven was modified by installing a precise temperature controller (model 2002 process controller made by LFE Corporation) capable of controlling and resolving to ±0.1°C. The original temperature controller in the oven was used as the high limit. The temperature was indicated by the digital readouts. Specimens were annealed at temperatures higher than the glass transition temperature for predetermined time periods, removed from the oven for dimensional measurements and returned to the oven for another period of annealing. The length and width of the specimen films were measured by using a conventional flexible plastic ruler along each of the four sides. The thickness of the film was measured by using a Brown and Sharp micrometer capable of resolving 0.1 mil (0.0001 inch, 2.5 μm), an average of five measurements being taken for each data recording. At the later stage of annealing, the length and width of some specimens were also measured by the micrometer for more precise readings.

Optical microscopy

Some specimens were observed under a Nikon Optiphot reflection light microscope. Specimens were cut under an LKB Ultra-tome III microtome with glass blades. Pictures were taken by using a Nikon UFX-II photographic system.

RESULTS AND DISCUSSION

Recovery of biaxially oriented films upon annealing

When a piece of biaxially oriented SAN film was annealed at temperatures higher than the glass transition temperature, both the length (MD) and width (TD) of the film gradually decreased with the annealing time. The shrinkage in length appeared to be faster than that of width during annealing. The film sometimes curled up, probably due to the non-uniform distribution of internal stresses during annealing. The irregularity of shape eventually disappeared at long annealing times. Films were flattened by a piece of glass plate for precise measurements of the dimensions at the initial stage of annealing. A flexible plastic ruler was used for measuring the slightly wavy boundaries at the later stage of annealing. The thickness of the film was found to be increasing with the annealing time. The cross-sections of a specimen during annealing are shown in *Figure 1*. The thickness increases dramatically during annealing. The change of the film thickness appeared to be uniform along the cross-section, indicating that the degree of orientation produced during the orientation process was uniform. The variation of the length (MD), width (TD) and thickness of the film with the annealing time at 112°C is shown in *Figure 2*. The rate of change of length and width is extremely high at the initial stage of annealing; it gradually decreased at long times. On the other hand, the thickness increased drastically in the beginning and gradually levelled off at long annealing times.

The large extent of dimensional change upon annealing indicated that a large amount of cold work was stored in the film during the orientation process. For an unoriented SAN film, e.g. films made by compression moulding, annealing above T_g caused no apparent dimensional changes. Like the recovery processes of shear bands and indentation in polystyrene[12,13], the driving force for the recovery process is probably the stored energy resulting from the biaxial deformation. Since the deformation caused the molecular chains to extend along two perpendicular directions, the energy was possibly stored with the introduction of conformational defects along the chains. The nature of the defects was not known; however, the defects were probably density variations generated from deformation, or conformational changes such as rotations of side groups along the main chain. These defects could carry opposite signs, such as rotational pendant groups with opposite twist angles, and be distributed uniformly over the oriented region. Therefore, a possible mechanism for recovery is the motion and elimination of such defect dipoles by cancelling with each other towards the equilibrium concentraton of the unoriented state. If this is true, the rate of elimination of such defects during annealing should be proportional to the concentration of both the positive and the negative defects present at any time t. The kinetics of recovery should therefore be second-order.

Since the defect concentration increased with the degree of orientation, it is reasonable to assume that the concentration is proportional to the linear dimensions of the film. During annealing, the defect concentration should decrease with the dimensions and approach an equilibrium state corresponding to the annealing temperature. This idea is consistent with that of shear strain[12], indentation[13] and volume recovery[12] in polystyrene. The kinetics of defect annealing can then be studied by dimensional recovery. Let the final length and width after an infinite time of annealing be l_∞ and w_∞ per specimen; the concentration of defects is then proportional to $l-l_\infty$ and $w-w_\infty$ in the length and width directions respectively, where l and w are length and width of the film at any time t during recovery. The second-order rate relationships in the respective directions are:

$$d(l-l_\infty)/dt = -k_l(l-l_\infty)^2 \tag{1}$$

$$1/(l-l_\infty) = k_l t \tag{2}$$

$$d(w-w_\infty)/dt = -k_w(w-w_\infty)^2 \tag{3}$$

$$1/(w-w_\infty) = k_w t \tag{4}$$

where k_l and k_w are the second-order rate constants. The final dimensions l_∞ and w_∞ are unknown quantities, and they need to be numerically adjusted before a second-order rate constant can be obtained. First of all, the relationships between length and width and the annealing time for different temperatures are shown in *Figures 3a* and *3b*. To see if second-order kinetics were obeyed, both $1/(l-l_\infty)$ and $1/(w-w_\infty)$ were plotted against time as shown in *Figures 4a* and *4b*. The fitted final equilibrium dimensions l_∞ and w_∞ were obtained using RS/1 software

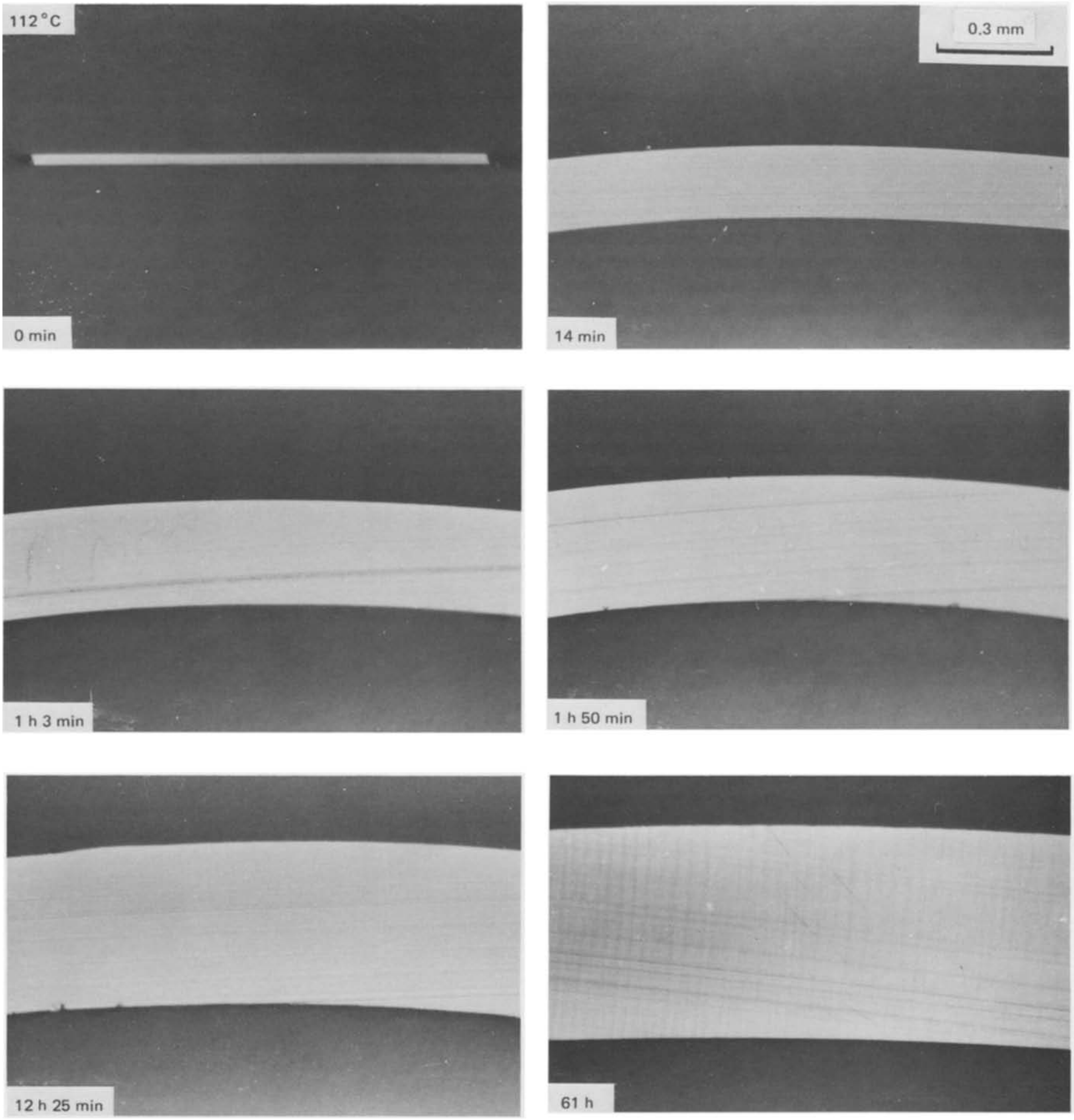

Figure 1 Cross-sectional views of films showing the increase in the thickness of film during annealing at 112°C

(licensed from Bolt Beranek and Newman Inc.). It is clear that the data follow second-order kinetics, at least for the later part of the recovery processes. The rate at the beginning seemed to be faster than what was required by the second-order kinetics. This discrepancy could be caused by the inhomogeneous distribution of conformational defects introduced by the orientation process and/or parallel recovery processes occurring at the initial stage of annealing. It disappeared rapidly with annealing at the later stage of recovery. The second-order rate constants k_l and k_w were obtained directly from the slopes.

The temperature dependence of the second-order rate constants showed Arrhenius relationships as shown in *Figure 5*. The activation enthalpy from the slopes are 120 kcal mol^{-1} for length (MD) recovery and 126 kcal mol^{-1} for width (TD) recovery. These values are smaller than that of the shear strain recovery and volume recovery in polystyrene obtained using the same type of analysis. The fact that the recovery of length and width gave consistent activation enthalpy indicated that a single process occurred during recovery.

Kinetics of area recovery

For studying the recovery kinetics of specimen area, the variation of film area with annealing time was examined. The area at any time t obtained from length and width measurements was plotted against that from thickness

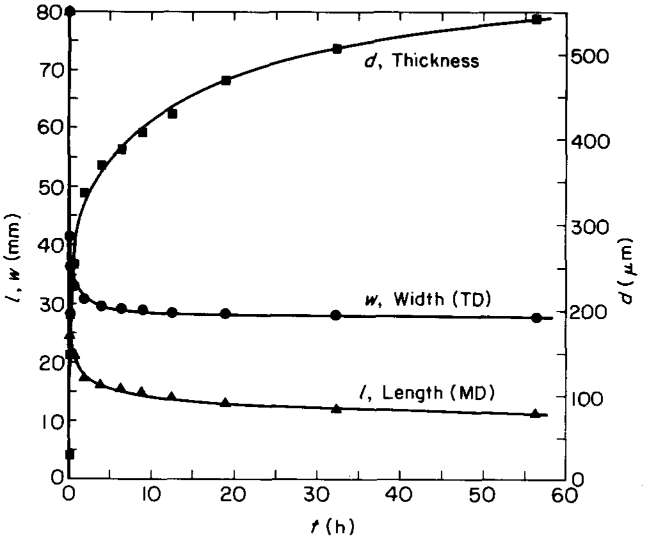

Figure 2 The variation of length *l*, width *w* and thickness *d* of films with annealing time at 112°C

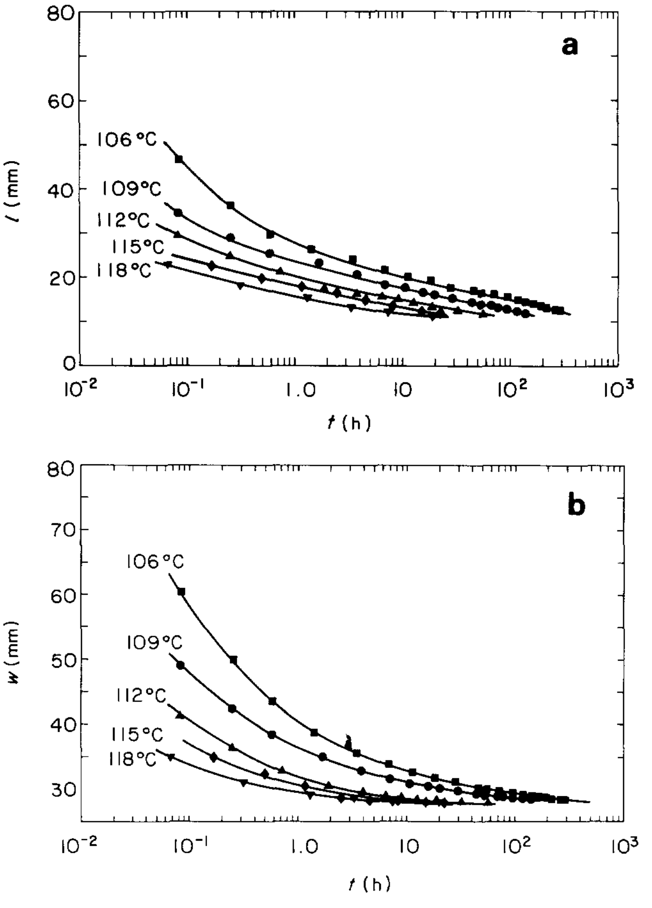

Figure 3 The variation of (a) length of films and (b) width of films with annealing time for five different temperatures

measurements as shown in *Figure 6*, in which area calculated from $l \times w$ was plotted against V/d, where V is the film volume before annealing and d is the thickness at any time t. A straight line passing through the origin is shown indicating the consistency between the measurements. The variation of area with time for different temperatures is shown in *Figure 7*. As expected, the area decreased rapidly at the beginning and gradually levelled off at long annealing times. The variation of area with time showed some similarity with that of the length and width recovery. However, since second-order kinetics were obeyed in linear dimensional recovery, the recovery of area was not expected to be second-order. Based on the second-order kinetics established for length and width recovery as shown in equations (2) and (4), the area

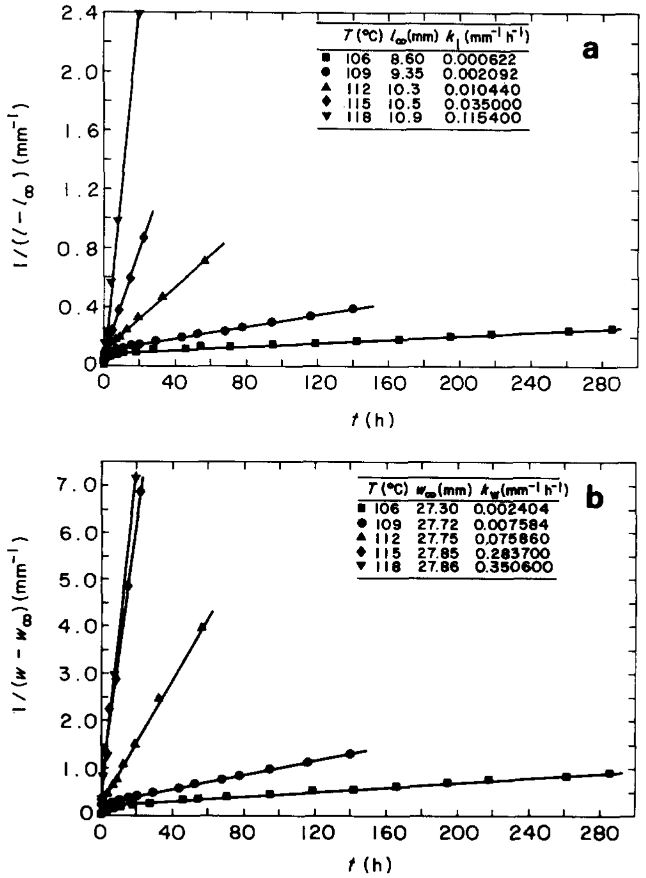

Figure 4 Second-order kinetics for the recovery of (a) film length and (b) film width at different temperatures

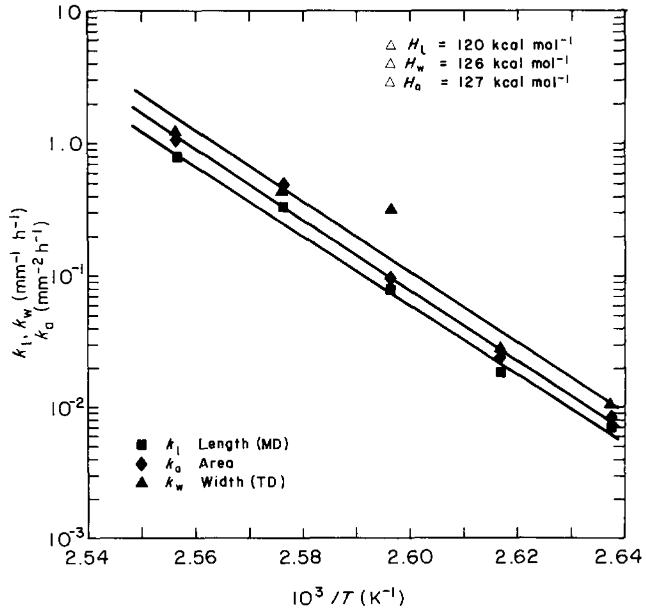

Figure 5 The temperature dependence of the second-order rate constant for length, width and area recovery

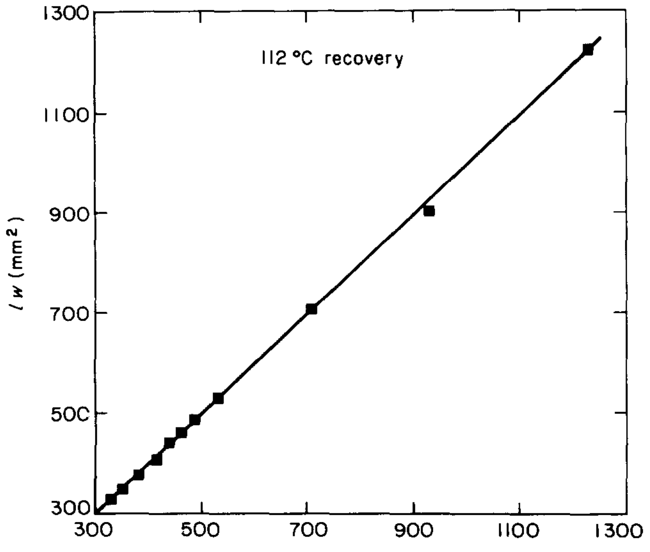

Figure 6 A plot of area obtained by length × width against volume/thickness during annealing at 112°C

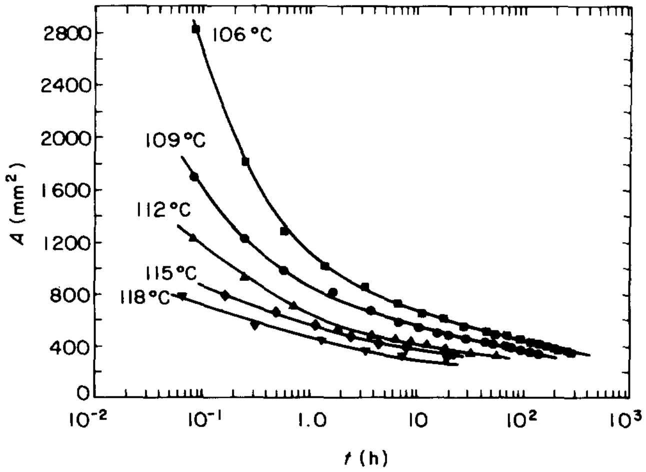

Figure 7 The variation of area with time during annealing for different temperatures

change in the oriented state $A - A_\infty$ can be expressed as:

$$A - A_\infty = \frac{l_\infty}{k_w t} + \frac{w_\infty}{k_l t} + \frac{1}{k_l k_w t^2} \tag{5}$$

$$\simeq \left(\frac{l_\infty}{k_w} + \frac{w_\infty}{k_l}\right)\frac{1}{t} \tag{6}$$

where A_∞ represents the final area which can approach the measured A at long annealing times. At later stages of the recovery process, i.e. when the annealing time is sufficiently long, the equation can be approximated as a simple relationship as shown in equation (6). The variation of the additional area with time during recovery was then found to follow second-order kinetics as shown in the following equations:

$$\mathrm{d}(A - A_\infty)/\mathrm{d}t = -k_a(A - A_\infty)^2 \tag{7}$$

and

$$1/k_a = l_\infty/k_w + w_\infty/k_l \tag{8}$$

where k_a is the second-order rate constant for area recovery. The relationships indicate that the recovery process of area can be second-order at later stages of the process provided that the linear dimensional change during recovery follows second-order kinetics.

To see if this is valid, the area recovery data were examined in terms of equation (7). The final area A_∞ is an unknown quantity, and it needs to be numerically adjusted before second-order kinetics can be obtained. Without fitting for A_∞ the recovery process did not follow second-order kinetics as shown in *Figure 8* in which the reciprocal of area, $1/A$, is plotted against the annealing time. The value of A_∞ was obtained from the best fir for second-order kinetics. The results of $1/(A - A_\infty)$ vs. t are shown in *Figure 9*. It is clear that the recovery of area appears to obey second-order kinetics at later stages of annealing. The fitted final area, A_∞, increases from 234 to 306 mm² with increase in annealing temperature. The slope of the curves gave the second-order rate constant for area recovery, k_a. The temperature dependence of k_a showed an Arrhenius relationship, as also shown in *Figure 5*, with an activation enthalpy of 127 kcal mol^{-1}. This value is very close to that of the length and width recovery, indicating that the recovery of length, width and area is a correlated process which probably involves a single recovery mechanism.

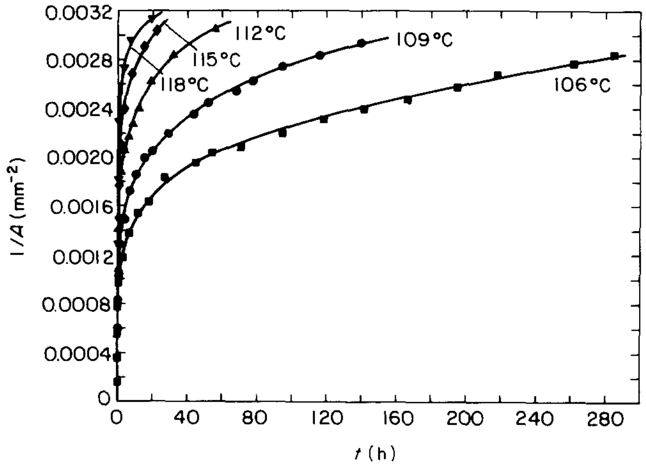

Figure 8 Plots of reciprocal of area, $1/A$, against annealing time for different temperatures

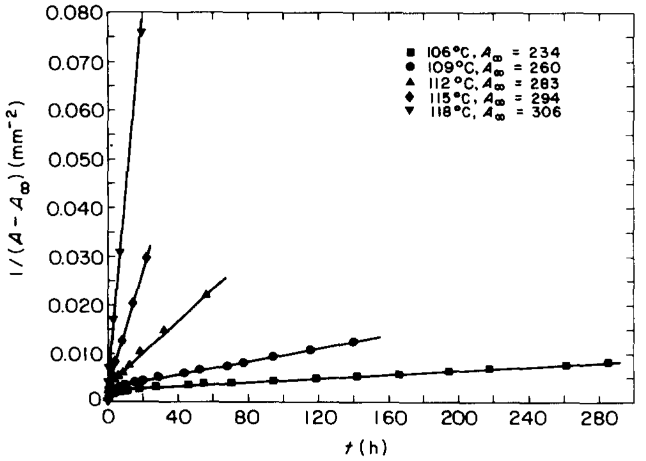

Figure 9 Second-order kinetics for area recovery at different temperatures

Table 1 The fitted final length l_∞, width w_∞ and area A_∞ and their relationship for SAN recovery at different temperatures

T (°C)	l_∞ (mm)	w_∞ (mm)	$l_\infty w_\infty$ (mm^2)	A_∞ (mm^2)	$\frac{\lvert l_\infty w_\infty - A_\infty \rvert}{A_\infty}$ (%)
106	8.60	27.30	234.78	234	0.3
109	9.35	27.72	258.182	260	0.7
112	10.30	27.75	285.825	283	1.0
115	10.55	27.855	293.870	294	0.04
118	10.98	27.860	305.903	306	0.03

The fitted final dimensions l_∞, w_∞ and A_∞ were obtained independently in this study. The fitted final area A_∞ was found to be consistent with that of $l_\infty w_\infty$ as shown in *Table 1*. The difference between them was within only 1%. This indicates the validity of the approximation used in equation (6). To see if the relationship between the second-order rate constants k_l, k_w and k_a is consistent with that predicted in equation (8), the value of $1/k_a$ is plotted against $l_\infty/k_w + w_\infty/k_l$, as shown in *Figure 10*. The result shows a straight line passing through the origin, indicating the validity of the suggested relationship between the three second-order rate constants.

Kinetics of volume recovery

Kovacs[14] studied volume contraction behaviour from polymers quenched from a temperature above the glass transition to a temperature below by isothermal annealing at the lower temperature. The volumetric data as analysed by Li[12] and coworkers were also found to follow second-order kinetics for the later part of the recovery process. A similar type of mechanism was proposed to have occurred with the quenched-in defects during recovery. Based on the second-order rate relationship established for linear dimensional recovery, the kinetics of volume recovery can be obtained. For a cubic element defined by length (l), width (w) and height (h), the second-order rate relationships for length and width were defined by equations (2) and (4); that for the height can be expressed as:

$$d(h - h_\infty)/dt = -k_h(h - h_\infty)^2 \tag{9}$$

The additional volume resulting from deformation or thermal quenching is

$$V - V_\infty = \left(\frac{w_\infty h_\infty}{k_l} + \frac{l_\infty h_\infty}{k_w} + \frac{l_\infty w_\infty}{k_h}\right)\frac{1}{t} + \left(\frac{w_\infty}{k_l k_h} + \frac{l_\infty}{k_w k_h} + \frac{h_\infty}{k_l k_w}\right)\frac{1}{t^2} + \frac{1}{k_l k_w k_h t^3} \tag{10}$$

or

$$V - V_\infty \simeq \left(\frac{w_\infty h_\infty}{k_l} + \frac{l_\infty h_\infty}{k_w} + \frac{l_\infty w_\infty}{k_h}\right)\frac{1}{t} \tag{11}$$

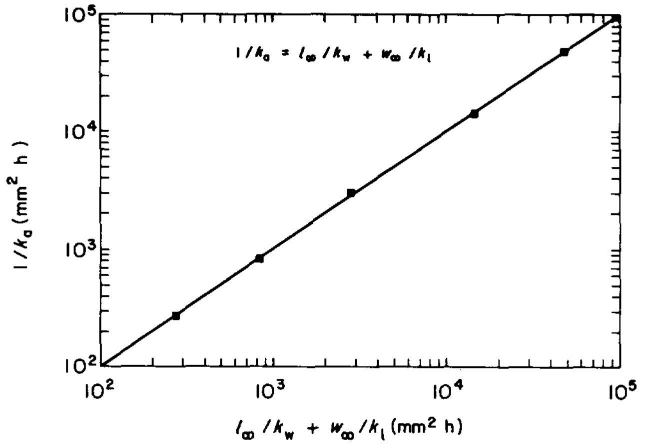

Figure 10 Plot of $1/k_a$ against $l_\infty/k_w + w_\infty/k_l$ showing the relationship between the three second-order rate constants, k_l, k_w and k_a

where V_∞ represents the final volume, which could be obtained by annealing of the deformed material for an infinite period of time. At later stages of the recovery process, both terms containing higher orders of t could be neglected, resulting in a simple relationship as shown in equation (11). The kinetics of recovery of the additional volume $V - V_\infty$ was then found to be second-order as shown below:

$$d(V - V_\infty)/dt = -k_v(V - V_\infty)^2 \tag{12}$$

where

$$\frac{1}{k_v} = \frac{w_\infty h_\infty}{k_l} + \frac{l_\infty h_\infty}{k_w} + \frac{l_\infty w_\infty}{k_h} \tag{13}$$

Kovacs *et al.*[19] proposed a multiparameter model to explain the complicated process in glassy polymers when subjected to various thermal treatments. The possibility of existence of a second-order rate process in a portion of the recovery of a volume element deformed three-dimensionally such as through simple quenching and annealing is suggested in the study.

CONCLUSIONS

When biaxially oriented styrene–acrylonitrile copolymer films were annealed above the glass transition temperature, both length and width decreased, while the thickness increased with time.

The recovery of length and width appeared to follow second-order kinetics for the later part of the recovery. The activation enthalpy was 120 kcal mol^{-1} for the length (MD) recovery, and 126 kcal mol^{-1} for the width (TD) recovery.

The kinetics of area (length × width) recovery was also found to be second-order for the later part of the process. The second-order rate constant k_a was related to k_l and k_w as $1/k_a = l_\infty/k_w + w_\infty/k_l$. The fitted final area was equal to the product of the fitted final length and width. The activation enthalpy of recovery was about 127 kcal mol^{-1}.

These observations suggested that conformational defects of opposite sign were introduced during biaxial deformation. The mechanism of recovery at the later stage was the cancellation of defect dipoles towards the equilibrium state.

ACKNOWLEDGEMENTS

The authors wish to thank Professor J. C. M. Li for his guidance during the course of the study, R. A. Wessling, D. E. McLemore and S. V. McKinley for reviewing the manuscript and encouraging the work, and D. Bank for helping with the experiments. Permission from the Dow Chemical Company to publish the work is deeply appreciated.

REFERENCES

1 Dismore, P. F. *Polym. Lett.* 1964, **2**, 1113
2 Dismore, P. F. *J. Polym. Sci. C* 1966, **13**, 133
3 Crystal, R. G. and Hansen, D. *J. Appl. Phys.* 1967, **38**, 3103
4 Wilson, W. P. W. *Polymer* 1974, **15**, 277
5 Statton, W. O., Koenig, J. L. and Hannon, M. *J. Appl. Phys.* 1970, **41**, 4290
6 Koenig, J. L. and Hannon, M. J. *J. Macromol. Sci.–Phys. B* 1967, **1**(1), 119
7 Ito, E., Horie, T. and Kobayashi, Y. *J. Appl. Polym. Sci.* 1978, **22**, 3193
8 Benbow, J. J. 'The Rheology of Elastomer' (Eds. P. Mason and N. Wookey), Pergamon, London, 1958, p. 164
9 Park, J. B. and Uhlmann, D. R. *J. Appl. Phys.* 1970, **41**, 2928
10 Uhlmann, D. R. and Park, J. B. *J. Appl. Phys.* 1971, **42**, 3800
11 Park, J. B. and Uhlmann, D. R. *J. Appl. Phys.* 1973, **44**, 201
12 Li, J. C. M. *Met. Trans.* 1978, **9A**, 1353
13 Chang, B. T. A. and Li, J. C. M. *J. Mater. Sci.* 1980, **15**, 1364
14 Kovacs, A. J. *J. Polym. Sci.* 1958, **30**, 131
15 Cleereman, K. J., Karam, H. J. and Williams, J. C. *Mod. Plastics* 1953, **30**(9), 119 (May)
16 Slone, M. C. and Reinhart, F. W. *Mod. Plastics* 1954, **31**(10), 203 (June)
17 Chau, C. C. and Rubens, L. C. *Polym. Eng. Sci.* 1987, **27**(14), 1095
18 Mauro, J. B. and Levitzky, J. J. 'The Science and Technology of Polymer Films', (Ed. O. J. Sweeting), Interscience, New York, 1968, Vol. 1, pp. 459–80
19 Kovacs, A. J., Aklonis, J. J., Hutchinson, J. M. and Ramos, A. R. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 1097