

# Properties of Syndiotactic-Rich Poly(vinyl Alcohol) Thin Films in Water. VI. Elastic Behavior of Undrawn / Annealed Thin Films by Repeated Elongation / Contraction in Water

KAZUO YAMAURA, AKIHIRO HAYAKAWA, TETSUYA TANIGAMI, and SHUJI MATSUZAWA, *Faculty of Textile Science and Technology, Shinshu University, Tokida 3-15-1, Ueda-city, Nagano-prefecture 386, Japan*

## Synopsis

The elastic behavior of undrawn/annealed swollen thin films of syndiotactic-rich poly(vinyl alcohol), derived from vinyl trifluoroacetate, was studied by repeated elongation/contraction in water. For the films annealed at temperatures below 175°C, the characteristic of deformation was divided into low-drawn and high-drawn regions. The elastic deformation was dominant over the plastic deformation in the low-drawn region and vice versa in the high-drawn region. The effect of heat treatment on the elastic behavior of the swollen films in water was almost independent of annealing temperatures below 125°C. The elastic deformation in water at 70°C was especially remarkable in the low-drawn region for the films annealed at temperatures below 125°C and at 80°C for the films annealed at 150°C. For the films annealed at 200°C, considerable plastic deformation occurred in addition to elastic deformation from the initial drawing; the films were broken in the low-drawn region.

## INTRODUCTION

In previous articles,<sup>1-5</sup> the authors have studied the deformation behavior of very thin and untreated, undrawn/annealed or drawn/annealed films of poly(vinyl alcohol) (PVA<sub>VTFA</sub>) derived from vinyl trifluoroacetate (VTFA) in water under a given load. Deformation behavior caused by repeated, forced elongation and contraction for untreated film was also reported. We have shown that the untreated thin films of PVA<sub>VTFA</sub> behaved as an elastomer in water. Moreover, even the undrawn PVA<sub>VTFA</sub> films annealed at temperatures below 125°C were considered to behave as an elastomer in water in the higher water temperature range.<sup>5</sup>

In this paper, the deformation behavior of undrawn/annealed thin PVA<sub>VTFA</sub> films in water was examined by repeated, forced elongation and contraction at each fixed water temperature in the range of 0 to 80°C and the elastic characteristic was investigated.

## EXPERIMENTAL

### Sample and Films

PVA<sub>VTFA</sub> derived from VTFA was used as a sample. The VTFA monomer was polymerized in bulk at 60°C employing benzoyl peroxide as an initiator.

Poly(vinyl trifluoroacetate) was converted to PVA<sub>VTFA</sub> by dissolving it in 2,2'-diamino diethylamine. The degree of polymerization and the content of syndiotactic diad were 1670 and 55.2%, respectively. PVA<sub>VTFA</sub> thin films (70 × 150 mm) were made by casting an aqueous solution at room temperature on a glass plate. The thickness of the films was about 0.017 mm. The films were cut to a width of 2 mm (length: 70 mm). The tape-like films were heat-treated in an oven with air for 10 min at fixed temperatures in the range of 50 to 200°C (every 25°C) fixing both ends of film at the length of 6.0 cm.

### Repeated Elongation and Contraction

The experimental procedure was similar to that shown previously.<sup>4</sup> The initial length of films was  $l_d = 4$  cm and the water temperature was in the range of 0 to 80°C (every 10°C).

### RESULTS

Figures 1-4 show the change in film length in water by repeated, forced elongation and contraction for the thin PVA<sub>VTFA</sub> films annealed at 100, 150,

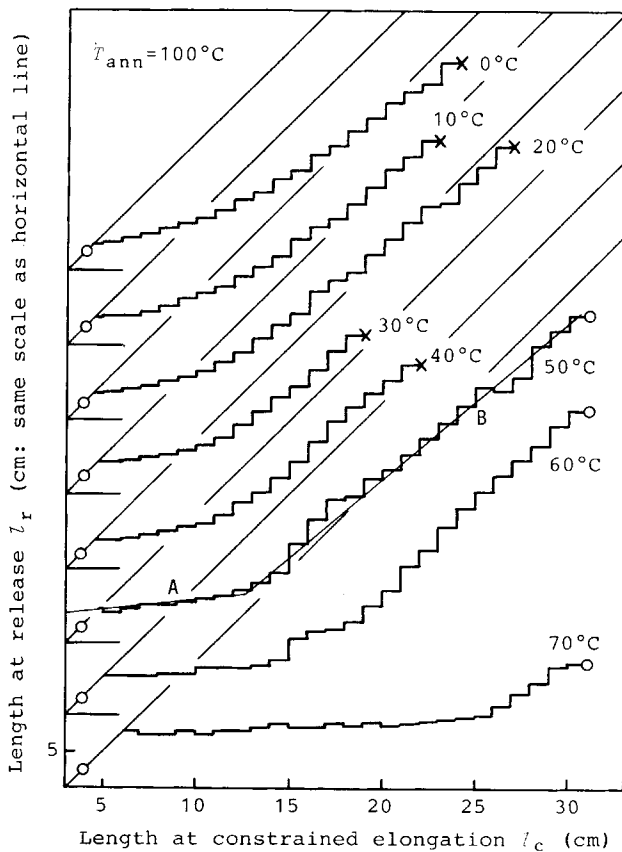


Fig. 1. Film length at release  $l_r$  versus film length at constrained elongation  $l_c$  at 0-70°C in water for PVA<sub>VTFA</sub> films annealed at 100°C.

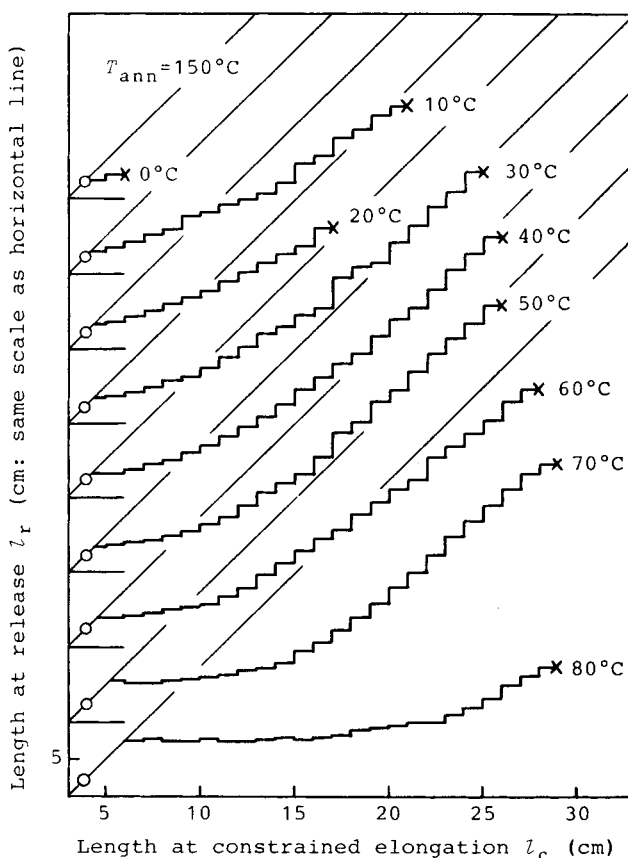


Fig. 2. Film length at release  $l_r$  versus film length at constrained elongation  $l_c$  at 0–80°C in water for PVA<sub>VTFA</sub> films annealed at 150°C.

175, and 200°C, respectively. The films in water reached equilibrium swellings at standing time within 4 min at water temperatures above 20°C independent on the annealing temperature of film, whereas at water temperatures of 0 and 10°C these were reached at the standing time above 5 min. Therefore, the repeated forced elongation and contraction were carried out after standing for 5 min in the former and after standing for 60 min in the latter. The initiation time of swelling for the films annealed at various temperatures did not differ from each other at the same water temperatures, that is, the difference in the diffusion rate of water into films was not apparent.

Figure 5 shows the relationship between the ratio  $l_s/l_d$  and the water temperature, where  $l_s$  is the film length after equilibrium swelling, and  $l_d (= 4 \text{ cm})$  in air. The relationship for the films annealed at temperatures below 125°C were almost same. For the films annealed at temperatures above 150°C, the ratio at the same water temperatures decreased with the increase in the annealing temperature. The swelling ratio increased steeply with an increase in water temperature above 60°C except for films annealed at 200°C.

The straight line shown in Figures 1–4 was termed a perfect plastic deformation line as described previously.<sup>4</sup> The stepwise lines shown in Figures 1–4 are divided roughly into two parts, that is, A and B regions shown in

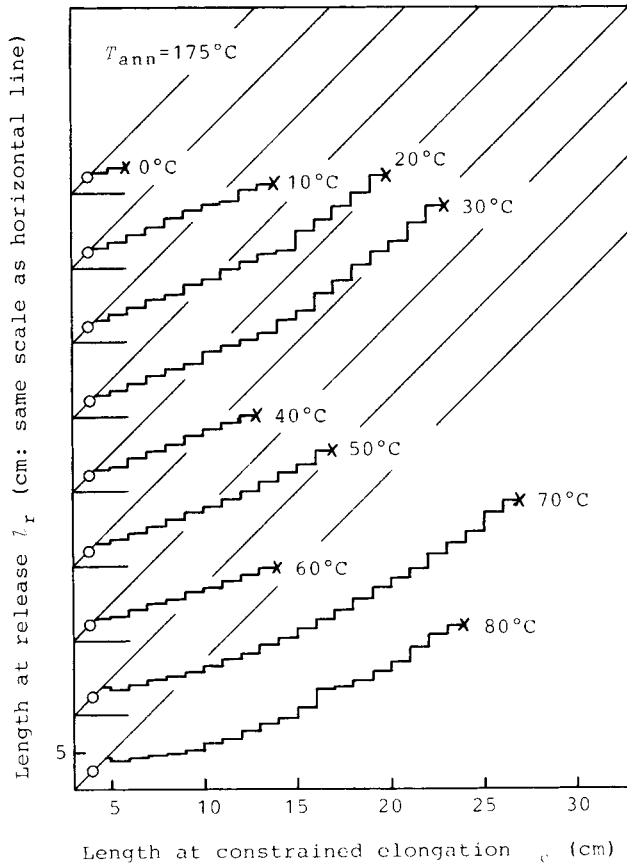


Fig. 3. Film length at release  $l_r$  versus film length at constrained elongation  $l_c$  at 0–80°C in water for PVA<sub>V</sub>TFA films annealed at 175°C.

Figures 1 and 4. The slopes of region A depended on both the water temperature and the annealing temperature, and decreased with the increase in the water temperature and the decrease in the annealing temperature. However, they were almost constant at the same water temperatures for the samples annealed at the temperatures below 125°C.

The ratio  $l_s/l_d$  or the difference  $\Delta l (= l_s - l_d)$  can be correlated to the slope of region A. Figure 6 shows the relation between  $\Delta l$  and the slope of region A. The slope decreased with the increase in  $\Delta l$ . When  $\Delta l$  exceeds 2.0 cm, that is,  $l_s/l_d$  exceeds 1.5, the swollen films behaved as an elastomer up to the constrained lengths within about 25 cm at a water temperature of 70°C for the samples annealed at the temperatures below 125°C and within about 23 cm at the initial temperature of 80°C for the sample annealed at 150°C. The plastic deformation was very small at the region and the slope was less than 0.06. However, even at region A the swollen films annealed at temperatures below 125°C and at 150°C were subject to considerable plastic deformation in addition to a large elastic deformation at water temperatures below 60 and 70°C, respectively. The plastic deformation increased with a decrease in water temperature. The slope for the former films was 0.075–0.34 and for the

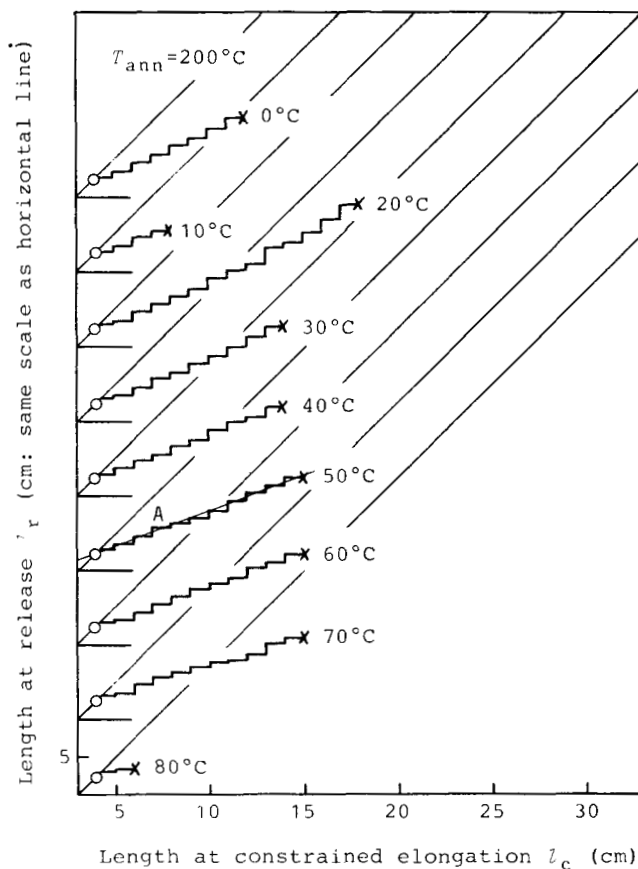


Fig. 4. Film length at release  $l_r$  versus film length at constrained elongation  $l_c$  at 0–80°C in water for PVA<sub>VTFA</sub> films annealed at 200°C.

latter films 0.079–0.33. For the films annealed at 175°C, the slope was 0.13–0.39. In the case of the sample annealed at 200°C, only region A was found and the slope was 0.29–0.49 and increased roughly with the decrease in the water temperature.

The slope of region B was 0.55–0.94, higher than that of region A. Generally the slope of region B increased with an increase in water temperature. However, since the range of region B was narrow at the highest water temperatures (70 or 80°C), the slope was not well defined (see Figs. 1 and 2).

## DISCUSSION

In the previous report,<sup>1</sup> we have shown that the untreated thin film of PVA<sub>VTFA</sub> obeyed Hooke's law under a certain fixed load even at 25°C in water. As described in the previous section, however, the film is considered not to have undergone small plastic deformation in addition to the large elastic deformation even in the region of low deformation. Both deformations are also considered to have increased roughly in proportion to load. We have also

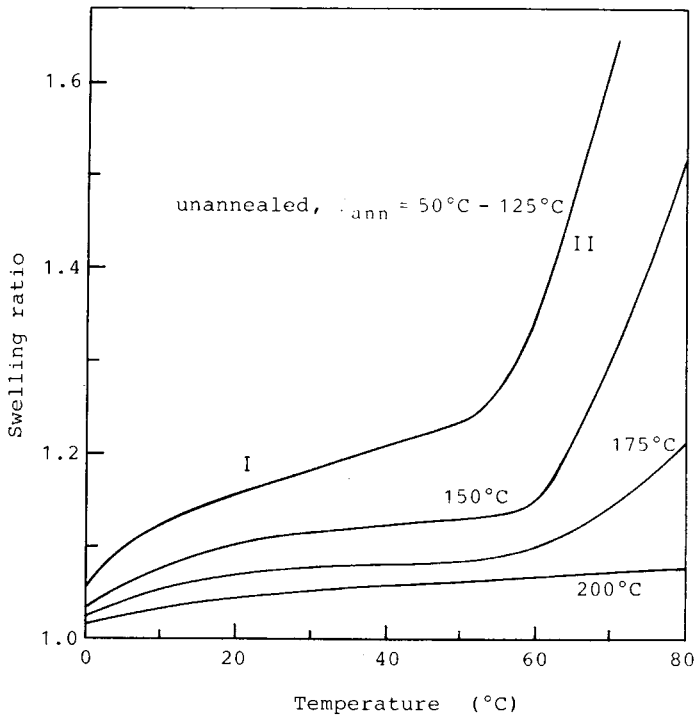


Fig. 5. Swelling ratio versus temperature in water for PVA<sub>VTFA</sub> films unannealed and annealed at 50–200°C.

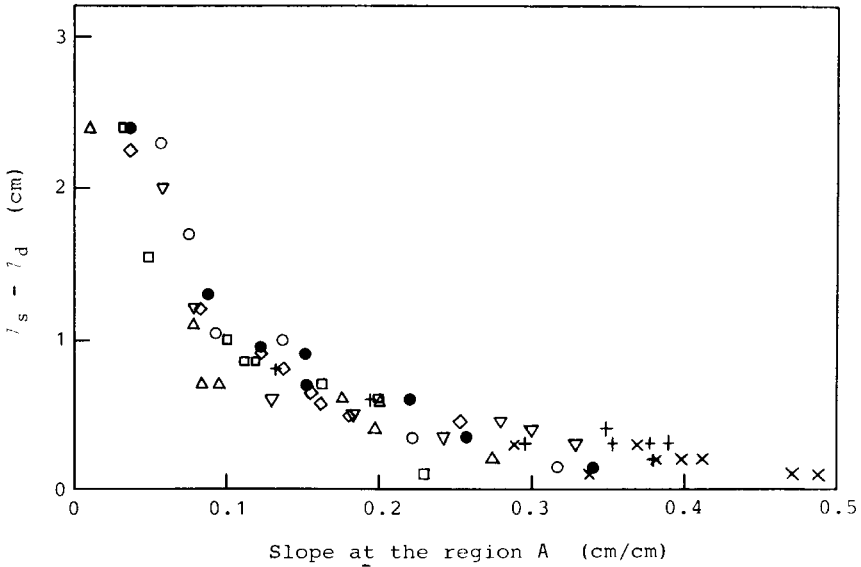


Fig. 6.  $\Delta l = l_s - l_d$  versus slope for region A shown in Figures 1–4: (○) unannealed; (●)  $T_{\text{ann}} = 50^\circ\text{C}$ ; (□) 75; (◇) 100; (△) 125; (▽) 150; (+) 175; (×) 200.

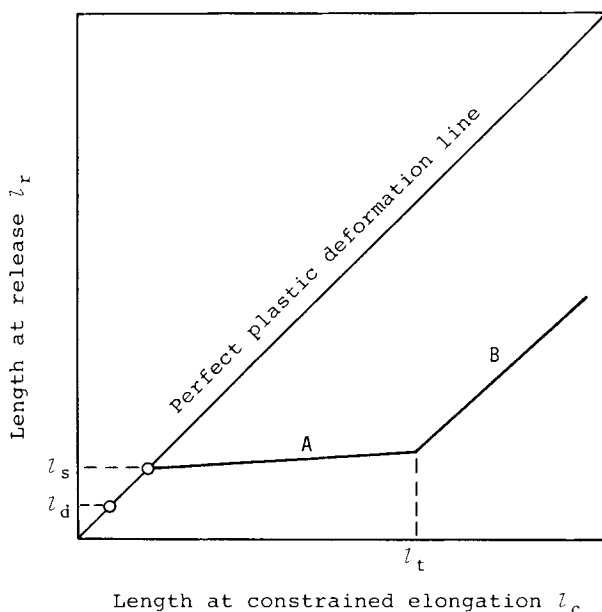


Fig. 7. Schematic diagram for the relations shown in Figures 1-4.

shown<sup>1</sup> that over a certain load the deformation of film did not occur. Therefore, under forced elongation the films are considered to be deformed plastically by drastic drawing. The characteristic of deformation was divided into regions **A** and **B** at the specific deformed length. The elastic and plastic deformations occurred chiefly in the **A** and **B** regions, respectively.

Figure 7 shows the schematic diagram for Figures 1-4. Lines **A** and **B** are described by the following equations:

$$l_r = a + bl_c \quad (\text{for line A}) \quad (1)$$

$$l_r = c + dl_c \quad (\text{for line B}) \quad (2)$$

As described in the previous section,  $b$  was 0.032-0.49 and  $d$  was 0.55-0.94. If  $b = 0$ , the swollen films behave as a perfect elastomer within  $l_t$ . However, the swollen films used in this experiment behaved as an imperfect elastomer. The  $b$  values depended on  $\Delta l = l_s - l_d$  (or  $l_s/l_d$ ) and the latter depended on the water temperature. Namely, the change in  $b$  values relates to the dissolution of microcrystals that play an important role as network junctions in the swollen films.

Sakurada et al.<sup>6</sup> and Shibatani<sup>7</sup> have investigated the effect of the stereoregularity on the thermoelastic behavior for the swollen PVA films cross linked lightly by irradiation. Shibatani<sup>7</sup> has reported that cross linking loci in PVA chains were syndiotactic sequences of different lengths and that the number of network chains formed by gelation of the waterswollen PVA films decreased with an increase in temperature in the higher temperature range, which led to the decrease in the number of network junctions. The PVA<sub>VTFA</sub> films used in this experiment are considered to be the network cross linked

only by syndiotactic sequences of different sequence lengths. As the junctions of different sequence lengths dissolve in accordance with water temperature, the  $l_s$  value (or  $\Delta l = l_s - l_d$ ,  $l_s/l_d$ ) increases with a decrease in the number of junctions as the temperature increases. The  $b$  value is also influenced by the change in the number of junctions. The change is brought about by breaking of junctions by drawing the film. The  $b$  value decreased rapidly after  $\Delta l$  exceeded 0.80, that is,  $l_s/l_d$  exceeded 1.20. When  $l_s/l_d$  exceeded 1.50, the swollen films could be drawn up to about  $4l_s$  by breaking small and few junctions.

For the PVA<sub>VTFA</sub> films annealed at temperatures below 125°C, the degree of crystallization increased with an increase in annealing temperature,<sup>8</sup> but the degree of swelling was roughly independent of annealing temperature shown in Figure 5. This suggests that the smaller microcrystals produced in film by the heat treatment and the microcrystals which existed already did not grow. Because the small microcrystals that are produced dissolve easily in water, the degree of swelling is considered to be independent on the annealing temperature below 125°C. The effect of heat treatment is recognized at annealing temperatures above 175°C, that is, larger microcrystals grow or are produced at the annealing temperatures. Therefore, the  $b$  value is greater than 0.1.

As shown in Figure 5, the plot between the swelling ratio and the water temperature can be divided into region I and region II. In the higher temperature range of region I, the swelling ratio was proportional to temperature and the slope was the same for the swollen PVA<sub>VTFA</sub> films annealed at temperatures above 150°C. For the swollen PVA<sub>VTFA</sub> films annealed at temperatures below 125°C, the slope was higher than that for the swollen PVA<sub>VTFA</sub> film annealed at temperatures above 150°C. The increase of swelling ratio for the latter films is attributable to the thermal motion of polymer chains between junctions in response to temperature, whereas for the former films it is attributable to both the dissolution of small microcrystals and the thermal motion of polymer chains between junctions in response to temperature. In the range of 0–25°C, as the initiation time of swelling of films in water decreased steeply with an increase in temperature, the penetrability of water into films is considered to increase with an increase in temperature. Because of this, the swelling ratio increases steeply with increased temperature. In region I, the steep increase of the swelling ratio is attributed to the dissolution of the smaller microcrystals. For the films annealed at 200°C, region II was not observed, that is, the dissolution of junctions scarcely occurs at temperatures below 80°C. Therefore, region B was not found in Figure 4 and a high  $b$  value was obtained, that is, the retardation of film was very slight. This means that larger microcrystals are destroyed by forced drawing even at high temperature. As shown previously,<sup>2</sup> microcrystals in the films annealed at 200°C began to dissolve in water at temperatures above 90°C.

In region B, the plastic deformation is dominant over the elastic one, that is, the junctions are mostly destroyed by forced drawing. The  $d$  value was higher than the  $b$  value and the sum of  $b$  and  $d$  was about one. The high  $b$  value was generally obtained for films elongated at the lower temperatures and for films annealed at higher temperatures. Although the films obtained under those conditions have a large amount of junctions and swelled insuffi-



ciently, drastic drawing was performed. Therefore, considerable large microcrystals are destroyed even in region A.

The elastic behavior of polymer films is influenced by the chain length between junctions, that is, the number of junctions. The stability of films in water is influenced by the size of junctions. Therefore, if the number and size of junctions in swollen PVA<sub>VTF</sub> films are estimated, the elastic behavior of the films in water might be better understood. Work is undertaken in our laboratory to study the size and number of junctions in swollen films.

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