Properties of Syndiotactic-rich Poly(vinyl Alcohol) Thin Film in Water. III. Contraction and Extension of Drawn and Annealed Thin Film in Water

KAZUO YAMAURA and SHUJI MATSUZAWA, *Faculty of Textile Science and Technology, Shinshu University, Ueda-city, Nagano-prefecture 386, Japan*

Synopsis

Contraction and extension behaviors in water for drawn (four times original length) and annealed (at 60–215°C) thin films of poly(vinyl alcohol) (PVA_{VTFA}) derived from vinyl trifluoroacetate have been examined. At a constant temperature of 25°C, drawn films annealed at 60–190°C contracted after a certain standing time. Length of films annealed at 200°C did not change after standing of 20 min and film annealed at 215°C extended very little. As the temperature was raised, the drawn films annealed at 60–190°C contracted further until a certain temperature and then extended. The drawn film annealed at 200°C first started contraction at 70°C. The drawn film annealed at 215°C extended further very little until 75°C and then contracted very little until 99°C (in boiling water). In standing at 99°C, it contracted very little with standing and resisted without breaking for 300 min.

INTRODUCTION

In the previous articles,[1,2] the authors studied the behavior in water of very thin and untreated or annealed/undrawn films of poly(vinyl alcohol) (PVA_{VTFA}) derived from vinyl trifluoroacetate (VTFA) and showed that the untreated thin PVA_{VTFA} film was insoluble in water and obeyed Hooke's law in water below a certain load at 25°C.[1] In this article, contraction and extension behaviors in water for drawn in air and annealed thin PVA_{VTFA} films are examined at a constant temperature and at elevated temperature. The effect of chain orientation-induced crystallization in air on the elastic behavior in water and water resistance for thin PVA_{VTFA} films is investigated.

EXPERIMENTAL

Sample and Films

PVA_{VTFA} sample used in this article is the same sample used in the previous articles.[1,2] PVA_{VTFA} thin films (70 × 150 mm) were made by a casting method on a glass plate from an aqueous solution at room temperature. Thickness of films was about 0.015 mm. The films were cut to a width of 2 mm (length 70 mm). The tape like films were drawn to four times their original length (40 mm) at 60, 80, and 100°C in an air-circulated oven. The drawn films were annealed for 10 min fixing both ends on a glass rod at a film length of 160 mm at 60–215°C. The films annealed at 100–200°C were obtained from the films drawn at 100°C.

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Measurement of Length in Water

The measurement of length of $\mathrm{PVA}_{\mathrm{VTFA}}$ film in water was carried out by the same method shown in the previous article.[1] A load of 1.78, g was used in water. Film lengths were about 76–116 mm.

RESULTS AND DISCUSSION

Contraction at a Constant Temperature of 25°C

Figure 1 shows the changes in film length in water with standing at a constant temperature of 25°C. Drawn films contracted in water at 25°C except the drawn films annealed at 200 and 215°C. The contraction at 25°C initiated after a certain standing time. The penetration of water molecules is considered to bring about the contraction. The initiation time of contraction depends on annealing temperature, that is, it increases with an increase in annealing temperature as shown in Figure 2. After onset of contraction, there is a rapid increase in contraction especially remarkable in the case of drawn films annealed at lower temperatures and then the contraction appears to level off after a certain standing time (time at arrow shown in Fig. 1). The time required for maximum contraction at 25°C, that is, minimum elongation ratio is shown also in Figure 2. Time increases with an increase in annealing temperature until annealing temperature of 170°C and decreases at annealing temperatures over 170°C. In the case of the drawn film annealed at 200°C, the length was constant even after standing 20 min in water at 25°C as shown in Figure 1. Figure 3 shows the relationship between minimum elongation ratio at 25°C and annealing temperature. The minimum elongation ratio at 25°C and annealing temperature. The minimum elongation ratio at 25°C has minimum at an annealing temperature of about 125°C. We have reported that the degree of crystallization and the birefringence for $\mathrm{PVA}_{\mathrm{VTFA}}$ film increased roughly with annealing temperature leading to the plateau in the range of annealing temperature between 100°C and 125°C.[3] Moreover, we have also reported

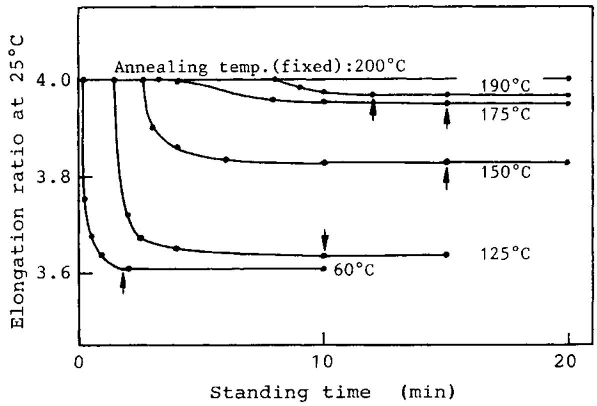

Fig. 1. Effect of annealing temperature on change of film length under load with standing time in water at 25°C for drawn $\mathrm{PVA}_{\mathrm{VTFA}}$ ($DP = 1850$) films.

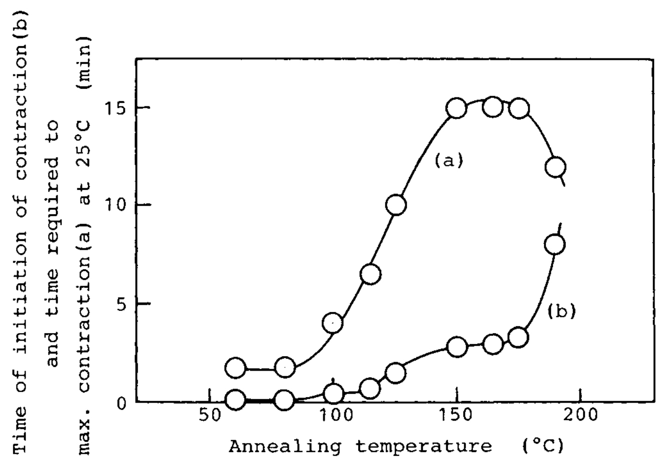

Fig. 2. Relations between initiation time of contraction or time required to maximum contraction in water at 25°C and annealing temperature for drawn PVA$_{\mathrm{VTFA}}$ films.

that the temperature at break in water for undrawn PVA$_{\mathrm{VTFA}}$ films had minimum at an annealing temperature of about 125°C, though it increased roughly with annealing temperature. For films annealed at temperatures below 80°C, reported as a glass temperature, under constant length, first, crystals propagate without melting of microcrystals, and then polymer chains and crystals are oriented. For those annealed at temperatures over 80°C microcrystals melt first, then the polymer chains in amorphous parts are oriented due to fixation of both ends of a film, and further the oriented chains crystallize easily at higher annealing temperature at which sufficient energy for crystallization is supplied. Therefore, in films annealed at 100–125°C there remain longer amorphous chains, and in films annealed at temperatures below 80°C there remains a shorter one; thus even films annealed at 120°C give rise to higher contraction in water.

The film annealed at 215°C extended only very little after standing for a certain time in water at 25°C (Fig. 4). As described above, the length of

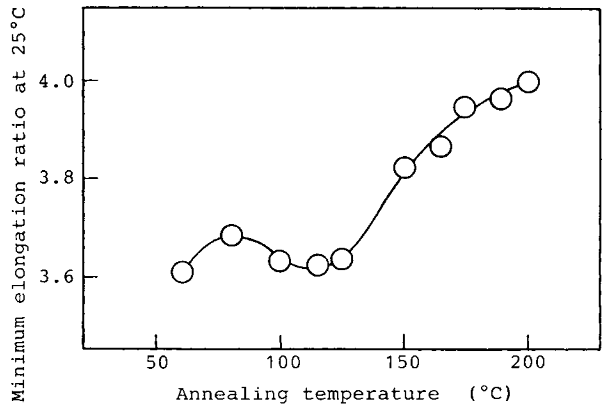

Fig. 3. Relation between minimum elongation ratio in water at 25°C and annealing temperature for drawn PVA$_{\mathrm{VTFA}}$ films.

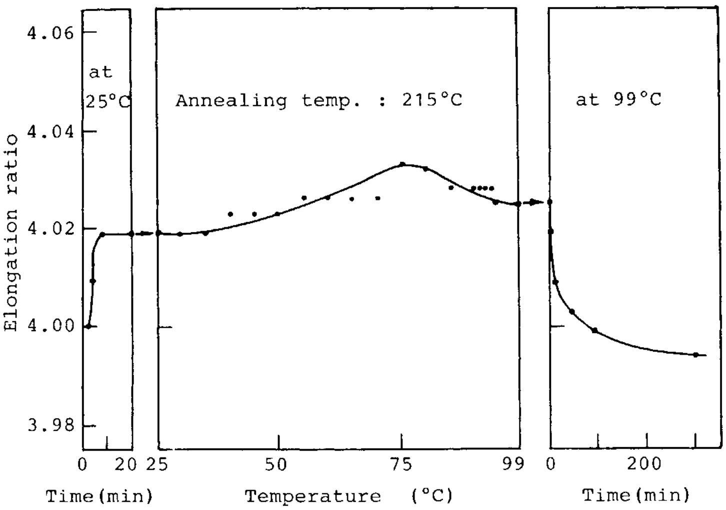

Fig. 4. Changes in film length with standing at a constant temperature of 25°C, in heating at a rate of 0.5°C/min and then with standing at a constant temperature of 99°C (in boiling water) for drawn PVA_{VTFA} films annealed at 215°C.

the films annealed at 200°C was constant in water at 25°C. Therefore, one can consider that very little of the polymer chains in the former film were broken owing to oxidative rupture by annealing at very high temperature in air. This fact must be ascertained by measurement for films annealed in an inert gas.

Contraction and Elongation by Elevation of Temperature

Figure 5 shows the changes in elongation ratio due to the elevation of temperature with a heating rate of 0.5°C/min after the contraction has ceased at 25°C. At first the contraction occurs mildly and then it occurs

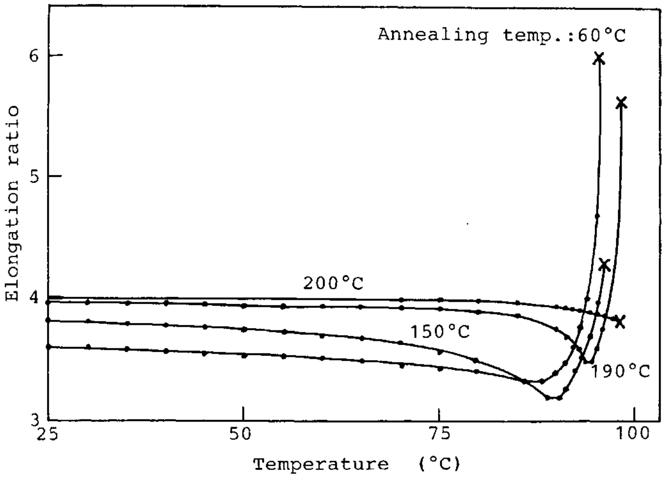

Fig. 5. Change in film length in heating at a rate of 0.5°C/min for drawn PVA_{VTFA} films annealed at 60–200°C.

remarkably except films annealed at 100–125°C. The contraction of PVA_{VTFA} film in water with heating is considered to be brought about by entropy elasticity, that is, rubberlike elasticity. For films annealed at 100–125°C, the elongation ratio decreased in proportion to temperature in heating. The contraction ceases at a certain temperature in heating, film length holds constant for a while, and then elongation initiates. Contraction and elongation are considered to take place simultaneously while film length remains constant. The elongation stops due to breaking at a certain temperature. In the case of film annealed at 200°C, the contraction began at 70°C, but the film broke at 97.7°C without elongating. Therefore, films annealed at temperatures below 190°C have weaker crystals than those annealed at 200°C. The former crystals are considered to dissolve at higher temperatures in heating. In the case of film annealed at 215°C, the film elongates very little until 99°C (see Fig. 4). Since the film does not break at 99°C (in boiling water), it was held in water at constant temperature of 99°C, contracting only very little with standing and did not break even after standing 300 min at 99°C. The change in length in water during heating for PVA_{VTFA} film annealed at 215°C was less than 1% after drawing in air, that is, it was insignificant in comparison to that of PVA_{VTFA} film annealed at temperatures below 200°C (see Figs. 1, 4, and 5). As described above, the drawn films annealed at temperatures below 200°C behave as a elastic material when heated in water up to a certain temperature. Figure 6 shows the relation between temperature of cessation of contraction in heating and annealing temperature. The temperature was constant, that is, about 85°C for drawn films annealed in the range of 60–125°C, and it increased, with an increase in annealing temperature, at annealing temperatures above 150°C. For the drawn films annealed in the range of 60–125°C, the water resistance is not influenced by the annealing temperature. However, the effect of the annealing on the water resistance of the films appears distinct for those annealed at temperatures above 175°C, suggesting the increase in the crystallites with the water resistance and with the annealing temperature.

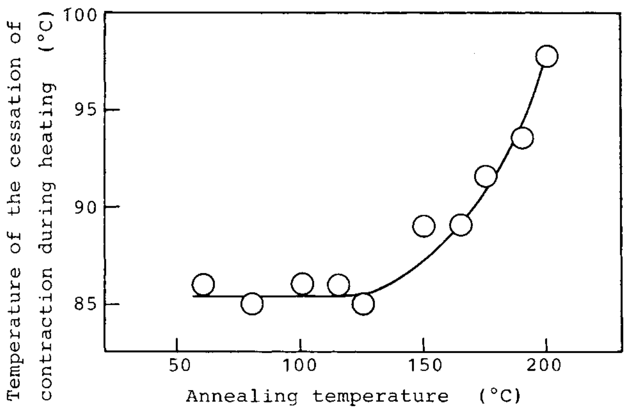

Fig. 6. Relation between temperature of cessation of contraction in heating and annealing temperature for drawn PVA_{VTFA} films.

The temperature at break in water in heating was about 95–96°C for drawn films annealed at temperatures below 175°C, and it was about 98°C for drawn films annealed at 190–200°C. Therefore, crystals in the latter films have higher water resistance than that in the former. For films annealed at temperatures above 175°C, the difference in temperatures at break for drawn films and undrawn films[2] in water was very little (about 1–2°C), but for films annealed at temperatures below 150°C the difference was great (about 4–7°C). There was no or slight difference in degrees of crystallization of undrawn and drawn films.[3] However, the difference in temperature at break was great for films annealed at temperatures below 150°C. Therefore, it is expected that the crystallization under higher orientation of polymer chains plays an important role for water resistance, but the increase in the degree of crystallization is not brought about for films annealed at temperatures below 150°C. When the degree of crystallization exceeds about 50%, temperatures at break in water were about 97–98°C independent of the content of crystals. That is, stable crystals are believed to be produced even in undrawn films annealed at temperatures above 175°C.

Fibers made from commercial poly(vinyl alcohol) ($\mathrm{PVA}_{\mathrm{VAc}}$), derived from vinyl acetate (VAc), are known as vinylon. The $\mathrm{PVA}_{\mathrm{VAc}}$ dissolves in boiling water, even if it has high crystallinity, due to heating accompanied with drawing. Therefore, vinylons of water resistance is improved by the formalization of $\mathrm{PVA}_{\mathrm{VAc}}$ fibers. As described above, however, drawn $\mathrm{PVA}_{\mathrm{VTFA}}$ films annealed at 215°C are resistant to boiling water without formalization. The high water resistance of drawn and annealed $\mathrm{PVA}_{\mathrm{VTFA}}$ films in comparison with that of $\mathrm{PVA}_{\mathrm{VAc}}$ is considered to be due to the longer sequence of intermolecular hydrogen bonding in the films as shown in previous articles.[4,5]

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