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PROPERTIES OF SYNDIOTACTIC-RICH POLY (VINYL ALCOHOL) THIN FILMS IN WATER(PART VIII. ELASTIC BEHAVIOR OF DRAWN/ANNEALED THIN FILM BY REPEATED ELONGATION/CONTRACTION CYCLES IN WATER)

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ABSTRACT

The elastic behaviors of the drawn/annealed thin films for syndiotactic-rich poly(vinyl alcohol), derived from vinyl trifluoroacetate, were studied by the repeated elongation/contraction cycles in water. For the drawn films annealed at temperatures below 125°C, the characteristic of deformation was divided into two regions in all cases, that is, low-elongated and high-elongated regions. The elastic deformation was dominant over the plastic deformation in the low-elongated region and vice versa in the high-elongated region. For the drawn films annealed at temperatures above 150°C, the characteristic of deformation was given roughly the high plastic deformation accompanying with elastic deformation.

1. INTRODUCTION

In the previous papers¹⁻⁷⁾, the authors studied the deformation behaviors of the very thin film of poly(vinyl alcohol) (PVA_{VTFA}) derived from vinyl trifluoroacetate (VTFA) in water under a given load or by repeated elongation and contraction cycles. Sakurada et al.⁸⁾ and Shibata⁹⁾ have investigated thermoelastic behavior for swollen films of radiation-crosslinked poly(vinyl alcohol) (PVA_{VAc}) derived from vinyl acetate (VAc). The elastic behavior in water is unable to study for thin PVA_{VAc} films without crosslinking by chemical reaction. The very thin films of PVA_{VTFA} used in this series have high water-resistance without chemical treatments. We have shown that the undrawn PVA_{VTFA} films annealed at temperatures below 125°C behaved as an elastomer with very low Young's modulus in water at 70°C²⁾. The drawn films which were allowed to reach equilibrium lengths in water at 25°C continued to contract in water until certain temperatures are reached during the elevation of temperature from 25°C³⁾. This fact also shows that the drawn films behaved as an elastomer in water.

The objects of this paper is to clarify the elastic behaviors of the drawn/annealed thin PVA_{VTFA} films and to develop the materials with extensive elastic property.

The deformation behaviors in water of drawn/annealed thin PVA_{VTFA} films were examined by repeated elongation and contraction at fixed temperatures in the range of 0°C to 80°C and were compared with the results described in the previous paper⁶⁾ for the undrawn/annealed films.

2. EXPERIMENTAL

2.1 Sample and films

PVA_{VTFA} derived from VTFA was used as a sample. VTFA monomer was polymerized in bulk at 60°C employing benzoyl peroxide as an initiator. Poly(vinyl trifluoroacetate) was converted to PVA_{VTFA}, by dissolving it in 2,2'-diaminodiethylamine. The degree of polymerization and the content of syndiotactic diad were 1670 and 55.2%, respectively. PVA_{VTFA} thin films (70 × 150 mm) were prepared by casting the aqueous solutions at room temperature on a glass plate. The thickness of the films was about 0.017 mm. The films were cut into 2 mm width (length: 70 mm). The tape-like films (original length: $l_d = 40$ mm) were drawn to three times its original length at 100°C in an air circulated oven. The thickness of drawn films was about 0.011 mm. The whitening of films according to drawing did not occur. The drawn films were annealed for 10 min fixing both

ends on a glass rod at a film length of 120 mm ($3l_d$) at 100–200°C.

2.2 Repeated elongation and contraction

The drawn tape-like films were fixed on a hand drawing machine in the state that the films were relaxed somewhat. A drawn film set to the drawing machine was immersed in water at the fixed temperatures. The initial temperatures were in the range of 0°C to 80°C (every 10°C). The start time of contraction, the time that the contraction ceased (named equilibrium contraction), and the film length at the equilibrium contraction, l_c , were measured. After the contraction ceased, the swollen film was left to stand for 20 min as it was. The degree of swelling (thickness and width) could not be determined because of the rolling tendency into tubes (staples) in water for the films annealed at temperatures below 150°C. The swollen film was elongated to an integer number length in cm nearest l_c named l_1 and then immediately the stress was removed until the film relaxed. Next, the relaxed film was again elongated to a length of $l_1 + 1$ cm and then the stress was immediately removed. Film length at elongation was increased in turn to $l_1 + 1$ cm, $l_1 + 2$ cm, $l_1 + 3$ cm, ...

3. RESULTS AND DISCUSSION

3.1 Equilibrium contraction

For the drawn films annealed at 100–150°C, contraction initiated at standing time of 10–30 min in water of 0°C. For the drawn films annealed at 100–175°C, it initiated at standing time of 5–10 min and 1–5 min in water of 10°C and 20°C, respectively. The induction period of contraction for the drawn films in water of 30–80°C were within 1 min⁻¹ sec. The drawn films contract with swelling to the direction of thickness and width in water. However, the drawn films annealed at 175°C and 200°C did not contract in water for a long time at 0–10°C and 0–20°C, respectively, and they hardly swelled. In general, the induction period of contraction increased with the increase in annealing temperature (T_{ann}) and with lowering of water temperature. The activation energy E_a was obtained by the same method shown in the previous paper³⁾. E_a for the drawn films annealed at 100°C was higher than that for the undrawn films annealed at 100°C, that is, the former and latter values were 35.7 and 31.0 kcal/mol, respectively. The drawing of PVA film in air gives rise to the interference of permeation of

water molecules into the films.

Figures 1–4 show the relations between the film length after the completion of contraction and the temperature of water for the drawn films annealed at 100–200°C. The relation between the equilibrium extension length and the temperature of water for the undrawn films⁶⁾ is for comparison also shown in Figures 1–4. For the drawn films annealed at temperatures below 125°C, the effect of annealing on contraction was not recognized and the film length after contraction was constant at water temperatures below 70°C (Fig. 1). Moreover, considerable plastic deformation occurred by drawing in air (Fig. 1). This is normal behavior for crystalline polymer materials drawn in the solid state, that is, the drawing brings about the propagation of crystals according to the orientation of polymer chains and the slippage in crystals.

In Figures 2–4, the effect of annealing temperatures over 150°C on the equilibrium contraction is shown. The equilibrium contraction depends on the annealing temperature and water temperature. This may be caused by the

Fig. 1 Relations between the film length at equilibrium extension or contraction and the temperature in water for the undrawn or drawn PVA_{VTFA} films annealed at temperatures below 125°C. ○ : undrawn films, original length $l_d = 4$ cm. ● : drawn films, drawn to three times its original length at 100°C in an air circular oven, 12 cm ($= 3l_d$).

Fig. 2 Relations between the film lengths at equilibrium extension or contraction and the temperature in water for the undrawn (○) or drawn (●) PVA_{VTFA} films annealed at 150°C.

Fig. 4 Relations between the film lengths at equilibrium extension or contraction and the temperature in water for the undrawn (○) or drawn (●) PVA_{VTFA} films annealed at 200°C.

Fig. 3 Relations between the film lengths at equilibrium extension or contraction and the temperature in water for the undrawn (○) or drawn (●) PVA_{VTFA} films annealed at 175°C.

propagation of stable crystallites at higher annealing temperatures as pointed out by Sakurada et al.¹¹⁾ from the results of wide and small angle X-ray diffraction patterns for PVA_{VTFA} casting films. For the drawn films

annealed at 200°C, the annealing effect appeared distinctly and the contraction did not take place in water at temperatures below 70°C (Fig. 4).

The drawn films annealed at temperatures below 125°C have many smaller unstable crystallites which do not increase crystallinity with increasing annealing temperature (<125°C). The unstable crystallites dissolve in water accompanying the contraction of the films. The contraction with swelling decreases with increasing annealing temperature above 150°C because of stable crystallites.

3.2 Repeated elongation and contraction

Figures 5-9 show the change in film length in water by repeated elongation and contraction for the drawn thin films annealed at 100, 125, 150, 175, and 200°C, respectively. The repeated elongation and contraction were carried out after standing films in water for 30 min. The symbols a, b, and c in Figure 5 indicate the length of original film, the length after drawing three times its original length in air, and the length (l_c) of equilibrium contraction in water, respectively. In the case of films which contracted highly, the step-wise lines shown in Figures 5-8 are divided roughly into two parts as well as the case of the swollen undrawn films^{5,6)}, that is, A and B regions shown in Figure 5. The slope of re-

Fig. 5 Film length at release l_r versus film length at constrained elongation l_e at 0-70°C in water for the drawn PVA_{VTFA} films annealed at 100°C. a: length of original film (=4 cm). b: drawn length in air (=12 cm). c: length of equilibrium contraction in water.

Fig. 6 Film length at release l_r versus film length at constrained elongation l_e at 0-80°C in water for the drawn PVA_{VTFA} films annealed at 125°C.

Fig. 7 Film length at release l_r versus film length at constrained elongation l_e at 10-80°C in water for the drawn PVA_{VTFA} films annealed at 150°C.

Fig. 8 Film length at release l_r versus film length at constrained elongation l_e at 10-80°C in water for the drawn PVA_{VTFA} films annealed at 175°C.

Fig. 9 Film length at release l_r versus film length at constrained elongation l_e at 0–80°C in water for the drawn PVA_{VTFA} films annealed at 200°C.

gion **A** decreased with the increase in the water temperature and the decrease in the annealing temperatures, respectively. Contrary to this, the width of region **A** increased. These results may be caused by the enhancement of the motion of polymer chains in amorphous regions with the increase in water temperature and by the decrease of amorphous regions induced by the crystallization, respectively. Region **B** is not recognized when there is no or very low contraction, that is, the parts which contribute to equilibrium contraction have a characteristic of elastic deformation. However, the elastic deformation of the drawn films is lower than that⁶⁾ of the undrawn films. Namely, the drawing in air did not promote an elastic property. Figure 10 shows the relations between the ratio of the maximum elastic length, l_m (see Fig. 5), to the equilibrium contraction length, l_c , and the temperature of water. For the films annealed at 100–125°C, no change of elastic property with water temperature is recognized whereas in those at 150°C the elastic property depends strongly on water temperature. The maximum ratio was about 1.9 at 70°C ($l_m/l_c = 16.3 \text{ cm}/8.5 \text{ cm}$). For the untreated PVA_{VTFA} films, the maximum ratio of l_m to the equilibrium swollen length, l_s (see

Fig. 10 Effects of the annealing temperature (●: 100–125°C, ○: 150°C) and the water temperature on the elastic behavior in water for the drawn PVA_{VTFA} films.

Fig. 1), was about 4.1 at 70°C ($l_m/l_s = 25.3 \text{ cm}/6.2 \text{ cm}$)⁶⁾. It is supposed that the amorphous parts decrease due to the crystallization caused by drawing/annealing and that slippage in crystals and the local breakage at the weak regions in film are induced by drawing.

The crystallization caused by drawing/annealing has an effect on ultimate length of films at break in water. The maximum ultimate length was 27 cm (Fig. 8). In the case of the undrawn films, the swollen films did not break even at the length of 32 cm in some cases⁶⁾. The ultimate length at break for the drawn films scatters more widely and is shorter than that for the undrawn films. This is attributed to the generation of local defects in the films and the decrease in number of tie molecules between crystals by drawing.

4. CONCLUSION

The pre-drawing of PVA_{VTFA} films in air did not promote the elastic property in water in comparison with the undrawn PVA_{VTFA} films. For the drawn films annealed at temperatures below 125°C, the characteristic of deformation due to the repeated elongation/contraction in water was divided into two regions in all cases. For the drawn films annealed at 200°C, the plastic deformation was recognized accompanying with elastic deformation from the initial drawing in water and the elastic deformation was still high.

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シンジオタクトに富むポリビニルアルコールの薄膜の水中での性質
(第8報 延伸・熱処理薄膜の水中での繰り返し伸長・収縮による弾性的挙動)

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トリフルオロ酢酸ビニルから誘導したシンジオタクトに富むポリビニルアルコールの延伸・熱処理薄膜の弾性的挙動を、水中での繰り返し伸長・収縮のもとで調べた。125°C以下で熱処理した延伸フィルムでは、水中70°C以下での平衡収縮量は同じで、どの場合も繰り返し変形で二つの領域すなわち低伸長と高伸長領域にわか

れた。低伸長領域では、弾性変形が塑性変形に優先するが、高伸長領域では逆になる。150°C以上で熱処理した延伸物では、水中での平衡収縮量は熱処理温度および水の温度に依存し、また繰り返し変形では弾性変形と塑性変形とが共存した。