

Mechanical Properties of Films of Poly(vinyl Alcohol) Derived from Vinyl Trifluoroacetate

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Synopsis

In order to study the influence of the stereoregularities of polymer chains on the mechanical properties of films of poly(vinyl alcohol) (PVA_(VTFA)) derived from vinyl trifluoroacetate, the strength of the film was measured. In the case of undrawn PVA_(VTFA) films, Young's modulus and strength at break were the smallest at the annealing temperature of about 100°C. It is considered to be due to the melt of small microcrystals and the increase in mobility of chains in amorphous parts. Young's moduli of undrawn PVA_(VTFA) films were in the range of 1.50–3.75 GPa and the values were higher than that (0.17–0.36 GPa) of undrawn film of commercial PVA with the low concentration of syndiotacticity and the high concentration of head-to-head bonds. In the case of drawn, annealed PVA_(VTFA) film, the maximum Young's modulus was about 20 GPa.

INTRODUCTION

It is well known that the film of poly(vinyl alcohol) PVA_(VTFA) derived from vinyl trifluoroacetate (VTFA) has higher water resistance than that of poly(vinyl alcohol) PVA_(VAc) derived from vinyl acetate (VAc).^{1–5} The marked difference in the water resistance depends on stereoregularity of polymer chains, namely, syndiotacticity. From results described above, it is considered that the strength of PVA_(VTFA) film is higher than that of PVA_(VAc). In this paper, the effects of drawing and heat treatment on the mechanical properties for PVA_(VTFA) films have been examined.

EXPERIMENTAL

Sample and Films

The PVA_(VTFA) 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_(VTFA), by dissolving it in 2, 2'-diaminodiethylamine. The degree of polymerization and the contents of syndiotactic diad were 1680 and 55.2%, respectively. The degree of polymerization, DP, was determined from the intrinsic viscosity in benzene of the acetylated PVA_(VTFA) using the formula $[\eta] = 8.91 \times 10^{-3} DP^{0.62}$ (dL g⁻¹, 30°C).⁶ The syndiotacticity of the PVA_(VTFA) was determined from the infrared spectra.⁷

The five films were made by the casting method from an aqueous solution on a framed glass plate (7 × 15 cm) at room temperature. The thickness

of films was about 0.06 mm. The films were cut to a width of 2 mm. Drawn and annealed films were obtained by the following method: The cast films were drawn to suitable times against its original length in an air-circulated oven and in water at 50°C. Annealing was carried out in an air-circulated oven. The annealing under constant length was carried out for 10 min fixing on the glass plate at the film length of 2 cm for the untreated film and on the glass tube at the film length after drawing for the drawn film.

Tensile Test

Tensile tests were performed using a Shinko Model TOM/5 tensile tester at a crosshead speed of 10 cm/min and an original sample length of 20 mm at the temperature of 25°C and under the relative humidity of 65%. The measurement was carried out for the five films obtained under same conditions.

Birefringence and Density

The birefringence Δn of PVA_(VTFA) film was estimated from the retardation determined using a Sénarmont compensator by a Nikon OPTIPHOT-POL polarizing microscope. The density of PVA_(VTFA) film, d , was determined by the floating method of benzene-carbon tetrachloride mixed solvents. The crystallinity, x , was determined from the density of the film using the equation $1/d = x/1.345 + (1 - x)/1.269$.⁸

RESULTS AND DISCUSSION

Undrawn Films

Figures 1 and 2 show the stress-strain curves for the undrawn films. The yield points were not recognized in the low strain region of the stress-strain curves for all those films. The curves have a maximum except for the undrawn films annealed at 100 and 125°C. After the curves exceeded the maximum, they reached a plateau or increase slightly. This is due to the fact that the undrawn films are deformed by necking after the curves exceeded the maximum, that is, the yield point. As described above, two

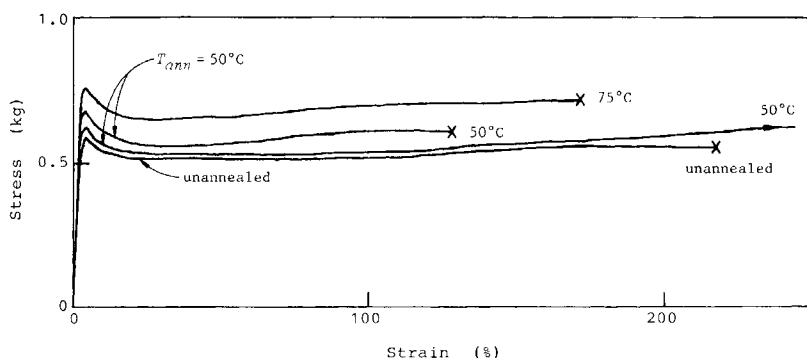


Fig. 1. The stress-strain curves for the undrawn PVA_(VTFA) films.

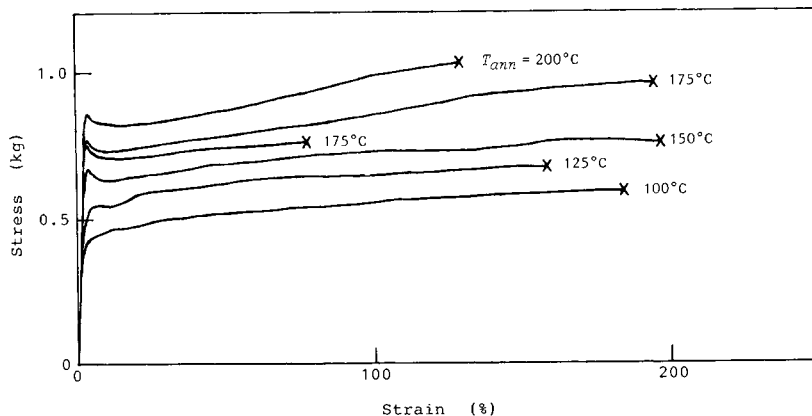


Fig. 2. The stress-strain curves for the undrawn PVA_(VTFA) films.

kinds of the stress-strain curves were obtained from the undrawn PVA_(VTFA) films. PVA has two second-order transition points (80, 120°C).⁹ Figure 3 shows the relations between the degree of crystallization or the birefringence and the annealing temperature. As shown in Figure 3, both the degree of crystallization and the birefringence became a plateau in the

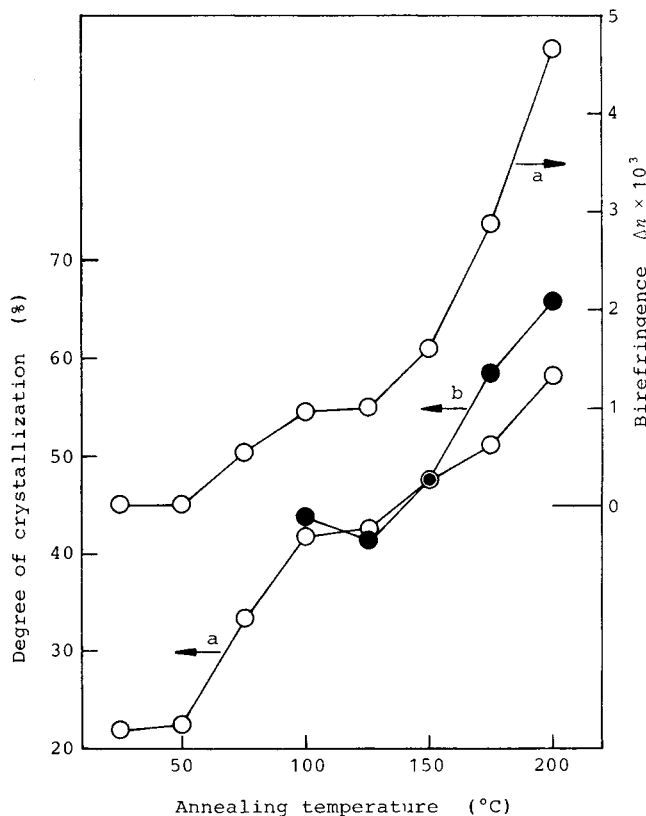


Fig. 3. The relations between the degree of crystallization or the birefringence and the annealing temperature for the undrawn or drawn PVA_(VTFA) films: (a) undrawn; (b) drawn ratio = 5.

range of the annealing temperature between 100 and 125°C. This is due to the fact that the glass transition point of PVA exists at the neighborhood of 80°C. In the range of the annealing temperatures below 80°C, although PVA molecules are in a glassy state, both the degree of crystallization and the birefringence increase with the elevation of annealing temperature. Namely, amorphous parts are incorporated into crystals with the elevation of annealing temperature. So the crystals and chains of residual amorphous parts turn parallel to the direction along the long axis of film fixed at both ends. In the range of the annealing temperatures above 80°C, the propagation of crystals and the destruction of microcrystals occur competitively according to the increase in mobility of amorphous parts. The incorporation of amorphous parts into crystals is considered to be influenced by the chain orientation of amorphous parts and the energy required to crystallization. When the annealing temperature is over 125°C, both the degree of crystallization and the birefringence increase steeply with the elevation of annealing temperature; therefore, sufficient energy for the crystallization is given to amorphous parts at annealing temperatures over 125°C. In the range of the annealing temperatures between 100 and 125°C, as the weak microcrystals are destroyed, the longer chains of amorphous parts remain unchanged. Figure 4 shows the relations between the Young's modulus, the

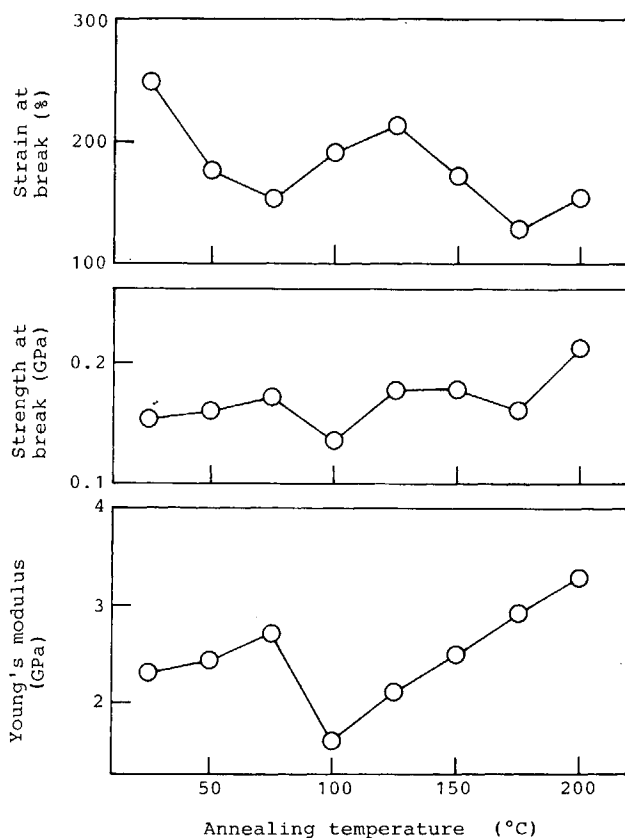


Fig. 4. The relations between the Young's modulus, the strength at break or the strain at break, and the annealing temperature for the undrawn PVA_(VTFA) films.

strength or the strain, and the annealing temperature. As shown in Figures 1 ($T_{ann} = 50^{\circ}\text{C}$) and 2 ($T_{ann} = 175^{\circ}\text{C}$), no similar stress-strain curves are obtained for samples annealed at same conditions. Therefore, the values shown in Figure 4 are mean values for five films. Generally, the Young's modulus and the strength are considered to increase with the elevation of the annealing temperature and the strain decreases in reverse. However, in the case of undrawn $\text{PVA}_{(\text{VTFA})}$ film, the Young's modulus and the strength are the smallest at the annealing temperature of 100°C and the strain is largest at the annealing temperature of 125°C . These results give support to the concept described above. This should be confirmed by other measures. Therefore, we shall continue the study on this point in future. The value at break in water for thin, undrawn $\text{PVA}_{(\text{VTFA})}$ film was also smallest at the annealing temperature of 125°C .¹⁰

Undrawn $\text{PVA}_{(\text{VTFA})}$ films unannealed or annealed at the temperatures below 150°C whiten in drawing by the tensile tester. The whitening occurs after necking, that is, in the plateau parts of Figures 1 and 2. Moreover, Young's modulus of undrawn $\text{PVA}_{(\text{VTFA})}$ films was in the range of 1.50–3.75 GPa and the values were higher than that (0.17–0.36 GPa)¹¹ of undrawn film of commercial PVA.

Drawn Films

In the case of undrawn $\text{PVA}_{(\text{VTFA})}$ films, the necking occurs as shown in Figures 1 and 2. Their films break already before the completion of necking.

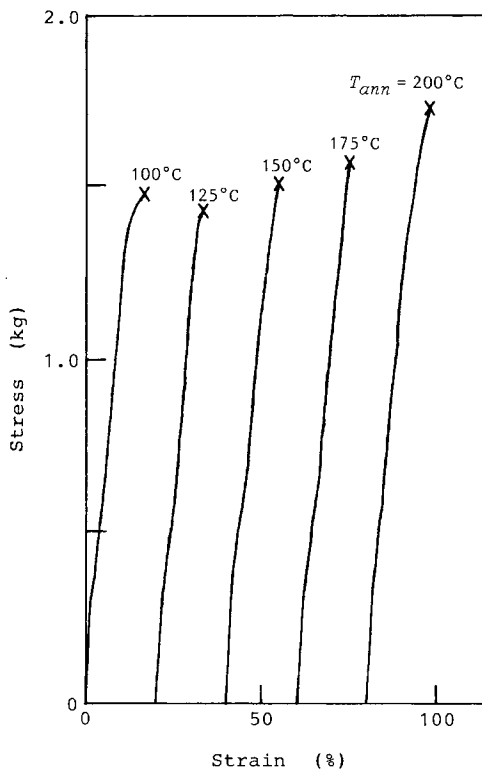


Fig. 5. The stress-strain curves for the drawn $\text{PVA}_{(\text{VTFA})}$ films (draw ratio = 5).

However, if the strain reaches to about 300%, necking parts are lost from the films. Therefore, in this section $PVA_{(VTFA)}$ films drawn to over four times its original length at 100°C were used. The maximum elongation of $PVA_{(VTFA)}$ film was 6.8 times at 100°C in air and 8 times at 50°C in water. $PVA_{(VTFA)}$ film breaks over their magnification. Figure 5 shows the stress-strain curves for $PVA_{(VTFA)}$ films drawn five times. The plateau parts found in the stress-strain curves of the undrawn $PVA_{(VTFA)}$ films (Figs. 1 and 2) were not recognized in the case of the drawn $PVA_{(VTFA)}$ films, but in the curves the yield point was recognized clearly. Figure 6 shows the relations between the birefringence, the strain at break, the strength at break or Young's modulus, and the annealing temperature for the $PVA_{(VTFA)}$ films drawn five times. The relation between the degree of crystallization and the annealing temperature for the $PVA_{(VTFA)}$ films drawn five times are already shown in Figure 3. The degree of crystallization was the lowest at the annealing temperature of 125°C and increases with the elevation of

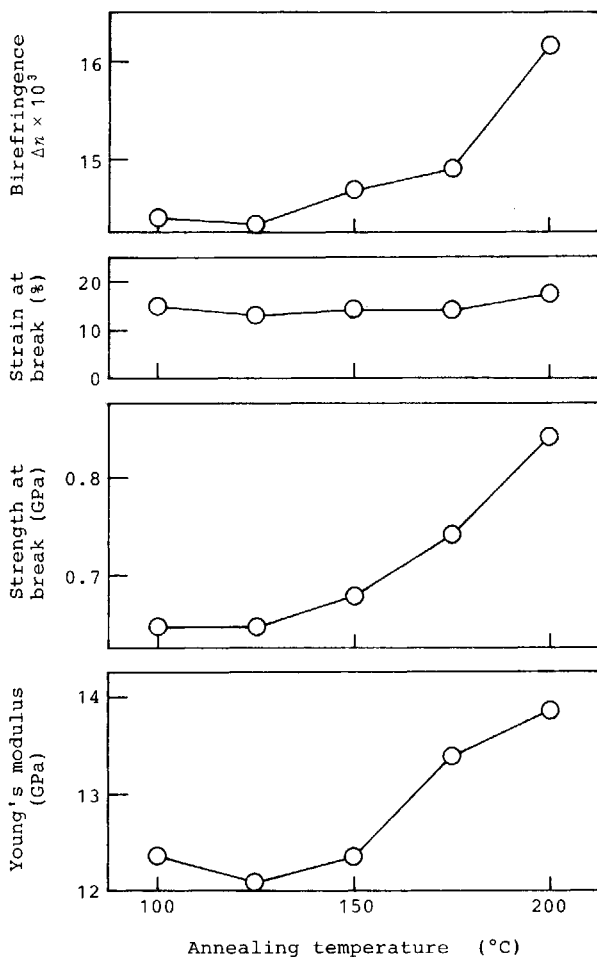


Fig. 6. The relations between the birefringence, the Young's modulus, the strength at break or the strain at break, and the annealing temperature for the drawn $PVA_{(VTFA)}$ films (draw ratio = 5).

nealing temperature at the annealing temperature above 125°C. The degree of crystallization increases about 25% with the elevation of annealing temperature from 100 to 200°C, but the increase in birefringence is small. The degrees of crystallization for the undrawn and drawn PVA_(VTFA) films were roughly equal at the annealing temperature between 100 and 150°C, but at the annealing temperatures above 175°C the degree of crystallization of latter was higher than that of former. The strength at break and Young's modulus increased slightly with the elevation of annealing temperature, but the strain at break was independent on it and about 15%.

Figure 7 shows the relations between the birefringence or the strength at break and the draw ratio and Figure 8 shows the relations between the Young's modulus or the strength at break and the draw ratio for the PVA_(VTFA) films drawn preliminarily in air or water and annealed at 200°C. Although the drawing in water (8 times) is higher than that in air (6.8 times), the birefringence of former films is lower than that of latter and the strain at break is the opposite. Namely, for drawing in water the slip in crystals is considered to occur. The mean values of Young's modulus and the strength at break at the annealing temperature of 200°C and the elongations of 6.8 times in air and 8.0 times in water about 17.3 and 0.85 GPa and 16.9 and 0.87 GPa, respectively. The maximum value of Young's modulus for PVA_(VTFA) film in this experiment was about 20.0 GPa. The maximum Young's modulus of normal vinylon filaments was about 9.5 GPa.¹² The physical properties of PVA is considered to be influenced by the stereoregularity of polymer chain, the 1, 2-glycol content in main chain and the branching, etc. The syndiotacticity of PVA_(VTFA) is higher than that of PVA_(VAc),⁴ and the 1, 2-glycol content¹ and the branching¹³ of PVA_(VTFA) are lower than that of PVA_(VAc). Recently, it was reported that the thermal

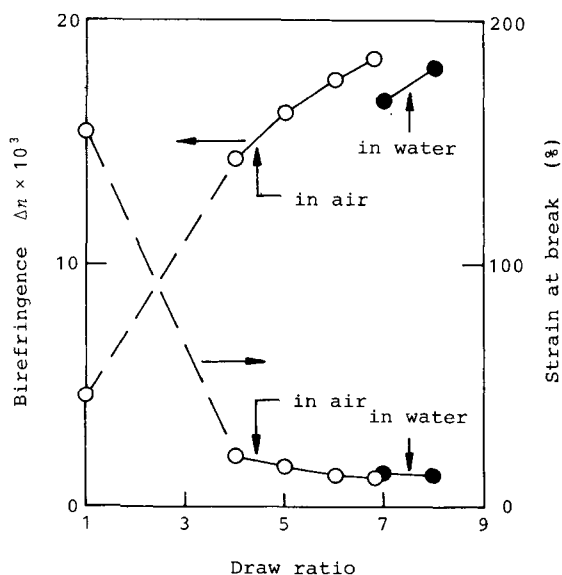


Fig. 7. The relations between the birefringence or the strain at break and the draw ratio for the PVA_(VTFA) films annealed at the temperature of 200°C.

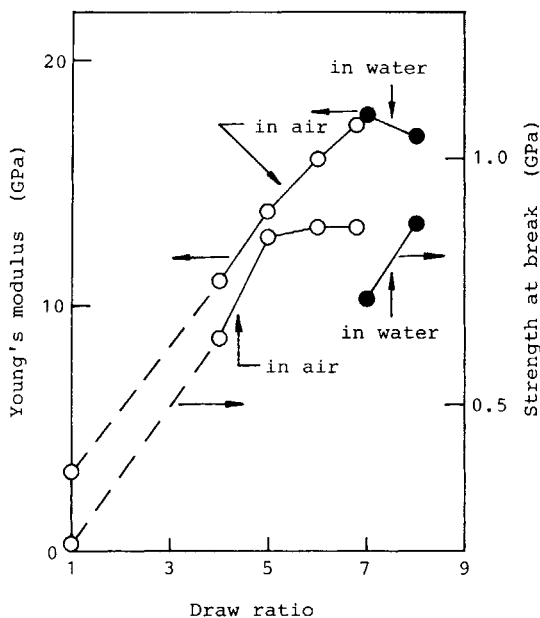


Fig. 8. The relations between the Young's modulus or the strength at break and the draw ratio for the PVA_(VTFA) films annealed at the temperature of 200°C.

expansion coefficients for crystals in PVA_(VTFA) were smaller than that those in PVA_(VAc) and that the formation of the intermolecular hydrogen bonds was hindered by the molecular configuration such as the high concentration of the head-to-head linkage and the low syndiotacticity.^{14,15} Therefore, the higher strength of PVA_(VTFA) film is considered to be due to the high syndiotacticity, high linearity, and low disorder of main chain.

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