

Properties of Syndiotacticity-rich Poly(vinyl Alcohol) Thin Film in Water. II. Effect of the Annealing Temperature on the Extension of Thin Film in Water

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Synopsis

The effect of the annealing temperature on the extension of thin film of syndiotacticity-rich poly(vinyl alcohol)(PVA_{VTF}) derived from vinyl trifluoroacetate is investigated in water. For the samples annealed at the temperature of above 125°C, the time of initiation of elongation and Young's modulus increase steeply with the elevation of annealing temperature, and the time required to maximum elongation and the maximum elongation ratio decrease quietly. The elongation ratio at break during the elevation of temperature of water decreases with the increase in the annealing temperature, that is, from 6.5 to 1.5. Reversely, the temperature at break increases from 85 to 97°C, but it is minimum at the annealing temperature of 125°C.

INTRODUCTION

Poly(vinyl alcohol) (PVA_{VTF}) derived from vinyl trifluoroacetate (VTF) has been well known to have the high water-resistance in comparison with commercial PVA.¹⁻⁶ In the previous paper,⁷ authors also showed that even the very thin, untreated film of PVA_{VTF} has considerable high water resistance.

Generally, the crystalline polymers can be heightened in the degree of crystallization and the mechanical properties by the heat treatment. In this paper, the effect of the annealing temperature on the extension of PVA_{VTF} thin film in water is investigated and in addition a few properties of annealed PVA_{VTF} thin film in air are shown.

EXPERIMENTAL

Sample and Film

The PVA_{VTF} sample used in this paper is the same sample used in the previous paper.⁷ The degree of polymerization and the content of syndiotacticity in diad were 1850 and 56.2%, respectively. The thin film was made by the same method shown in the previous paper.⁷ The heat treatment of film was carried out in air for 10 min fixing both ends of film at the length of 5.7 or 6.0 cm.

Birefringence and Density

The birefringence Δn of PVA_{VTFA} film was estimated from the retardation determined using a SÉNARMONT compensator by the polarizing microscope of NIKON OPTIPHOT-POL. The density of PVA_{VTFA} film was determined by the floating method in benzene-carbon tetrachloride mixed solvents.

Measurement of Length of Film in Water

The measurement of length of PVA_{VTFA} film in water was carried out by the same method shown in the previous paper.⁷ The thickness and width of film in air were about 0.015 mm and about 2 mm, respectively. In the previous paper,⁷ authors have recognized that the relation between the load and the elongation for the untreated film of the same sample coincides with Hooke's law in the range of loads 0.9–4.4 g. Therefore, in this paper, the load of 1.78₁ g was used in water.

RESULTS AND DISCUSSION

Properties of PVA_{VTFA} Film in Air

Unfixed, Heated Film

The retardation of square, unfixed film appeared hardly even by the heat treatment. The degree of crystallization of PVA_{VTFA} film was reported to increase with the elevation of annealing temperature.⁸ Therefore, the occurrence and growth of crystals in the square, unfixed film make an isotropic progress, and the direction of molecular chains in film is random. The retardation of rectangular, unfixed film is appeared by the heat-treatment. Figure 1 shows the change of the degree of orientation with the elevation of annealing temperature for the rectangular, unfixed film. The degree of

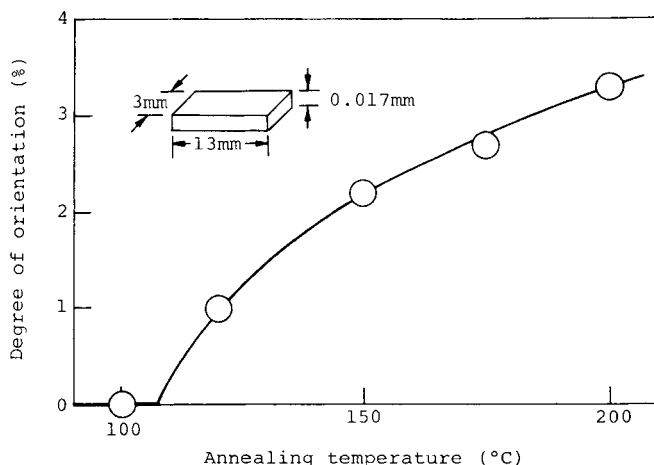


Fig. 1. The effect of the annealing temperature on the degree of orientation to the direction of length for unfixed, annealed PVA_{VTFA} (DP = 1850) films.

orientation of polymer chain in film was obtained by the connection of the birefringence obtained in this paper and the results of Okajima et al.⁹ Until the annealing temperature about 100°C, the degree of orientation is zero. At the temperature above 125°C, it increases slightly with the elevation of annealing temperature. The thickness of the rectangular, unfixed film increases with the elevation of temperature and the width decreases. The anisotropic change of shape of film is considered to lead to the orientation of polymer chains.

Fixed, Heat-Treated Film

Figure 2(a) shows the change of the width of film with the elevation of annealing temperature for the fixed film (film length 5.7 cm). The annealing time is 10 min at the fixed temperature. The thickness of film increases with the elevation of annealing temperature and the thickness of film annealed at 200°C was about 1.13 times as large as that of untreated film. The width of film annealed at 200°C decreases to about 70% as large as that of untreated film. At the annealing temperatures between 80 and 125°C, the decrease of the width of film with the elevation of annealing temperature is slow. Figures 2(b) and 3 show the changes of the birefringence and the degree of crystallization with the elevation of annealing temperature, respectively. Both the birefringence and the degree of crystallization increase with the elevation of annealing temperature, but their increase is quiet in the range of annealing temperatures between 80 and 125°C. Kenney and Willcockson¹⁰ have reported that the temperatures of 62 and 133°C correspond to the glass transition and lattice variation, respectively. Therefore, the molecular motion of amorphous part is enhanced in the range of annealing temperature between 80 and 125°C.

In the case of the fixed film, the degree of orientation for PVA_{VTFA} film heat-treated at the temperature of 200°C was about 16%. As shown in Figure

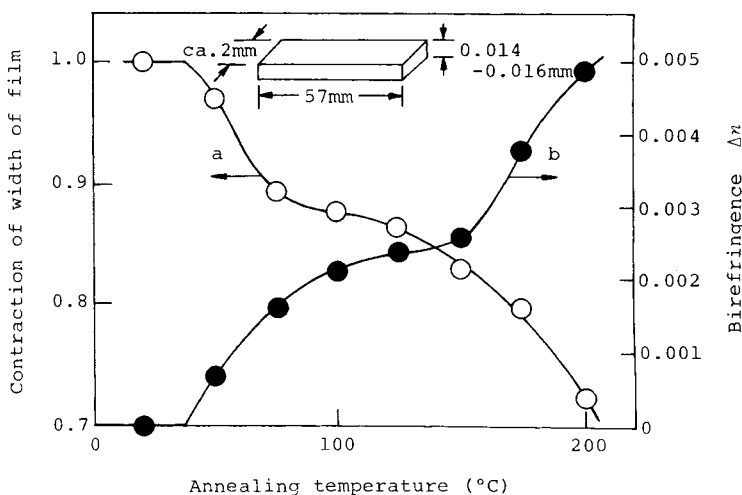


Fig. 2. The effect of the annealing temperature on the contraction to the direction of width of film and the birefringence for fixed, annealed PVA_{VTFA} films.

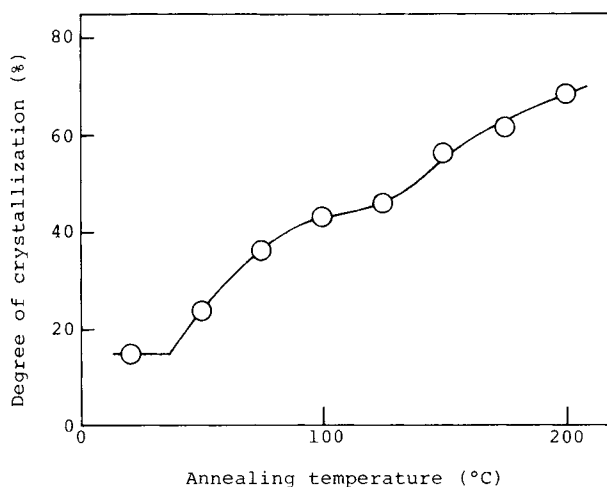


Fig. 3. The relation between the degree of crystallization and the annealing temperature for PVA_{VTFA} films shown in Figure 2.

1 for the rectangular, unfixed PVA_{VTFA} film annealed at the temperature of 200°C, it was about 3%. The degree of crystallization for former is about 67% and for the latter about 57%.⁸ These results are due to the fact that the former film cannot contract to the direction of length. Figure 4 shows the polarizing micrographs for the rectangular, untreated film [Fig. 4(a)] and for the rectangular, fixed film annealed at the temperature of 218°C [Fig. 4(b)]. PVA_{VTFA} films are inclined 45° to polarizers. The latter [Fig. 4(b)] shows clearly the orientation of polymer chain to the direction of length. Even for the former, the birefringence appears in both sides of film. This

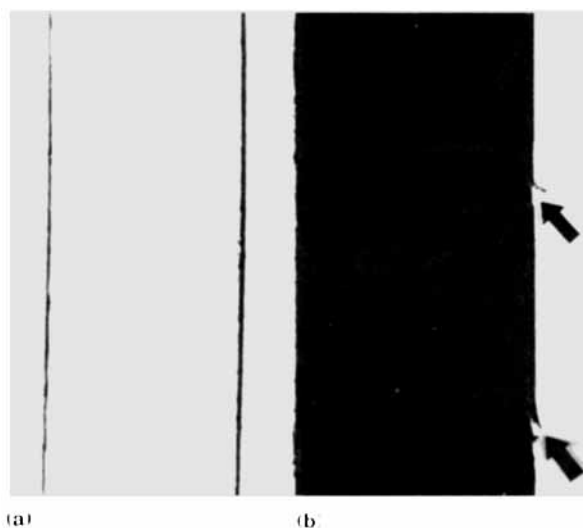


Fig. 4. The micrographs of PVA_{VTFA} films observed between crossed polarizers (samples inclined 45° to polarizers). (a) untreated film; (b) film annealed at 218°C under fixing both ends (the right side of film was cut after annealing).

is due to the orientation of polymer chains by the stress during the cutting of film. The cracks on the right hand side of the fixed film [Fig. 4(b)] is due to the cutting after the heat treatment. Therefore, all the film used to measure the film length in water was cut before the heat treatment.

Properties of PVA_{VTFA} Film in Water

The Extension at the Fixed Temperature of 25°C

Figure 5 shows the change of film length with standing time. The stretch does not occur until any standing time, over that time it occurs suddenly, steeply, and then quietly. The time of initiation of elongation [Fig. 6(a)], the time required to maximum elongation [Fig. 6(b)], and the maximum elongation ratio [Fig. 7(a)] are dependent on the annealing temperature. At the annealing temperatures of above 125°C, the time of initiation of elongation increases steeply with the elevation of annealing temperature, and the time required to maximum elongation and the maximum elongation ratio decrease quietly. This is due to the orientation of polymer chain [Fig. 2(b)] and the crystallization (Fig. 3). As described in the previous paper,⁷ considering the diffusion of water molecules from both sides of film and postulating that the initiation of elongation first occurs after the perfect diffusion to whole of film, the rate of diffusion of water molecules for the untreated film is about 8.5×10^{-5} cm/s and for the film heat-treated at 200°C 1.6×10^{-5} cm/s, the rate of diffusion decreasing with the elevation of heating temperature. The orientation of polymer chains in the amorphous parts, the intermolecular hydrogen bonds in the amorphous parts and the propagation of crystals interfere with the permeation of water molecules into the film.

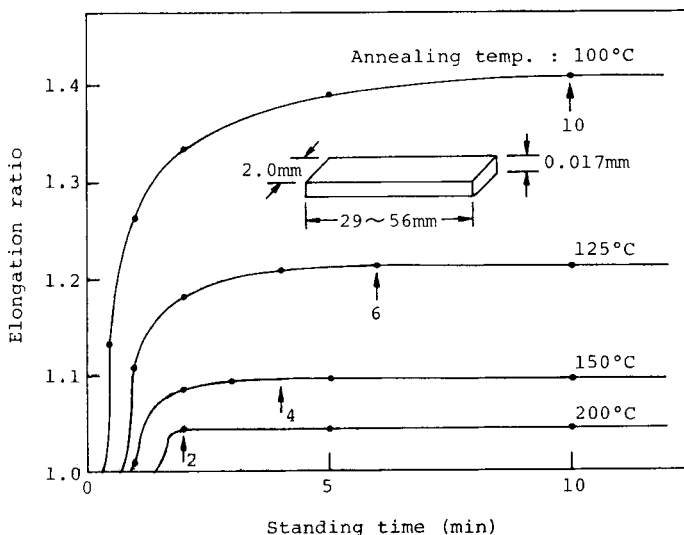


Fig. 5. The effect of the annealing temperature on the change of film length with the standing time in water at 25°C and a load of 1.78_g for PVA_{VTFA} films annealed fixing both ends of film at the length of 6.0 cm.

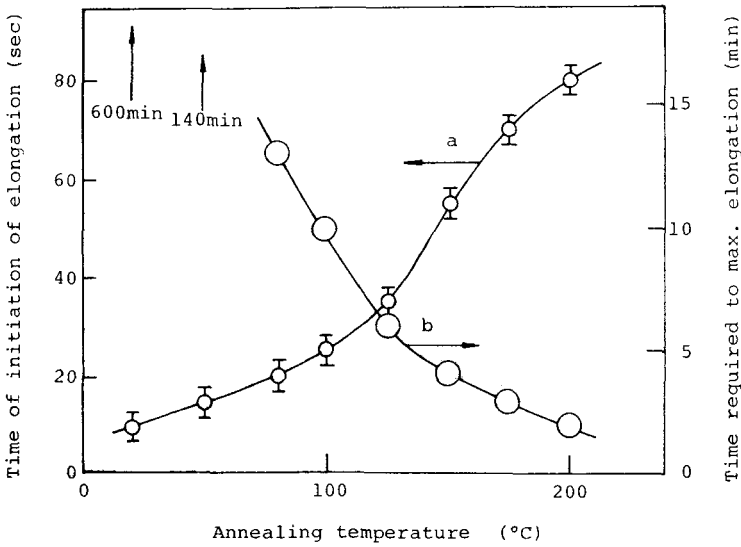


Fig. 6. The effect of the annealing temperature on the time of initiation of elongation or the time required to maximum elongation for PVA_{VTFA} film in water at 25°C.

For the samples heat-treated at low temperature, the time required to maximum elongation is considerably long. This is due to the complicated entanglement in amorphous regions of film. The stretch of film in water occurs uncoiling the entanglements. For the samples heat-treated at high temperature, the entanglements are inserted tightly into the crystals owing to the orientation of polymer chains and the propagation of crystals. Therefore, the entanglements are not uncoiled satisfactorily even by the permeation of water molecules into the film.

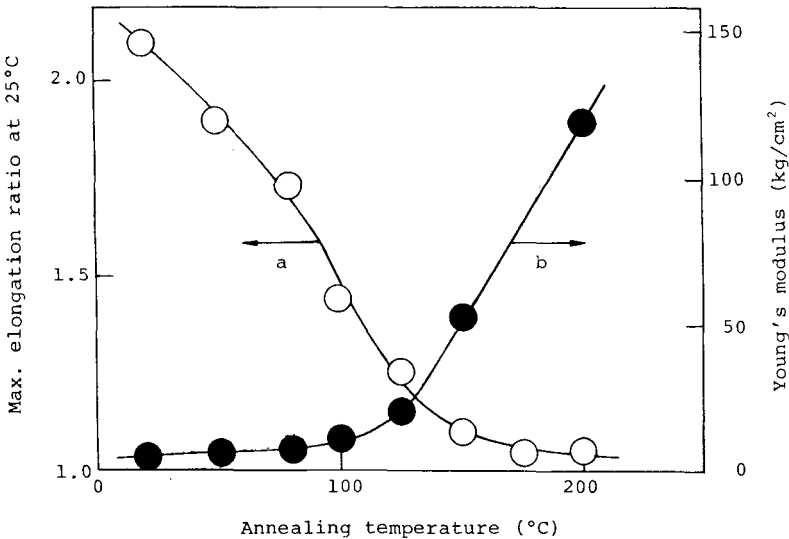


Fig. 7. The effect of the maximum elongation ratio on the annealing temperature, and the relation between Young's modulus and the annealing temperature for PVA_{VTFA} film in water 25°C.

Figure 7(b) shows the relation between Young's modulus and the annealing temperature for the film in water at 25°C. The cross section of film obtained from the dried film in air was used in order to evaluate Young's modulus. Young's modulus increases with the elevation of annealing temperature, especially suddenly over the annealing temperature of 125°C.

The Extension by the Elevation of Temperature

Figure 8 shows the changes of the elongation ratio by the elevation of temperature with the heating rate of 5°C/10 min after the elongation has ceased at 25°C. It was analogous to the curves shown in the previous paper.⁷ Namely, first the elongation occurs remarkably in the range of temperatures between 35 and 45°C, and then it occurs mildly in the range of temperatures between 45 and 60°C. Following the subsequent elevation of temperature, it occurs more remarkably than that in the range of temperatures between 35 and 45°C. For the samples heat-treated at higher temperatures, the appearance is not distinct, but it is recognized by the magnification of Figure 8. Such a result is consistent with that for the changes of the bending or shear moduli of aqueous PVA_{VTF} gel,^{11,12} produced at lower temperatures. The modulus decreases until about 30°C, increases in the range of temperature between 30 and 60°C and then decreases again above about 60°C. The decreases in modulus are considered to correspond to the dissolution of microcrystals that constitute the networks of gel and the increases in modulus are considered to correspond to the production and propagation of microcrystals. Such a dissolution and production of microcrystals in film are considered to correspond to the remarkable increase and the mild increase in elongation, respectively.

Figure 9 shows the relations between the temperature at break [Fig. 9(a)] or the elongation ratio at break [Fig. 9(b)] and the annealing temperature.

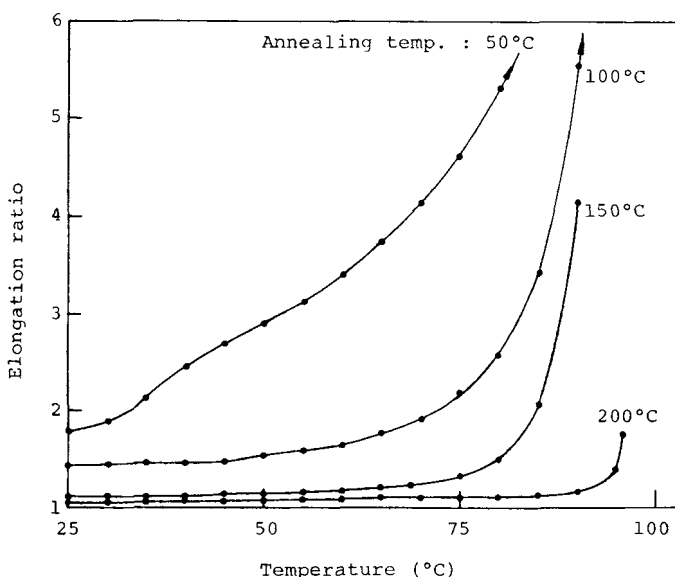


Fig. 8. The effect of the annealing temperature on the change of the elongation ratio of PVA_{VTF} films in heating water at a rate of 0.5°C/min.

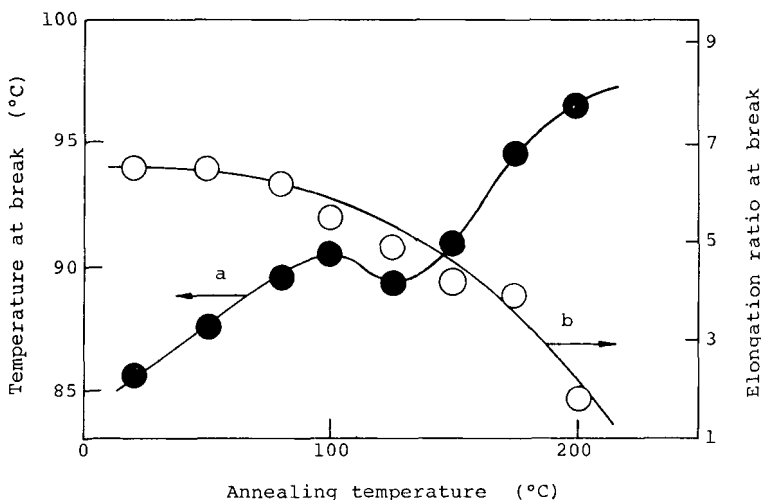


Fig. 9. The effect of the annealing temperature on the temperature at break or the elongation ratio at break for PVA_{V_{TFA}} films in heating water.

For the heat-treated films at lower temperatures, the elongation ratio at break is about 6.5–6.0, but at the annealing temperature of 200°C it is extremely low. In the contrary, the temperature at break increases with the increase in the annealing temperature from 85 to 97°C, but it is minimum at the annealing temperature of 125°C. As described in previous section, in the range of annealing temperatures between 62 and 133°C both the orientation of polymer chain and the crystallization of amorphous parts can occur, but the former occurs preferentially and crystals produced in amorphous parts are very few. Especially, in the case of the sample annealed at the temperature of about 125°C the behavior is considered to occur preferentially.

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