Properties of Syndiotactic-Rich Poly(vinyl Alcohol) Thin Film in Water. V. Effect of Initial Temperature of Heating on Elongation

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Synopsis

The effect of the initial temperature of heating on the elongation of syndiotactic-rich poly(vinyl alcohol) thin films was investigated in water under a load. The elongation ratios E_i after 4 h at fixed temperatures increased roughly with an increase in the initial temperature T_i and a decrease in the annealing temperature. E_i after 4 h was the smallest at $T_i = 45°C$ for the films annealed at temperatures below 100°C. E_i was 6.8 at $T_i = 60°C$ for the unannealed film and 1.12 at $T_i = 70°C$ for the film annealed at 200°C. The elongation at break decreased and the temperature at break increased with an increase in annealing temperature, but those at the annealing temperature of 100°C were the smallest. The films annealed at 200°C did not break even at 98°C (boiling temperature) in water and the elongation ratio was 1.42–1.97 in the initial temperature range of 10–70°C. From these results, the relation between the elongation in water and the state of polymer chains in film was discussed.

INTRODUCTION

Poly(vinyl alcohol) (PVA_{VTFA}) derived from vinyl trifluoroacetate (VTFA) has been well known to have high water resistance in comparison with commercial PVA.[1,2] Very thin unannealed PVA_{VTFA} film was able to withstand up to 76–90°C whereas the films annealed at 200°C did not break up to 98°C in water under load.[3,4] Further, very thin PVA_{VTFA} films elongated to four times its original length and then annealed at 215°C did not break in boiling water under load.[5] The untreated PVA_{VTFA} film obeyed Hooke's law in water below a certain load at 25°C. The film reached to an equilibrium length under the low load at 25°C elongated again with increasing temperature, though the elongation was slight in the range of 45–60°C.[3] The mild increase in elongation with increasing temperature was explained by the production of microcrystals in film, based on the studies of the temperature dependency of bending or shear moduli of PVA_{VTFA} hydrogels.[6,7]

To clarify the abnormal elongation behavior around 50°C, we chose the temperatures between 10 and 70°C (every 5°C) as the initial temperature and measured the elongation in water for very thin unannealed and annealed PVA_{VTFA} films.

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EXPERIMENTAL

Sample and Films

The PVA$_{\mathrm{VTFA}}$ sample and PVA$_{\mathrm{VTFA}}$ thin films were made by the same method described in the previous papers.[3-5,8] The thickness and width of films were about 18 μm and 2 mm, respectively.

Measurement of Length in Water

The measurement of length of PVA$_{\mathrm{VTFA}}$ film in water was carried out as previously described.[3-5] A load of 1.781 g was used in water. Film lengths were 18–40 mm.

RESULTS AND DISCUSSION

Elongation at Constant Temperature

Figure 1 (left side) shows the changes in the length of untreated PVA$_{\mathrm{VTFA}}$ thin film in water at various temperatures between 15 and 55°C with standing time. The initiation time of elongation t_e under the load depended on the temperature in the initial temperature range of 10–35°C for the unannealed and annealed PVA$_{\mathrm{VTFA}}$ thin films in water. The activation energy ΔE_a for the initiation time of swelling was estimated from the plots of the logarithm of $1/t_e$ against the reciprocal T_i. The value of ΔE_a for films annealed at temperatures below 150°C was 25.1 kcal/mol and for films annealed at temperatures over 175°C, 34.2 kcal/mol. The value of ΔE_a for the unannealed PVA$_{\mathrm{VTFA}}$ films under free load was 30.3 kcal/mol.[8] The ΔE_a obtained in the previous paper[8] is higher than that obtained in this paper for the same PVA$_{\mathrm{VTFA}}$ film. The difference is caused by the difference in the state of load.

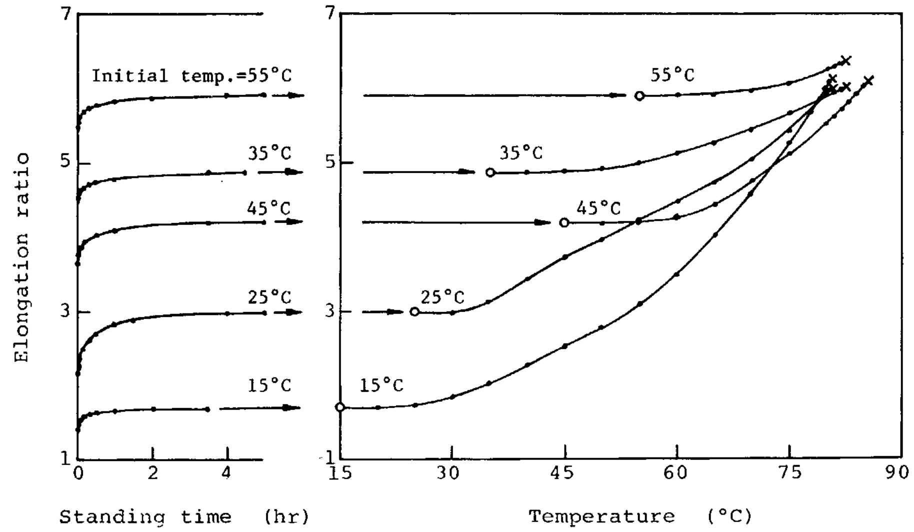

Fig. 1. Changes in film length of PVA$_{\mathrm{VTFA}}$ at various initial temperatures and at increasing temperature in water.

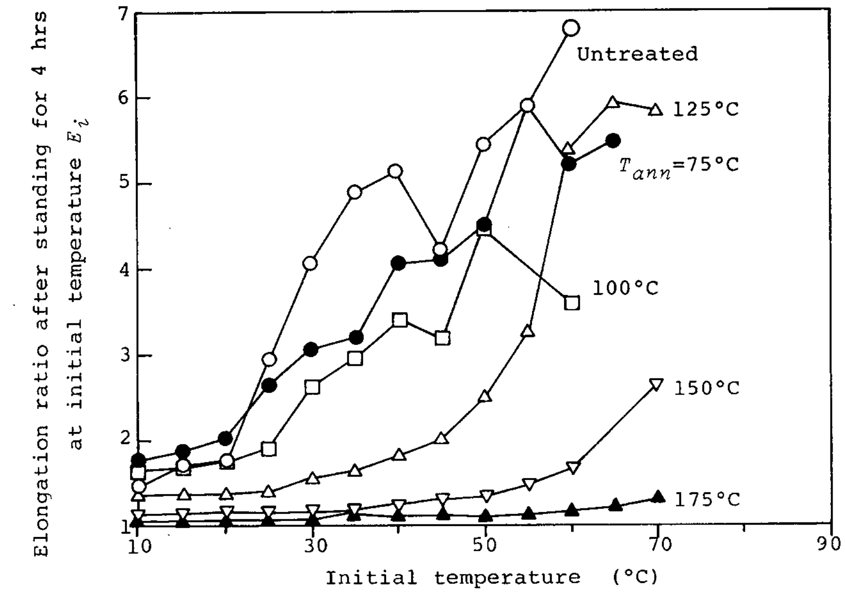

Fig. 2. Relation between the elongation ratio and the initial temperature in water for PVA_{VTFA} film annealed at various temperatures.

The value of t_e at initial temperatures over 40°C was roughly zero irrespective of unannealed and annealed films. The equilibrium length was reached after 4 h at each initial temperature. Figure 2 shows the relation between the elongation ratio E_i after 4 h and the initial temperature T_i. E_i increased with an increase in the initial temperature, but the increase was slight in the vicinity of T_i = 45°C for the films annealed at temperatures below 100°C. For the unannealed films E_i was the smallest at T_i = 45°C. This is discussed in detail below.

The value of equilibrium E_i at T_i = 60°C was about 6.8 for the unannealed PVA_{VTFA} film as shown in Figure 2. For the unannealed PVA_{VTFA} film in air the highest elongation ratio was about 6.8 at 100°C.[9] For PVA_{VTFA} films annealed at temperatures below 125°C, E_i was considerably higher at T_i values over 60°C. For PVA_{VTFA} film annealed at temperatures over 150°C, E_i was low, and for PVA_{VTFA} films annealed at 175 and 200°C, E_i values of 1.07–1.29 and 1.07–1.12, respectively, were obtained. Thus, annealing at temperatures over 175°C would result in a structure formation that is able to withstand water, and it is considered to reflect the activation energy as described above.

Elongation with Increasing Temperature

Figure 1 (right side) shows the changes in elongation for the unannealed PVA_{VTFA} film at the heating rate of 0.5°C/min after the elongation has ceased at various initial temperatures. In the case of initial temperatures below 30°C, significant elongation occurred in the range of 30–45°C and less elongation occurred in the range of 45–55°C. At increased temperature, significant elongation occurred again. However, in the case of initial tempera-

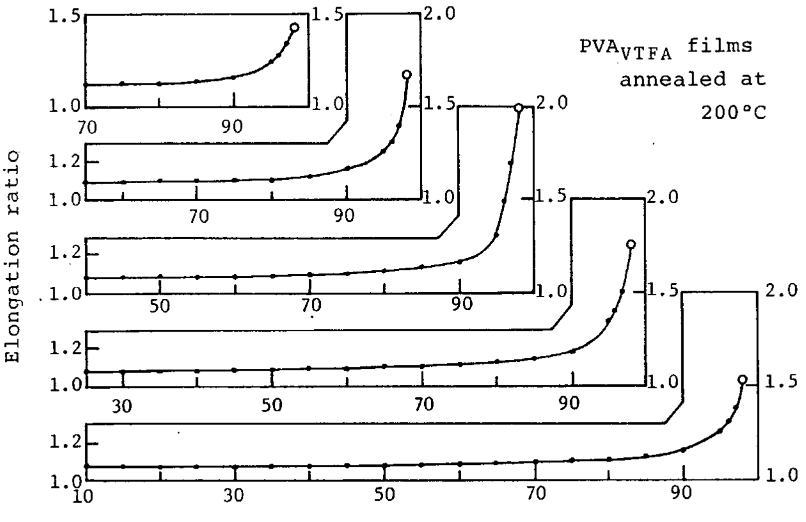

Fig. 3. Changes in film-length with increasing temperature for PVA$_{VTFA}$ film annealed at 200°C. Initial temperature differs (10, 25, 40, 55, and 70°C).

tures over 35°C, no or slight elongation occurred up to a certain temperature beyond which significant elongation occurred. For the annealed PVA$_{VTFA}$ films, the abnormal elongation found for the unannealed PVA$_{VTFA}$ film scarcely appeared. These films finally broke at certain high temperatures. Figure 3 shows the changes in elongation ratio for PVA$_{VTFA}$ films annealed at 200°C with increasing temperature after the elongation has ceased at various initial temperatures. First no or slight elongation occurred up to a certain temperature, and significant one occurred from about 90°C. The films did not break even at 98°C (boiling water).

The slight elongation in the range of 45–55°C and the minimum value of E_i at 45°C are related to the production or growth of microcrystals in the swollen PVA$_{VTFA}$ films during heating or keeping them at about 45°C. Such a result is consistent with that for the changes during heating in the bending or shear moduli of hydrogels of PVA$_{VF}$ derived from vinyl formate or PVA$_{VTFA}$.[6,7] The modulus of PVA$_{VF}$ hydrogel chilled at 0°C decreased up to about 10°C, increased dramatically in the range of 60–80°C, and then decreased again above about 80°C. The decrease in modulus and the increase in elongation are considered to correspond to the dissolution of smaller microcrystals that constitute the networks in gel or swollen film. The increase in modulus and the mild increase in elongation are considered to correspond to the production and growth of microcrystals. The change in E_i for the unannealed PVA$_{VTFA}$ film in Figure 2 is considered as follows: Microcrystals with various sizes exist in swollen films. The water resistance and the elongation are considered to be influenced by the size of microcrystals. As E_i increases sharply up to T_i = 40°C, numbers and sizes of dissolved microcrystals increase with an increase in the initial temperature accompanied by that in the chain length between junctions. However, in the range of 0–40°C the thermal energy does not contribute to the crystallization of reoriented polymer chains in water. Around 45°C, the thermal energy contributes to the recrystallization of reoriented polymer chains and the growth of microcrystals as supported by the modulus change[6,7] for PVA hydrogels with increasing temperature. For the PVA_{VTFA} films annealed at 75 and 100°C, the decrease of E_i at T_i = 45°C is smaller than that for the unannealed. The advance of crystallization by annealing brings about a decrease in the chain length between junctions.

Elongation and Temperature at Break

Figure 4 shows the relations between the elongation ratios at break E_b or at 98°C E_{98} (for films annealed at 200°C) and the initial temperature. The elongation ratios showed some scatter and did not show a distinct tendency to the initial temperature. The elongation ratio at break E_b for the films annealed at each temperature was plotted against the annealing temperature in Figure 5. The open circles in Figure 5 are the mean values of the elongation ratio at each annealing temperature. The mean elongation ratio decreased roughly with an increase in the annealing temperature. This is due to the decrease in the chain length between junctions with an increase in annealing temperature and to the defect parts that were not removed by annealing.

Figure 6 shows the relations between the ratios of E_b or E_{98} to E_i and the initial temperature. Since the elongation at initial temperatures increased dramatically with an increase in the initial temperature for films annealed at lower temperatures as shown in Figure 2, the ratio of E_b to E_i decreased with an increase in the initial temperature. For the unannealed PVA_{VTFA} films, the ratio at initial temperatures over 35°C was very small. On the contrary, the ratio for PVA_{VTFA} films annealed at 150 or 175°C was approximately constant. This suggests that the elongation in water occurs chiefly with increasing temperature. This fact is due to the production of stable microcrystals which

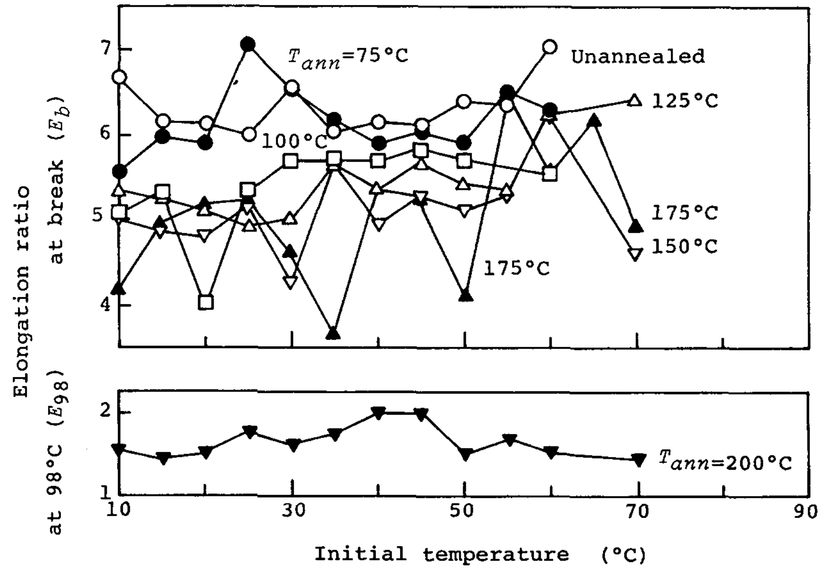

Fig. 4. Relations between the elongation ratio at break or at 98°C (for films annealed at 200°C) and the initial temperature.

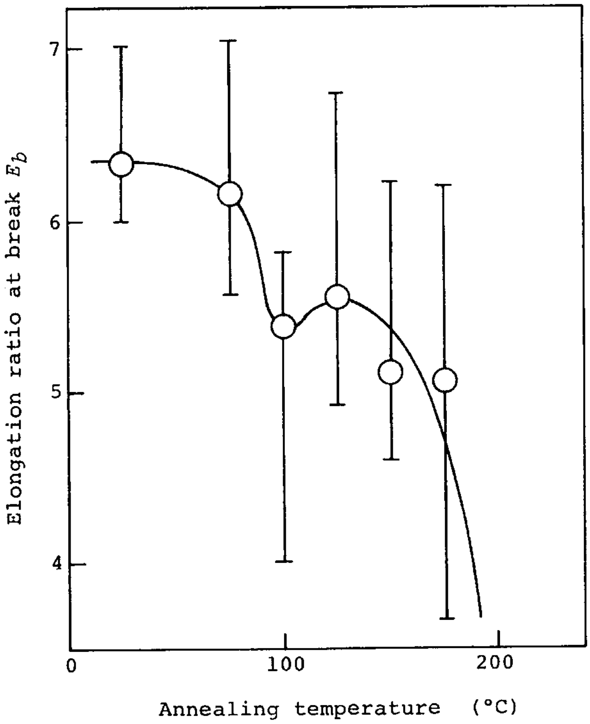

Fig. 5. Relation between the elongation ratio at break and the annealing temperature: (○) mean values of the elongation ratio at break at each annealing temperature.

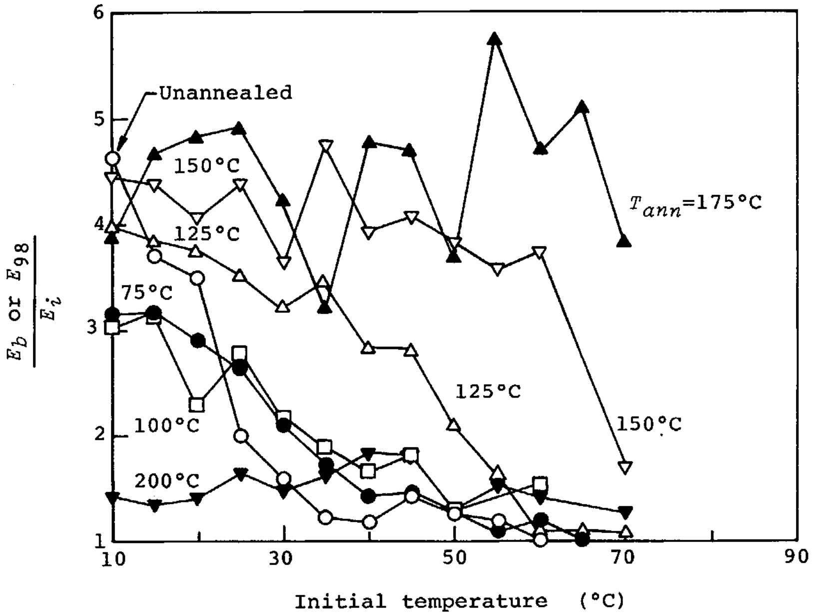

Fig. 6. Relations between the ratios of the elongation ratios at break or at 98°C (for films annealed at 200°C) with increasing temperature to the elongation ratio after 4 h at the initial temperature and the initial temperature for PVA_{VTFA} films annealed at various temperatures.

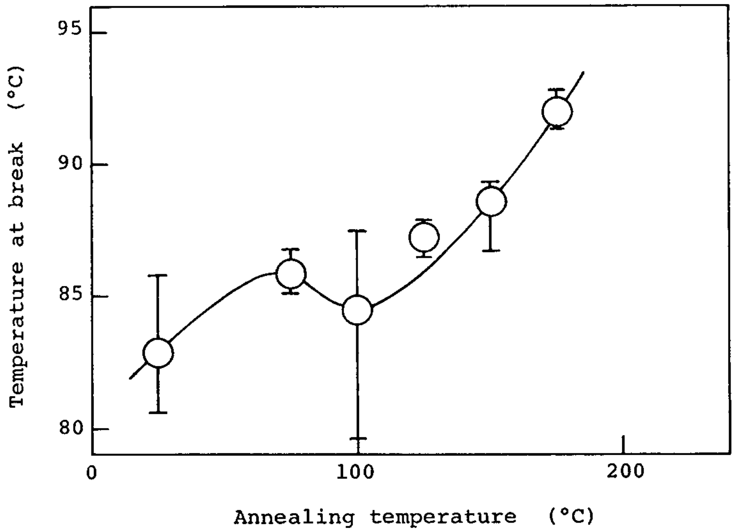

Fig. 7. Relation between the temperature at break and the annealing temperature: (○) mean values at each annealing temperature.

are able to withstand water at 70°C. For PVA$_{VTFA}$ films annealed at 200°C the elongation in water was very small even with increasing temperature as shown in Figure 3.

The temperature at break for PVA$_{VTFA}$ films annealed at each temperature showed some scatter but was approximately constant in the initial temperature range of 10–70°C. Figure 7 shows the relation between the temperature at break and the annealing temperature. The open circles in Figure 7 are the mean values of the temperature at break at each annealing temperature. The mean temperature at break increased roughly with an increase in annealing temperature. However, the temperature at break was the smallest at the annealing temperature of 100°C and was similar to the elongation ratio as shown in Figure 5. In the previous paper,[9] we found that in the case of undrawn PVA$_{VTFA}$ films in air the degree of crystallization became a plateau in the range of the annealing temperature between 100 and 125°C, and Young's modulus and the strength at break was smallest at the annealing temperature of about 100°C. PVA has two second-order transition points (80 and 120°C).[10] In the region of 80–120°C the mobility of chains in amorphous parts rises significantly; thus the stress at both ends of fixed film becomes lower than that in the glass state (below 80°C). Therefore, the degree of crystallization plateaus in the range of the annealing temperature between 100 and 125°C. These results are considered to have brought about the minimum elongation ratio at break (in Fig. 5) and the minimum temperature at break (in Fig. 7) at the annealing temperature of 100°C.

CONCLUSION

The length of PVA$_{VTFA}$ thin film under a load in water increased roughly with increasing temperature, but the equilibrium elongation was smallest at the initial temperature of 45°C for the unannealed films and plateaus in the vicinity of 45°C with increasing temperature. Since the unannealed PVA_{VTFA} thin films ware able to withstand water up to high temperature as shown in Figure 7, the PVA_{VTFA} thin films have more stable microcrystals than films of commercial PVA. The abnormal elongation of PVA_{VTFA} film in water in the vicinity of 45°C is considered to be as follows: If unstable small microcrystals in swollen films are supposed to dissolve depending on the temperature, free chains between junctions become longer. The free chains that emerged from stable long microcrystals would be expected to grow to longer microcrystals by the participation of the long microcrystals as a seed. This consideration must be confirmed by other methods.

References

1. H. Haas, E. S. Emerson, and N. W. Schuler, *J. Polym. Sci.*, **22**, 291 (1956).
2. T. Itoh, K. Noma, and I. Sakurada, *Kobunshi Kagaku*, **16**, 115 (1959).
3. K. Yamaura and S. Matsuzawa, *J. Appl. Polym. Sci.*, **29**, 4009 (1984).
4. K. Yamaura and S. Matsuzawa, *J. Appl. Polym. Sci.*, **30**, 3225 (1985).
5. K. Yamaura and S. Matsuzawa, *J. Appl. Polym. Sci.*, **31**, 2139 (1986).
6. K. Ogasawara, T. Nakajima, K. Yamaura, and S. Matsuzawa, *Colloid Polym. Sci.*, **254**, 553 (1976).
7. S. Matsuzawa, K. Yamaura, R. Maeda, and K. Ogasawara, *Makromol. Chem.*, **180**, 229 (1979).
8. K. Yamaura, T. Tanigami, and S. Matsuzawa, *J. Appl. Polym. Sci.*, **32**, 4343 (1986).
9. K. Yamaura, M. Tada, T. Tanigami, and S. Matsuzawa, *J. Appl. Polym. Sci.*, **31**, 493 (1986).
10. Y. Yano, *Busseiron Kenkyu*, **94**, 163 (1956).

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