

Properties of Syndiotacticity-Rich Poly(vinyl Alcohol) Thin Film in Water. I. Effect of the Load on the Extension of Untreated Thin Film in Water

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Synopsis

The effect of the load on the extension of untreated thin film of syndiotacticity-rich poly(vinyl alcohol) (PVA_{VTFA}) derived from vinyl trifluoroacetate was examined in water. The untreated thin film obeys Hooke's law under a certain constant load at 25°C. Young's modulus of untreated PVA_{VTFA} film in water at 25°C was about 4.8×10^{-4} GPa. The maximum elongation of PVA_{VTFA} film in water at 25°C is achieved for a short time under high load, whereas not under low load. The expansion of PVA_{VTFA} thin film by the elevation of temperature of water occurs mildly in the range of temperature of 45–55°C under low load, whereas not under high load. The temperature at break T_b is in the range of 70–90°C and increasing load roughly tends to decreasing T_b . The elongation at break decreased with the increase in load.

INTRODUCTION

The untreated film of commercial poly(vinyl alcohol) (PVA_{VAc}) derived from vinyl acetate(VAc) dissolves easily in water, however the untreated film of PVA_{VTFA} derived from vinyl trifluoroacetate(VTFA) does not dissolve completely even in boiling water. The marked difference in solubility depends on the stereoregularity of polymer, namely, the syndiotacticity. The water resistance of PVA_{VTFA} has been studied by the measurement of the dissolution temperature, the solubility and the swelling.¹⁻⁵

The crystallinity of the untreated PVA film made by the casting method from an aqueous solution is about 10% and that of the film heat-treated at 200°C is about 50%. However, PVA is well known not to produce the single crystals from an aqueous solution and the spherulites in the film prepared from an aqueous solution. Therefore, the conformation of polymer molecules in PVA film cannot be considered definitely even now. It is very interesting to know in which state the crystals and the molecules of the amorphous parts exist in the film. As described above, the water resistance of PVA_{VTFA} is very high in comparison with that of PVA_{VAc}, so that in the papers of this series we would consider the conformation of polymer molecules in the PVA_{VTFA} film from the extension-contraction behaviors of the thin film in water under load. In this paper, the effect of the load W on the extension of the untreated thin films in water has been examined.

EXPERIMENTAL

Sample and Film. 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'-diamino diethylamine. The degree of polymerization and the contents of syndiotactic diad (%) were 1850 and 56.2, respectively. The PVA_{VTFA} thin films were made by the casting method on the glass plate from an aqueous solution at room temperature. The thickness of film was about 0.017 mm.

Measurement of Length in Water. The experimental apparatus for the measurements of elongation and shrinkage in water consisted of a glass tube containing the film and water, surrounded by a continuously stirred polyethylene glycol bath which could be regulated to keep either a constant temperature (25°C) or a constant heating rate (0.5°C/min). First, the film to which the weight (ca. 1–10 g in air) was attached at the end were inserted hanging in the glass tube without water, and then water of 25°C was poured in the glass tube. The time when the film sank completely in the water was indicated as zero for the standing time. The extension was determined by measuring the increase or decrease in length of the film in water with a cathetometer at the suitable time intervals. If the elongation or shrinkage at 25°C ceased, the polyethylene glycol bath was heated at a rate of 0.5°C/min, and the elongation was measured at the suitable temperature.

Tensile Test in Air. 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 room temperature.

RESULTS AND DISCUSSION

The Expansion at the Constant Temperature at 25°C

Figure 1 shows the changes of the length of film in water with standing time at 25°C. The values of load W shown in Figure 1 were calculated by

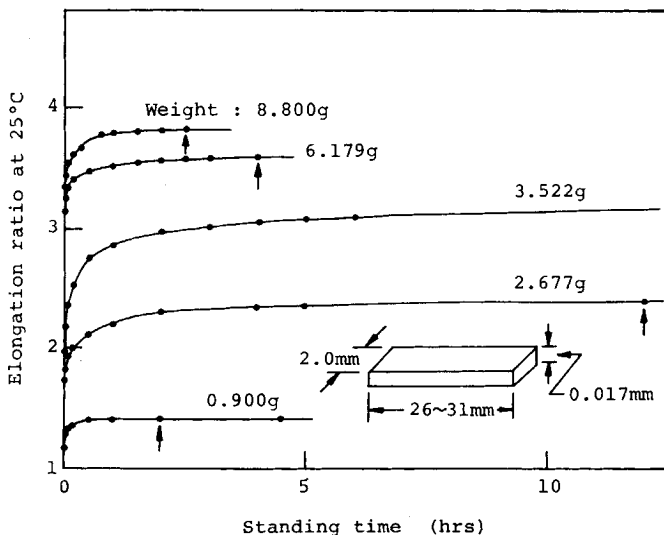


Fig. 1. The effect of the load on the change of film-length with the standing time in water at 25°C for untreated PVA_{VTFA} ($DP = 1850$) films.

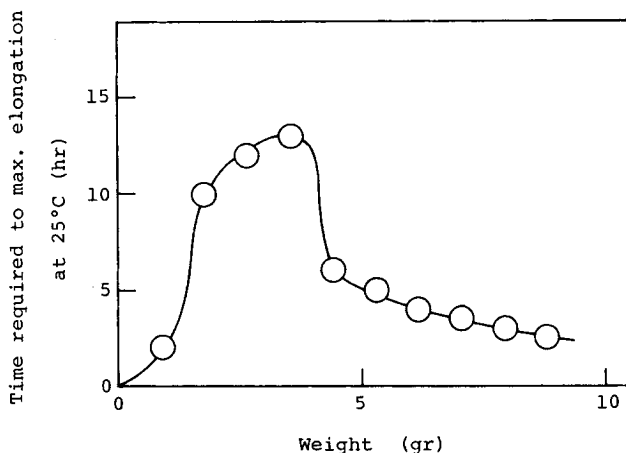


Fig. 2. The effect of the load on the time required to maximum elongation for untreated PVA_{VTFA} films in water at 25°C.

considering the buoyancy in water. The time of initiation of elongation, t_i , was 7–12 s, though it cannot be read from Figure 1. It was independent of load and about 10 s on the average. The diffusion of water molecules into the film is considered to be an important factor for t_i . By 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 the whole of film, the rate of diffusion of water molecules for the untreated film is about 8.5×10^{-5} cm/s at 25°C.

After the onset of elongation, there is a rapid increase in elongation, which is load-dependent as shown in Figure 1. Furthermore, the elongation appears to level off after a certain standing time (arrow points in Fig. 1), t_m . Figure 2 shows the effect of the load W on the time t_m required to reach the maximum elongation ratio E_{rm} at 25°C. Figure 3 shows the relationship between E_{rm} and W at 25°C, E_{rm} is proportional to W under $W = 4.4$ g and

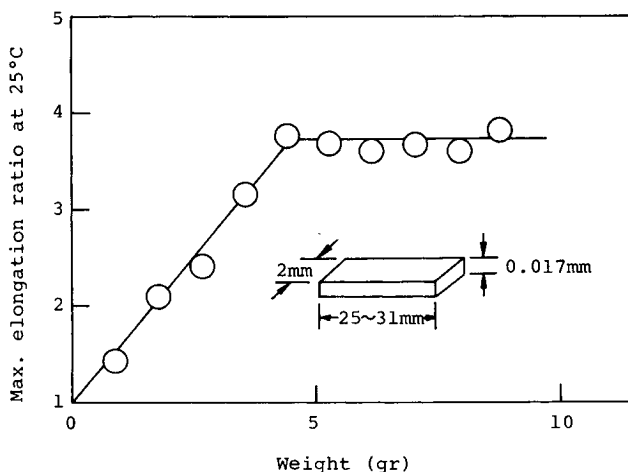


Fig. 3. The relation between the maximum elongation ratio and the load for untreated PVA_{VTFA} films in water at 25°C.

Hooke's law holds; but, over $W = 4.4$ g, E_{rm} is constant independent of W . Young's modulus of PVA_{VTF}A film in water at 25°C obtained from Figure 3 was about 4.8×10^{-4} GPa. Young's modulus of PVA_{VTF}A film in air at room temperature was 6.6 GPa. The latter Young's modulus was about 10,000 times as large as the former. Therefore, water molecules in film are considered to play an important role as a plasticizer. Water is a solvent of PVA. The untreated thin PVA_{VAc} film dissolves easily in water at room temperature or has only very low strength even if it did not dissolve. On the contrary, the untreated thin PVA_{VTF}A film does not dissolve in water at room temperature. The difference in solubility in water for PVA_{VAc} and PVA_{VTF}A is due to that in the hydrogen bonding force in crystals.⁶

The elongation of film in water under 4.4 g is considered chiefly to relate with the uncoiling of amorphous parts in film. However, under low load the maximum elongation is not achieved for a short time as rubber. This is considered as a reason to be due to weak intra- and intermolecular hydrogen bonds which are broken by load. Over $W = 3.7$ g, t_m decreases slightly with increasing W , whereas E_{rm} is constant. These results are understood from the mechanism of uncoiling of macromolecules in amorphous parts, that is, the weak intermolecular hydrogen bonds of amorphous parts are easily broken by higher W or the intermolecular entanglements are easily uncoiled by higher W . As E_{rm} is about 3.75, that is, constant at loads of over $W = 3.7$ g, amorphous parts are fully uncoiled. However, crystals are presumed to be broken at weaker parts when load exceeds some high value.

The Expansion by the Elevation of Temperature

Figure 4 shows the changes of elongation ratio E_r by the elevation of temperature with the heating rate of 0.5°C/min after the elongation has

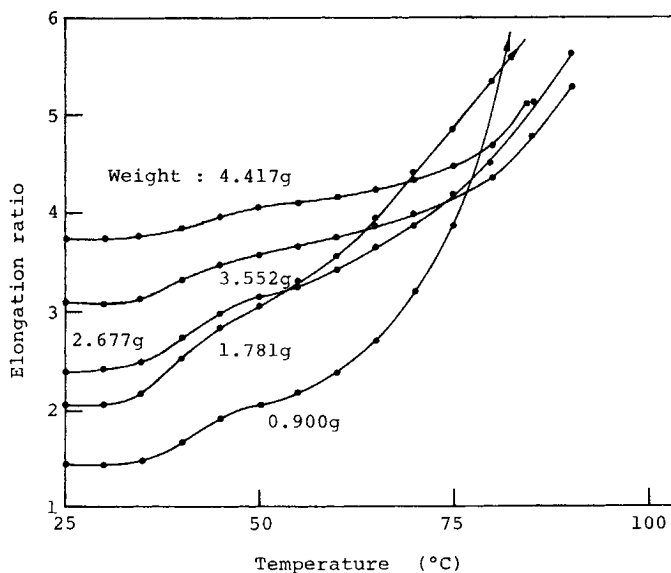


Fig. 4. The effect of the load (lower) on the change of the elongation ratio of untreated PVA_{VTF}A films during heating water at a rate of 0.5°C/min.

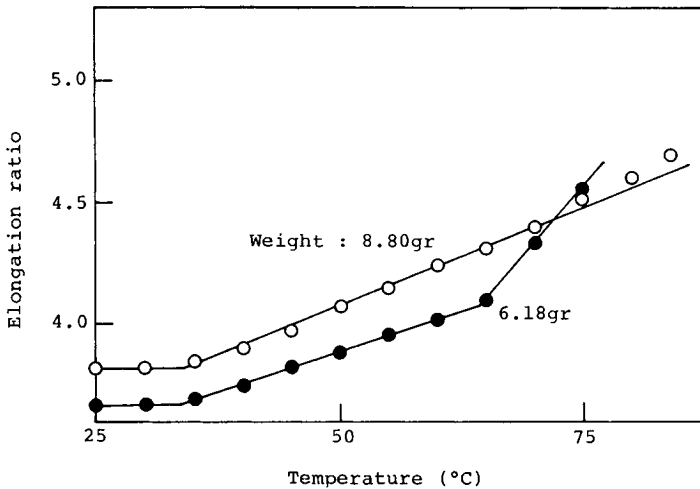


Fig. 5. The effect of the load (higher) on the change of the elongation ratio of untreated PVA_{VTFA} films during heating water at a rate of 0.5°C/min.

ceased at 25°C. First, the elongation occurs remarkably in the range of temperature of 35–45°C, and then it occurs mildly in the range of temperature of 45–55°C. Following the subsequent elevation of temperature it occurs more remarkably than that in the range of temperature of 35–45°C. Such a result is consistent with that for the change of the bending or shear moduli of aqueous PVA_{VTFA} gels, produced at lower temperature, with the elevation of temperature.^{7,8} With the elevation of temperature, the modulus of PVA_{VTFA} gel decreases until about 30°C, increases in the range of temperature of 30–60°C, and then decreases again above 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 are considered to cor-

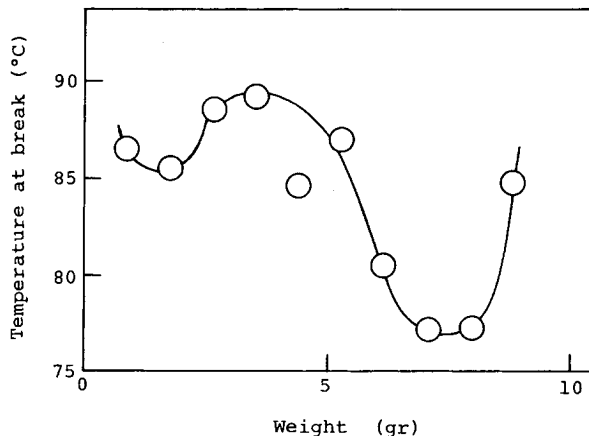


Fig. 6. The effect of the load on the temperature at break for untreated PVA_{VTFA} films in heating water.

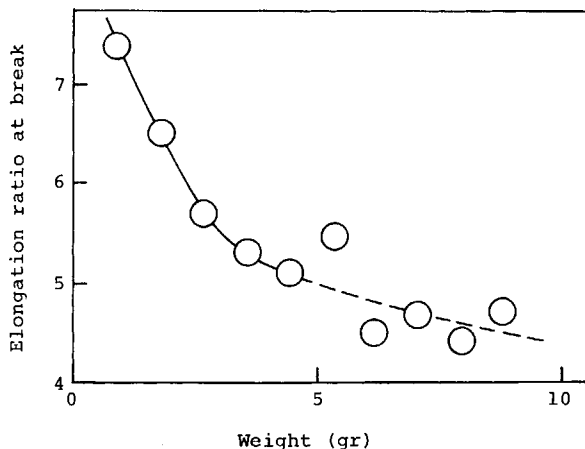


Fig. 7. The effect of the load on the elongation ratio at break for untreated PVA_{VTFA} films in heating water.

respond to the remarkable increase and the mild increase in the elongation of PVA_{VTFA} film in water with the elevation of temperature, respectively. In the case of higher load (Fig. 5), the mild change of elongation in the temperature range 45–55°C did not occur, that is, E_r is constant until 35°C, increases in proportion to the elevation of temperature at above 35°C, and then increases remarkably at above 65–80°C; the temperature is dependent on load. The elongation under high load at 25°C is very large, so that the weak, small crystals are broken under high load. Therefore, the elongation at first stage of the elevation of temperature is due to the thermal motion, and the elongation at above 65–80°C is due to the dissolution of crystals.

Figure 6 shows the relation between the temperature at break, T_b , and the load W . T_b is in the range of 70–90°C and increasing W roughly tends to decreasing T_b . Compared with the untreated film of PVA_{VAc} that cannot resist even to cold water, the film of PVA_{VTFA} has a high resistance to water.

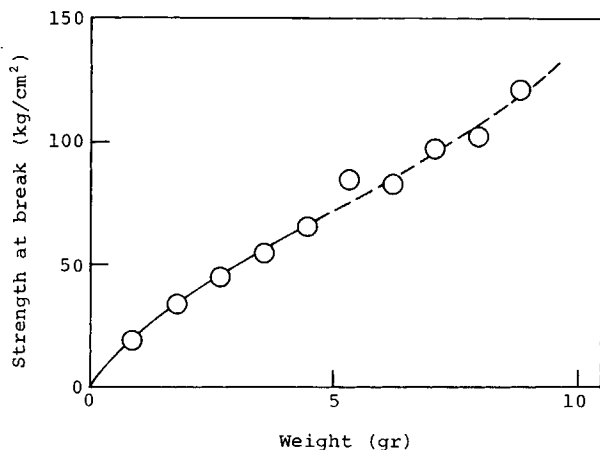


Fig. 8. The relation between the strength at break and the load for untreated PVA_{VTFA} films in heating water.

Figure 7 shows the relation between the elongation ratio at break, E_{rb} , and the load W . E_{rb} decreases with the increase in W . In the case of elongation at 25°C under high load, the film is elongated in short time to high E_r before the entanglement in amorphous part uncoil fully, and so the mobility of polymer molecules of amorphous part is interfered. Therefore, the production of microcrystals during the elevation of temperature does not occur, that is, the orientation of polymer molecules and the production of microcrystals in the film of high load are low. Moreover, the film under higher load suffers more strength per cross section. From the results described above, it can be understood that increasing W tends to lowering T_b and E_{rb} . The strength at break, S_b , increases with increasing load W (Fig. 8). S_b in Figure 8, however, is estimated on the assumptions that PVA_{VTFA} film is incompressible material and does not swell in water. As described above, S_b increases with increasing load W . Actually, PVA_{VTFA} film swells in water and so S_b obtained for PVA_{VTFA} film in water is expected to locate wholly under the curve shown in Figure 8.

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