JOURNAL OF Applied Polymer SCIENCE

High Strength Poly(vinyl alcohol) Films Obtained by Drying and then Stretching Freeze/Thaw Cycled Gel

Taishi Fukumori, Takahiko Nakaoki
Department of Materials Chemistry, Ryukoku University, Seta, Otsu 520-2194, Japan
Correspondence to: T. Nakaoki (E-mail: nakaoki@rins.ryukoku.ac.jp)

ABSTRACT: The mechanical properties of stretched poly(vinyl alcohol) (PVA), which is formed by stretching a film prepared from a freeze/thaw cycled gel, were investigated as a function of the stretching ratio. The tensile strength and Young's modulus of 800% stretched PVA annealed at 130°C were 3.4 and 119 GPa, respectively. These values were much higher than those for a PVA film prepared without freeze/thaw cycling. For a film stretched more than 600% before annealing, two melting peaks, assignable to folded and extended chain crystals, were observed around 220°C and 230°C, respectively. This indicates that a shish-kebab structure is formed as the stretching ratio increases. After annealing at 130°C, the folded-chain crystal transformed to an extended-chain crystal if an extended-chain crystal was present in the stretched film before annealing. High tensile strength and Young's modulus after annealing were due to the formation of extended-chain crystal. Therefore, the presence of extended-chain crystal for annealing is important to provide good mechanical properties. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41318.

KEYWORDS: crystallization; films; mechanical properties; thermal properties

Received 25 March 2014; accepted 21 July 2014
DOI: 10.1002/app.41318

INTRODUCTION

Recently, the development of organic polymer materials that are stronger than inorganic materials has received considerable attention. Research and development with regard to high strength and high elastic modulus materials is underway in various attempts to meet market needs. However, the high cost of these materials limits their practical application, so the development of less expensive high-strength polymers is strongly desired. General-purpose polymer materials such as poly(vinylalcohol) (PVA) and polyethylene (PE) have the potential for improving mechanical properties through regulation of their molecular morphology.

It has been reported that a repeated cycling process of freezing at −20°C followed by thawing at room temperature can provide a thermoreversible hydrogel from a PVA/water system.[1,2] PVA film prepared by excluding water from freeze/thaw cycled gel demonstrated dramatically improved mechanical properties.[3,4] The highest tensile strength and Young's modulus were 255 MPa and 13.5 GPa, respectively, for nonstretched PVA with 99.9% saponification.[2] This is because small crystallites formed during the freeze/thaw cycling process can act as nucleation sites for crystallization through a water-excluding process. These results were comparable with those obtained for PVA film with additives.[5–11] For example, significant improvements in the mechanical properties of PVA films were reported after using Na^{+}-montmorillonite+Cu^{2+} and nanodiamond+SWNTs, of which the tensile strength were as high as about 320 MPa (original PVA: 40 MPa)[10] and 534.3 MPa (38.0 MPa),[11] respectively.

Film stretching is another method that can be used to obtain a high modulus, because the molecular chains align along the stretching direction. For example, gel spinning is known to provide strong fibers, and PE fibers prepared by gel spinning have high tensile strength and Young's modulus.[12–17] Litvinov et al. reported that the Young's modulus of these fibers can be as high as 160 GPa,[17] which is comparable to or larger than that of aramid fibers. The molecular morphology obtained by gel spinning is characterized by extended chains and high crystallinity. However, PE has a relatively low melting temperature around 130°C, which corresponds to a low heat resistance. In contrast, PVA has a higher melting temperature around 220°C. It has been reported on the mechanical properties of PVA fibers prepared by gel spinning.[18–26] Ikada et al. reported that additive-free PVA, gel-spun from a dimethyl sulfoxide/water mixture, had a tensile strength of 2.8 GPa and a Young's modulus of 64 GPa.[19–21] Kunugi et al. successfully prepared high-modulus PVA using a zone-drawing method and achieved a dynamic modulus of 115 GPa at 20°C.[27]

In this work, we stretched films prepared from freeze/thaw cycled gel, and then investigated their mechanical properties. We then discuss the molecular morphology of these stretched films on the basis of their thermal behavior.

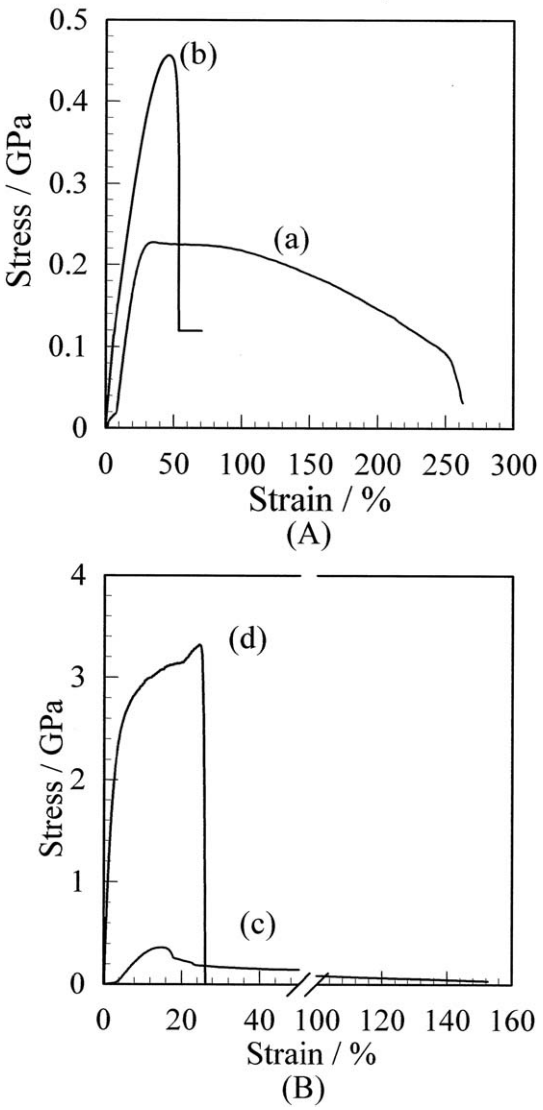

Figure 1. Stress–strain curves of stretched PVA, before (A) and after (B) annealing at 130°C. (a) and (c) represent 200% stretched PVA, whereas (b) and (d) represent 800% stretched PVA.

EXPERIMENTAL

Sample Preparation

PVA with a saponification of 99.9 mol % was provided by Kuraray Co., Ltd. Stretched films were prepared as follows: A 10 wt % PVA aqueous solution was dissolved in an autoclave at 120°C, and then a PVA hydrogel was formed by seven cycles of freezing at −20°C for 15 min followed by thawing at 25°C for 45 min. A film was obtained by drying the gel *in vacuo* for over 1 week, and then stretched at room temperature. It took 30–60 min to obtain the desired stretching ratio. After annealing, the samples without tension were annealed at 130°C for 30 min in a thermostatic oven to increase the crystallinity.

Measurements

Differential scanning calorimetry (DSC) was performed using a Rigaku 8230D instrument at a heating rate of 5°C/min. The crystallinity was determined by defining 138.6 J/g as representing 100% crystallinity.[28]

The mechanical properties were measured using a tensile testing instrument (Shimadzu Instron 5566). The PVA films had a lateral shape, with dimensions of 3.0 × 1.0 cm^2 and a thickness of 0.1–0.3 mm. The film thickness was measured by micrometer more than five places and the averaged value was adopted. Tensile measurements were conducted with a head speed of 0.5 mm/min, repeated at least three times, and the average value was adopted. The distance between clamps was about 2 cm.

Dynamic mechanical analysis (DMA) was performed using a dynamic viscoelasticity instrument (I.T. Instruments DVA-200). The heating rate was 3°C/min in the range from −100 to 200°C. The glass transition temperature (T_g) was determined as the temperature at which the storage modulus first began to decrease.

RESULTS AND DISCUSSION

Mechanical Properties

In our previous report, nonstretched PVA prepared via freeze/thaw cycling provided good mechanical properties. Therefore, after preparing PVA films from freeze/thaw cycled gels, these films were stretched and their mechanical properties were measured. Figure 1 shows stress–strain curves for 200% and 800% stretched PVA films before and after annealing. Before annealing, the 200% stretched film had a tensile strength of 220 MPa, whereas that of the 800% stretched film was 480 MPa. The closed circles in Figure 2(A) show the tensile strength as a function of stretching ratio. Although the tensile strength increased with increasing stretching ratio, the results were comparable with the previous reported values for nonstretched film; for example, our previous result was 255 MPa,[4] and 534.3 MPa was reported for PVA with nanodiamond+SWNTs.[11] When the stretched film was annealed at 130°C, the tensile strength increased significantly, as shown in Figure 1(B). The tensile strength of the annealed, 800% stretched film was as high as 3.4 GPa. To date, there have been few reports on the mechanical properties of stretched PVA, but Ikada et al. reported the mechanical properties of a 4500% stretched sample, which was prepared by gel spinning from a dimethyl sulfoxide/water mixture.[19–21] Our result of 3.4 GPa for an annealed, 800% stretched film was higher than their result of 2.8 GPa. This is because crystallites are formed during freeze/thaw cycling, and act as nucleation sites for crystal growth during annealing. Better results would probably be obtained if the films were stretched further, but the crystallinity is so high, as will be described later, that the films are too rigid to stretch more than 800%. It is worth noting that a significant increase in tensile strength was observed with increasing stretching ratio. This can be understood by considering both the crystallinity and the molecular morphology. Thermal analysis clarified the molecular morphology, as will be discussed in the following section.

Regarding the Young's modulus, the present experimental results are plotted as a function of stretching ratio in Figure 2(B). Before annealing, the Young's modulus increased from 5.2 GPa for the 200% stretched film to 20.2 GPa for the 800% stretched

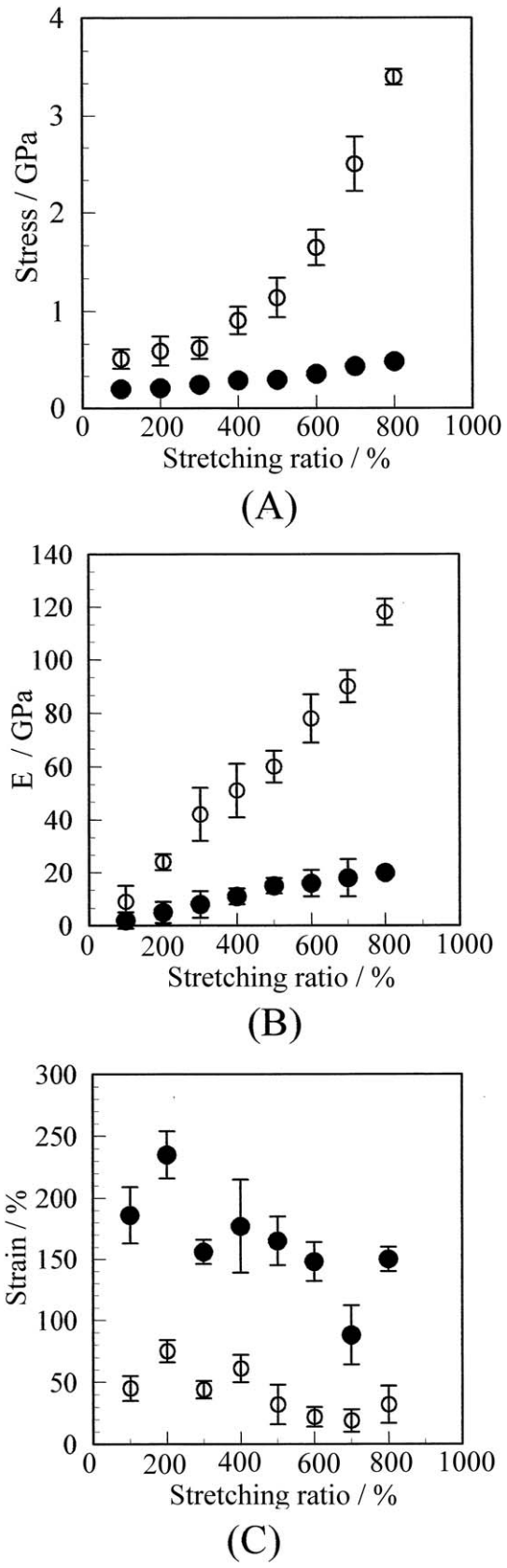

Figure 2. Tensile strength (A), Young's modulus (B), and the elongation at break (C), before (●) and after (○) annealing as a function of stretching ratio.

film. After annealing, the Young's modulus increased from 24.4 GPa for the 200% stretched film to 119 GPa for the 800% stretched film, a nearly five-fold increase. Sakurada et al. estimated a Young's modulus of crystal to be 255 GPa based on X-ray diffraction measurements.[29] Our result was approximately one-half of this value, which suggests that a higher Young's modulus would be expected with additional stretching, if a higher crystallinity was realized.

The elongation at break is shown in Figure 2(C). Before annealing, the elongation at break was about 200% for low stretching ratios, and the elongation at break decreased with increasing stretching ratio. This is because the molecular chains were extended along the stretching direction. After annealing, the

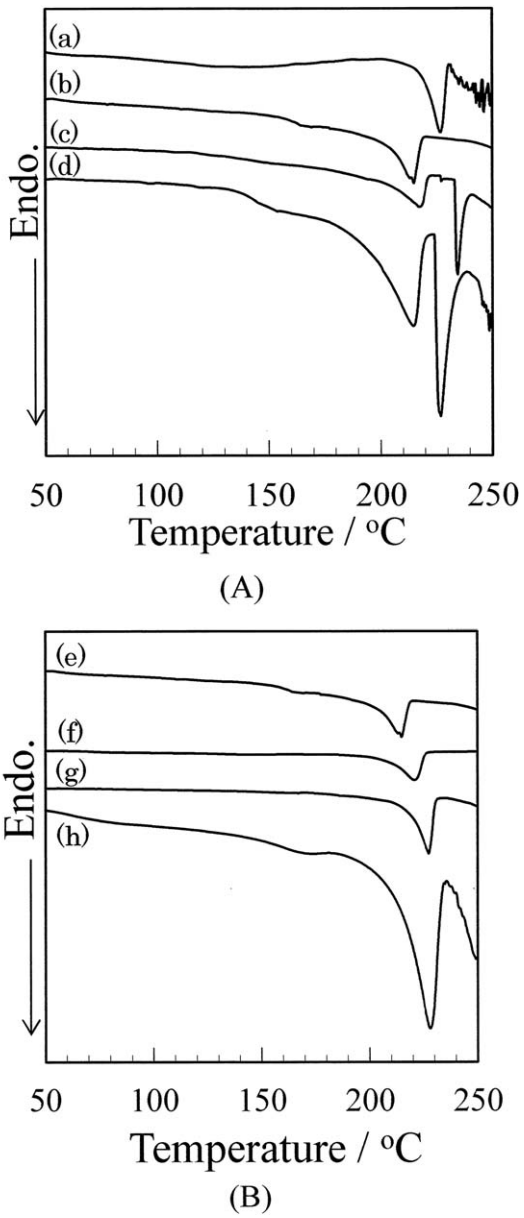

Figure 3. DSC profiles of stretched PVA, before (A) and after (B) annealing at 130°C. The stretching ratios were (a, e) 200%, (b, f) 400%, (c, g) 600%, and (d, h) 800%.

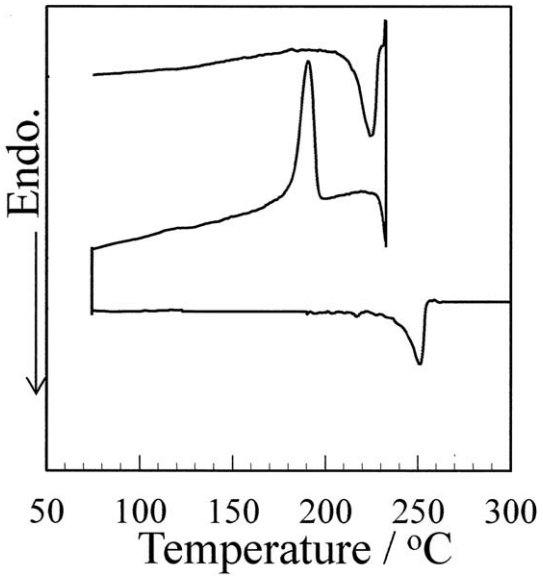

Figure 4. DSC thermogram of 800% stretched PVA. The first heating was scanned from 30°C to 230°C, and then the sample was cooled. The bottom profile shows the second heating process.

elongation at break decreased by less than 80% due to crystallization. This indicates that noncrystalline domains were present to be extended.

Thermal Behavior of Films Prepared with Different Stretching Ratios

Figure 3 shows DSC charts for different stretching ratios, before (A) and after (B) annealing. Before annealing, the nonstretched film provided a single endothermic peak around 220°C, whereas an additional peak was observed around 230°C for the stretched films. To confirm the reversibility of the melting peak around 220°C, a second scan was performed after heating at 230°C, which was above the mow melting temperature, as shown in Figure 4. During cooling, an exothermic peak due to recrystallization was observed, but in the second heating process, only one endothermic peak was observed, at 224°C. This suggests that the molecular morphology was different between them. Ikada et al. also observed two endothermic peaks, and suggested that a shish-kebab structure was formed in their stretched film, and that the low and high temperature melting peaks correspond to folded and extended chain crystal, respectively.[19–21] Therefore, the folded chain crystal melted around 220°C. The melting temperature is plotted with respect to the stretching ratio in Figure 5. Before annealing, the low melting temperature was a nearly constant 220°C, irrespective of the stretching ratio, and a high melting temperature peak was observed for 600% or more stretched samples. This indicates that extended chain crystals were induced by stretching. After annealing, the melting temperatures of the less than 600% stretched samples were comparable with the low melting temperature of ~220°C before annealing. This shows that the morphological structure of the folded chains was unchanged before and after annealing. However, the melting temperature for the films stretched more than 600% became higher than 230°C, which is comparable with the high melting temperature before annealing. It is worth noting

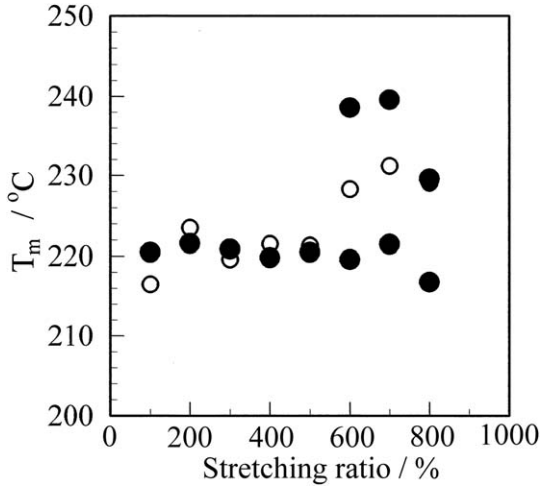

Figure 5. Melting temperature dependence on stretching ratio. ● and ○ denote the melting temperature before and after annealing, respectively.

that no low melting temperature was observed, even at annealing temperatures as low as 130°C. This result shows that the folded chain transformed to extended chain when an extended-chain crystal was present.

The total crystallinity of the folded and extended chain crystal is plotted in Figure 6. For the films less than 600%, the crystallinity after annealing was higher than that before annealing. This indicates that crystallization was promoted by the annealing. For the films stretched more than 600%, the total crystallinity due to the low and high melting peaks before annealing were almost the same as that of the extended chain crystal after annealing. These results are summarized in Table I. This can be explained by a morphological transformation from folded-chain to extended-chain crystals without further crystallization. This

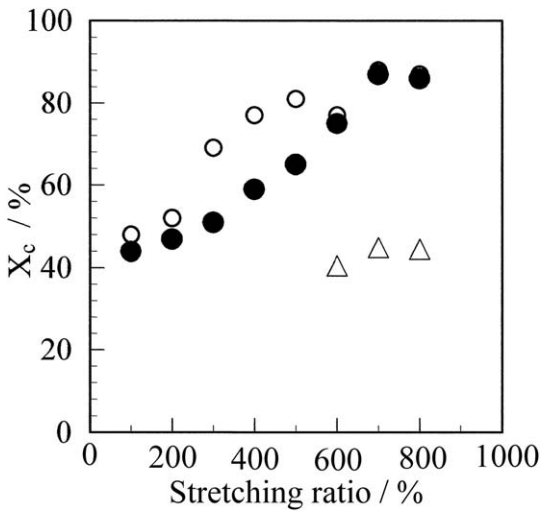

Figure 6. Degree of crystallinity dependence on stretching ratio. ● and ○ denote the melting temperature before and after annealing, respectively. Since two melting peaks were observed for PVA samples stretched more than 600%, the crystallinity of total crystal of folded and extended chain crystals and folded chain crystal are indicated by ○ and Δ, respectively.

Table I. Degree of Crystallinity of Nonannealed and Annealed PVA by Stretching Ratio

	Nonannealed			
Stretching ratio	X_c(Low)/%	X_c(High)/%	X_c(Total)/%	Annealed X_c
600%	40.5	36.7	77.2	78.4
700%	44.9	45.3	90.2	91.8
800%	44.6	43.7	88.3	90.6

X_c(Low) and X_c(High) denote the crystallinity of low and high melting peaks, respectively. X_c(Total) corresponds to the addition of X_c(Low) and X_c(High).

constant level of crystallinity suggests a shish-kebab-type morphological structure before annealing.

Another important result is that the crystallinity of the 800% stretched samples after annealing was as high as 90.6%. This indicates that the extended chain crystal occupied 90.6% of the films. This led to the high tensile strength and high Young's modulus.

Glass Transition Temperatures of the Gel Films

In our previous report, it was shown that there is a correlation between tensile strength and glass transition temperature (T_g). Therefore, T_g was observed and its relationship to tensile strength was investigated. Figure 7 shows the dependence of the storage modulus on temperature, as observed by DMA for non-stretched and 800% stretched films before and after annealing

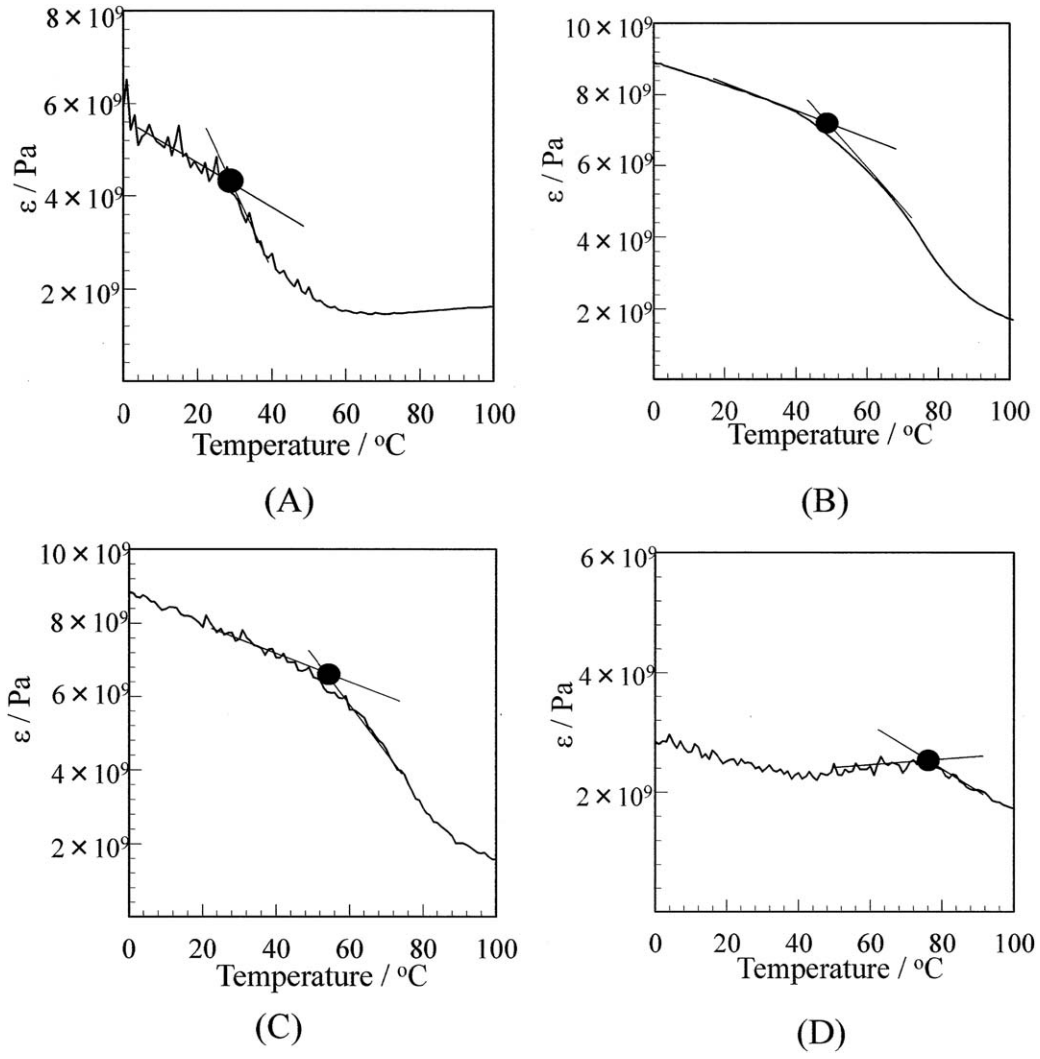

Figure 7. Dynamic mechanical analysis for (A) 200% and (B) 800% stretched samples before annealing, and (C) 200% and (D) 800% stretched samples after annealing.

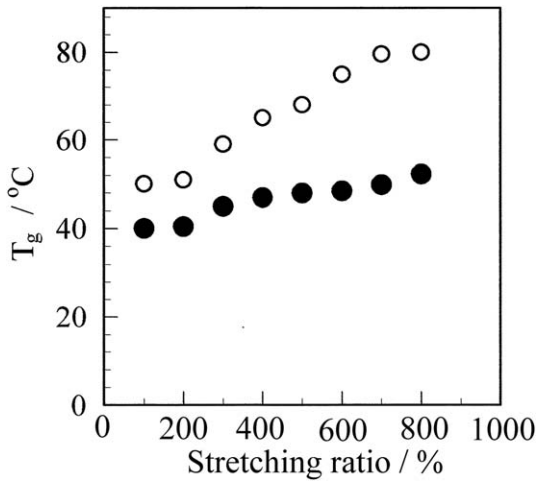

Figure 8. T_g of stretched PVA vs. stretching ratio, before (●) and after (○) annealing.

at 130°C. T_g of the nonstretched films was 40.1°C, whereas that of the 800% stretched film was 49.9°C. The noncrystalline chain between the crystallites for the stretched film would be more distorted than in the nonstretched film, so the T_g was higher. When the films were annealed, T_g increased for both nonstretched and 800% stretched films. Crystal growth due to annealing reduces the size of the noncrystalline region, causing the noncrystalline chain to become more distorted. This resulted in a higher T_g. Figure 8 shows T_g as a function of the stretching ratio. T_g increased with the stretching ratio, both before and after annealing. T_g of the annealed films increased from 50.1°C for the nonstretched film to 79.5°C for the 800% stretched film. This can be explained by the increase in distorted noncrystalline chains between the crystallites. Figure 9 shows a plot of tensile strength vs. T_g. These experimental results were fitted by the following equation.

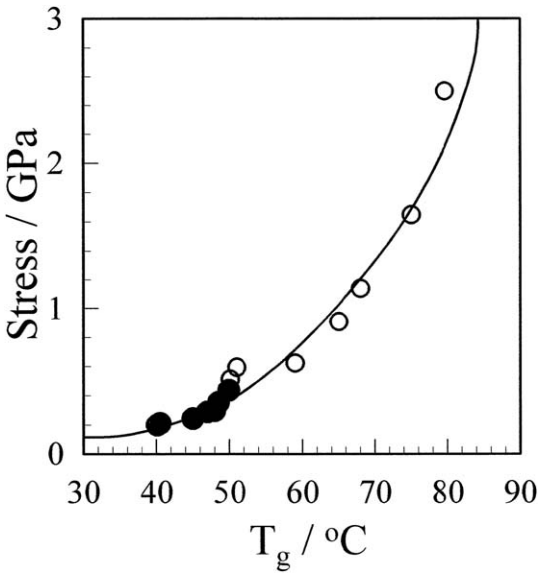

Figure 9. Relationship between the tensile strength and T_g of stretched PVA vs. stretching ratio, before (●) and after (○) annealing.

$$S_{max} = 1.45 \times 10^{-3} T_g^2 - 0.123 T_g + 2.88 \quad (1)$$

In our previous report on nonstretched PVA, it was shown that there is a correlation between the tensile strength and T_g,[3,4] but the fitted equation was completely different from eq. (1). The tensile strength depends on the noncrystalline chain between crystallites. The noncrystalline chain is extended by stretching the film, so the chain structure in stretched PVA would be different from that of nonstretched PVA. This led to the differences in the fitting equations of nonstretched and stretched PVA's.

CONCLUSIONS

The relationships between the molecular structure and mechanical properties of stretched PVA films were investigated. PVA films were prepared by evaporating water from hydrogel throughout a freeze/thaw cycling process. The highest tensile strength and Young's modulus were observed in an annealed, 800% stretched sample, and were 3.4 GPa and 119 GPa, respectively. These values were much higher than those for a conventional sample prepared using a gel-spinning method.

The thermal behavior before annealing showed two melting peaks for more highly stretched PVA. The low and high melting peaks correspond to folded-chain and extended-chain crystals, respectively. When stretched PVA with two melting peaks was annealed at 130°C, a single melting peak was observed at the high melting temperature, corresponding to the transformation of the folded-chain crystal to the extended-chain crystal. It is worth noting that the presence of a pre-existing extended-chain crystal is required for this transformation. The molecular morphology of the extended-chain crystal led to improved mechanical properties.

A good correlation between tensile strength and T_g was obtained, but the fitting curve was completely different from that of nonstretched PVA. This is because the noncrystalline states of nonstretched and stretched PVA's are different.

ACKNOWLEDGMENTS

The authors thank Dr. Ohgi of Kuraray Co., Ltd., for kindly providing the PVA samples.

REFERENCES

1. Peppas, N. A. *Makromol. Chem.* **1975**, *176*, 3433.
2. Hassan, C. M.; Peppas, N. A. *Adv. Polym. Sci.* **2000**, *153*, 37.
3. Fukumori, T.; Nakaoki, T. *Open J. Organ. Polym. Mater.* **2013**, *3*, 110.
4. Fukumori, T.; Nakaoki, T. *J. Appl. Polym. Sci.* to appear.
5. Konidari, M. V.; Papadokostaki, K. G.; Sanopoulou, M. *J. Appl. Polym. Sci.* **2011**, *120*, 3381.
6. Mbhele, H.; Salemane, M. G.; van Sittert, C. G. C.; Nedeljkovic, J. M.; Djokovic, V.; Luyt, A. S. *Chem. Mater.* **2003**, *15*, 5019.
7. Johnsy, G.; Datta, K. K. R.; Sajeevkumar, V. A.; Sabapathy, S. N.; Bawa, A. S.; Eswaramoorthy, M. *Appl. Mater. Interfaces* **2009**, *12*, 2796.

8. Zhao, X.; Zhang, Q.; Chen, D. *Macromolecules* **2010**, *43*, 2357.
9. Zhang, X.; Liu, T.; Sreekumur, T. V.; Kumar, S.; C.Moore, V.; Hauge, R. H. *Nano. Lett.* **2003**, *3*, 1285.
10. Morimune, S.; Kotera, M.; Nishino, T.; Goto K.; Hata, K. *Macromolecules* **2011**, *44*, 4415.
11. Podsiadlo, P.; Kaushik, A. K.; Shim, B. S.; Agarwal, A.; Tang, Z.; Waas, A. M.; Arruda, E. M. *J. Phys. Chem. B* **2008**, *112*, 14359.
12. Kamamoto, T.; Tsuruta, A.; Tanaka, K.; Takeda, M.; Porter, R. S. *Macromolecules* **1988**, *21*, 470.
13. Anandakumaran, K.; Roy, S. K.; Manley, R. *Macromolecules* **1988**, *21*, 1746.
14. Yeh, J.-T.; Lin, S.-C.; Tu, C. W.; Hsie, K.-H.; Chang, F.-C. *J. Mater. Sci.* **2008**, *43*, 4892.
15. Hoogsteen, W.; Kormelink, H.; Eshuis, G.; Brinke, G.; Pennings, A. J. *J. Mater. Sci.* **1988**, *23*, 3467.
16. Porter, R. S.; Kanamoto, T.; Zachariades, A. E. *Polymer* **1994**, *35*, 4979.
17. Litvinov, V. M.; Xu, J.; Melian, C.; Demco, D. E.; M€oller, M.; Simmelink, *J. Macromolecules* **2011**, *44*, 9254.
18. Cebe, P.; Grubb, D. *J. Mater. Sci.* **1985**, *20*, 4465.
19. Hyon, S.-H.; Cha, W.-I.; Ikada, Y. *Polym. Bull.* **1989**, *22*, 119.
20. Cha, W.-I.; Hyon, S.-H.; Ikada, Y. *Die Makromol. Chem.* **1992**, *193*, 1913.
21. Cha, W.-I.; Hyon, S.-H.; Ikada, Y. *J. Polym. Sci. Part B: Polym. Phys.* **1994**, *32*, 297.
22. Yamaura, K.; Tanigami, T.; Hayashi, N.; Kosuda, K.; Okuda, S.; Takemura, Y.; Ito., M.; Matsuzawa, S. *J. Appl. Polym. Sci.* **1990**, *40*, 905.
23. Yamaura, K.; Suzuki, M.; Yamamoto, M.; Shimada, R.; Tanigami, T. *J. Appl. Polym. Sci.* **1995**, *58*, 1787.
24. Yamaura, K.; Kumakura, R. *J. Appl. Polym. Sci.* **2000**, *77*, 2872.
25. Uddin, A. J.; Narusawa, T.; Gotoh, Y. *Polym. Eng. Sci.* **2011**, *51*, 647.
26. Uddin, A. J.; Araki, J.; Gotoh, Y. *Biomacromolecules* **2011**, *12*, 617.
27. Kunugi, T.; Kawasumi, T.; Ito, T. *J. Appl. Polym. Sci.* **1990**, *40*, 2101.
28. Hickey, A. S.; Peppas, N. A. *Membr. Sci.* **1995**, *107*, 229.
29. Sakurada, I.; Nukushina, Y.; Ito, T. J. *Polym. Sci.* **1962**, *b57*, 651.