

Effect of Gel Spinning Accompanied with Cross-Linking Using Boric Acid on the Structure and Properties of High-Molecular-Weight Poly(vinyl alcohol) Fiber

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ABSTRACT: To enhance the thermal stability of poly(vinyl alcohol) (PVA) fiber, the fiber was prepared from the gel spinning of high molecular weight (HMW) PVA by using dimethyl sulfoxide/water (8/2, v/v) as a solvent, accompanied with the cross-link by boric acid (B-PVA). In addition, the structure and properties of the B-PVA fiber were compared with those of the HMW PVA fiber obtained by using the same spinning system without cross-linking (NB-PVA). Through a series of experiments, it turned out that cross-linking actualized by an optimum amount of boric acid (0.3 wt % based on PVA) and zone drawing caused significant changes in the properties of HMW PVA gel fiber. That is, cross-linking increased ther-

mal degradation temperatures at each degradation step and amounts of final residues, resulting in improving thermal properties of the PVA fiber. On the contrary, it was found that in the case of the B-PVA fiber, some broadening of the original PVA unit cell occurred, which was identified by the peak shift to lower angle in X-ray diffractogram. The tensile strength and Young's modulus of B-PVA fiber with draw ratio of 15 are 23.1 and 308.3 g/d, respectively. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1733–1738, 2009

Key words: thermal stability; PVA fiber; cross-linking; boric acid

INTRODUCTION

Poly(vinyl alcohol) (PVA) PVA had many OH side groups causing strong intermolecular hydrogen bonds, which is beneficial for properties, providing a high melting point of 228–240°C but it is a limitation for processability, such as drawability.^{1–4} Thus many researchers have made an effort to obtain the high strength and high modulus PVA fibers by improved spinning and drawing methods such as gel spinning,^{5,6} cross-linking-wet spinning,^{7,8} and zone drawing.^{9,10} Among these methods, it was well known that the gel spinning of PVA solution of water/dimethyl sulfoxide (DMSO) and the subsequent drawing was an effective method. Cha and

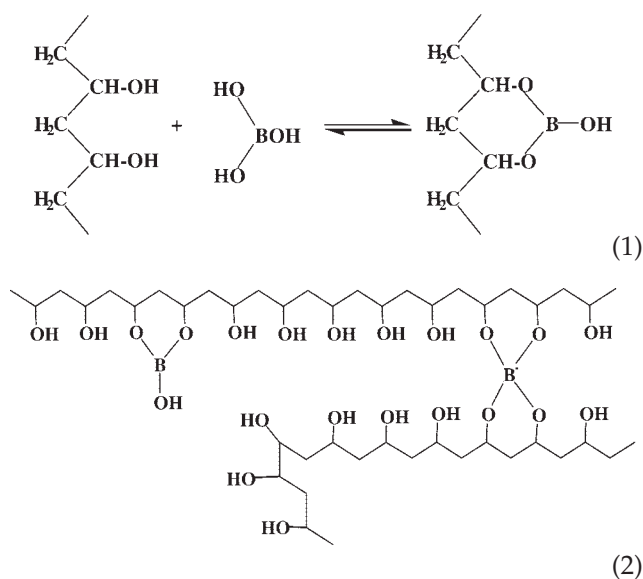
coworkers² reported on the gel spinning of PVA dope prepared from the mixture of DMSO and water. The DMSO/water (8/2 v/v) mixture and methanol were found to be the best spinning solvent and coagulant, respectively.

The cross-linked PVA gel has attracted particular attention because of its high degree of swelling in water, good biocompatibility, inherent low toxicity, and desirable physical properties.^{11–14} In general, the effect of cross-linking of PVA, especially in the case of fiber, is to reduce water sensitivity and to increase the dimensional stability in solution. The cross-linking is usually formed by chemical reaction and/or complex formation with organic or inorganic compounds.

It is known that boric acid causes thickening and gelation of PVA by chemically bonding with PVA. Boric acid is presumed to form monodiol-type bond, as shown by eqs. (1) and (2). The structure indicated is the simplest form of intramolecular bonding as eq. (1), but intermolecular borate esters are also likely to be formed by eq. (2)¹⁵

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In this article, we focused on the gel-spinning of high molecular weight (HMW) PVA from a water/DMSO mixture accompanied by the cross-linking with boric acid and the examination of thermal properties of the gel containing various concentrations of boric acid. To precisely elucidate the effect of cross-linking during spinning on the structure and physical properties of fibers prepared, we compared the fiber prepared from spinning of HMW PVA with cross-linking by using boric acid (B-PVA) with the fibers obtained from spinning of HMW PVA without cross-linking (NB-PVA).

MATERIALS AND METHODS

Materials

Vinyl acetate (VAc) (Shin-Etsu, Tokyo, Japan) purchased from Shin-Etsu was washed with an aqueous solution of NaHSO_3 and dried with anhydrous CaCl_2 (Duksan Pure Chemical Co., Ltd., Ansan, Korea), followed by distillation in nitrogen atmosphere under reduced pressure. The initiator, 2,2-azobis(2,4-dimethylvaleronitrile) (ADMVN) (Wako Co., Osaka, Japan) was recrystallized twice from absolute methanol before use. PVA with number-average molecular weight of 127,000 and degree of saponification (DS) of 88% (Aldrich, St. Louis, MO) was used as a suspending agent. Other extra-pure grade reagents were used without further purification. Deionized water was used.

Preparation of HMW PVA

To synthesize HMW α -PVA, having a P_n of 4000, DS of 99.9%, and syndiotactic diad content of 52.4%, VAc was suspension polymerized at 40°C with ADMVN as an initiator, followed by subsequent saponification.^{16–19}

Solution preparation and measurement of rheological properties

Two types of solutions were prepared by dissolving the PVA in a mixture of DMSO/water (8/2, v/v) and in a mixture of DMSO/water/boric acid (Duksan Pure Chemical Co.) at 80°C for 2 h. The concentrations of PVA were 13 g/dL in both solutions. The concentrations of boric acid in PVA solution were 0.1–0.6%. PVA solutions prepared were maintained for 30 min to ensure homogenization. The shear and dynamic rheologic properties of solutions of PVA in DMSO/water and in DMSO/water/boric acid were measured at 25°C in frequency between 0.1 and 100 rad/s, using a physical USD 200 rheometer (Physica Messtechnik GmbH, Stuttgart, Germany), with a coquette geometry having outer and an inner diameters of 23.50 and 22.75 mm, respectively, at maximum strain amplitude of 10%. The strain level was determined in the strain sweep test so that all measurements were carried out within the linear viscoelastic regime.

Gel spinning and zone drawing

HMW PVA gel fibers were prepared by a dry-jet wet spinning. The dope kept at 80°C was first extruded through a nozzle having a hole size of 0.6 mm (boric acid concentration of 0.3%) with air gap of 50 mm at 30°C, and then immediately coagulated in methanol at 0°C; the sample was washed with methanol several times and dried at 50°C for 24 h. Dried fibers were zone-drawn at 150°C. Zone drawing was carried out between a pair of narrow-band heaters with dimensions of 7 cm length, 2.5 cm width, and 1 mm thickness and moving at a speed of 10 mm/min using an Instron Model 4201 (Instron Co., Canton, MA). The band heater assembly and zone drawing apparatus was represented in our previous article.²⁰

Characterization

Differential scanning calorimetric (DSC) thermogram was obtained by DSC (Perkin-Elmer, Norwalk, CT DSC 7) from 30°C up to 280°C with heating rate of 10°C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) (TA Instruments, New Castle, DE) was performed on a TGA (TA Instruments, 2950) from 100°C up to 500°C. The sample weight for DSC and TGA analysis were about 2 and 5 mg, respectively. $\theta/2\theta$ diffractometer scans were recorded by using a Rigaku D/MAX-2200H (Tokyo, Japan). Diffractometer with scintillation counter in the transmission mode. $\text{Cu K}\alpha$ radiation was used in all measurements. Load-elongation curves were recorded by an Instron 4201. The width and length of the sample were 0.14 and 100 mm, respectively, and the test speed was 40 mm/min.

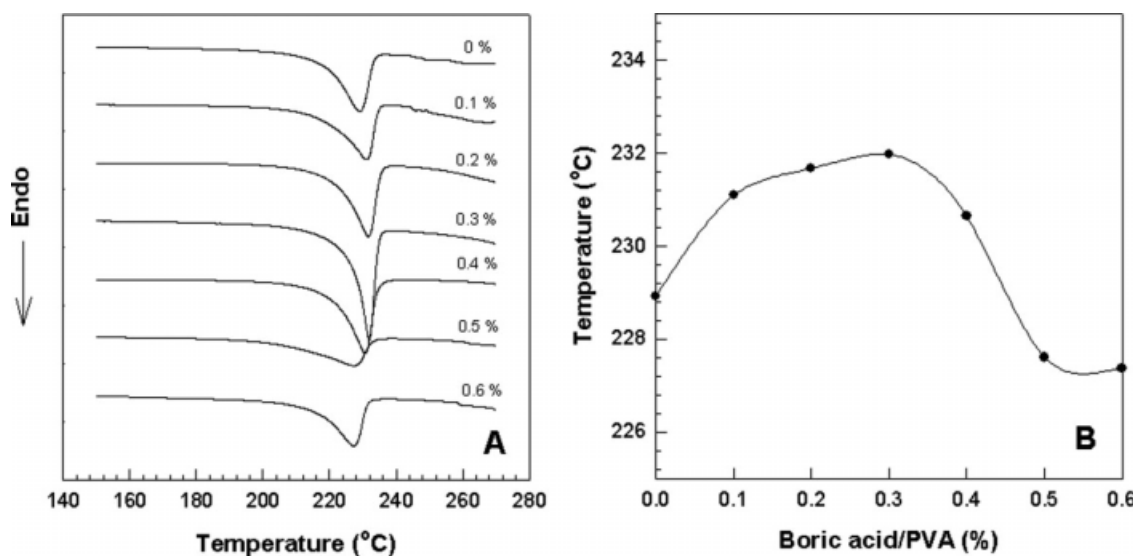


Figure 1 DSC thermograms (A) and melting temperatures (B) of the PVA hydrogels with different concentrations of boric acid.

RESULTS AND DISCUSSION

Characterization of PVA gel

It is well known that cross-linking spinning by using inorganic matter like boric acid is nearly impossible on account of a rapid change of viscosity under spinning process. Thus, to make a suitable spinning solution, prior to spinning, the preceding study on gel made from different concentrations of cross-linking agent should be conducted to control gelation and viscosity by cross-linking reaction.

Figure 1(A) shows the DSC thermograms of gels with different concentrations of boric acid. Until a boric acid concentration of 0.3%, the melting temperature (T_m) was increased with an increase in the boric acid concentration, and after that T_m was decreased and broadened gradually. The variations of the (T_m)s are simply shown in Figure 1(B). In this study, the boric acid concentration of 0.3% was chosen as a reasonable concentration to have cross-linking spinning. In case the concentration is over 0.3%, it was nearly impossible to realize spinning produce owing to very high viscosity.

Figure 2 shows the variation of storage modulus (G') and loss modulus (G'') of NB-PVA gel and B-PVA gel with boric acid concentration of 0.3% at 25°C. In the case of B-PVA gel, with increasing frequency, liquid-like viscoelasticity decreased and a solid-like property evolved that accompanied a crossover between G' and G'' . Such a crossover between G' and G'' is usually found in gelation systems. The G' was increased over a whole ω range measured and the G' of B-PVA gel was higher than that of NB-PVA gel, especially high ω . In the Casson-type plot, the intercept of G'' axis could be considered as a standard of yield stress in

heterogeneous system.^{21,22} The B-PVA gel shows the behavior of an obvious yield stress, accordingly as a formation of a strong sham structure. In other words, a powerful gel structure was formed by complexation as well as cross-linking reaction between PVA and boric acid. The frequency dependence of loss tangent ($\tan \delta$) is plotted in Figure 3. The $\tan \delta$ of the B-PVA was low and simply decreased with an increase in the shear rate. It means that coherence of the formed sham structure was so strong that did

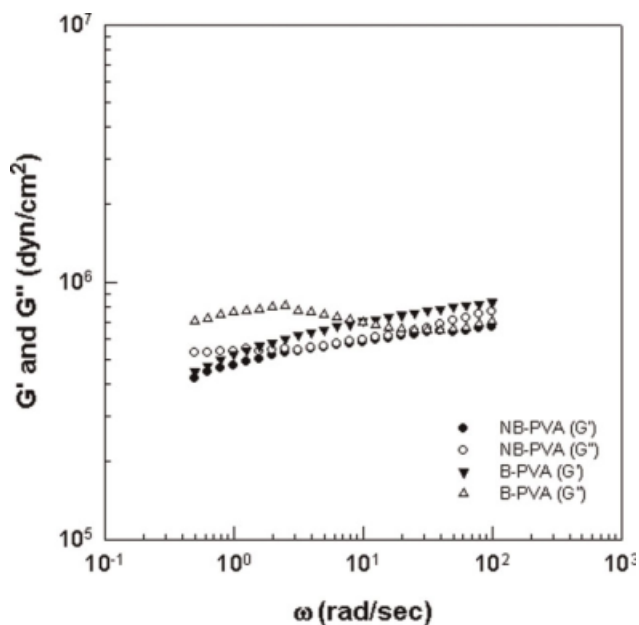


Figure 2 Storage modulus (G') and loss modulus (G'') of NB-PVA gel and B-PVA gel with boric acid (0.3 wt % based on PVA) in DMSO/water (8/2, v/v) at 25°C with frequency.

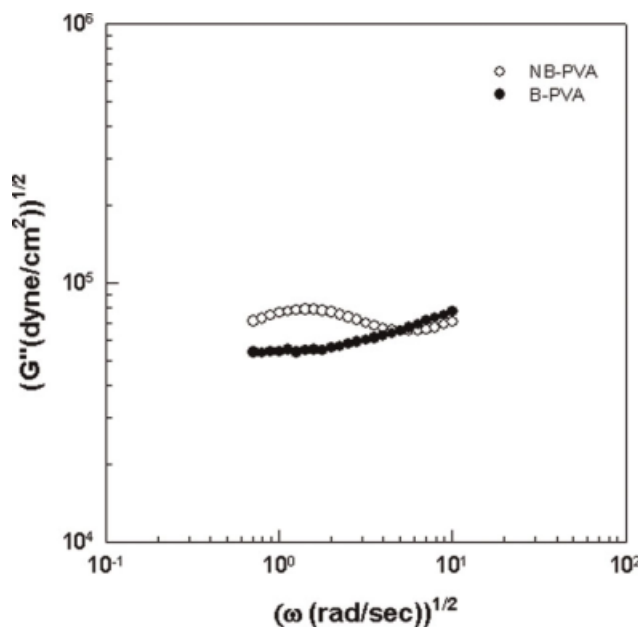


Figure 3 Loss tangent ($\tan \delta$) of 13 wt % PVA solution containing boric acid (0.3 wt % based on PVA) in DMSO/water (8/2, v/v) at 25°C with frequency.

not perfectly destroyed of molecular units in frequency ranges measured.

Comparison between NB-PVA and B-PVA fiber

DSC curves of the fibers from NB-PVA and B-PVA are shown in Figure 4. It is well known that T_m of drawn fiber is higher than that of as-spun fiber and with increasing the presented draw ratio, the T_m increases and the melting range becomes narrower, as in Figure 4. The T_{ms} of the B-PVA fibers were

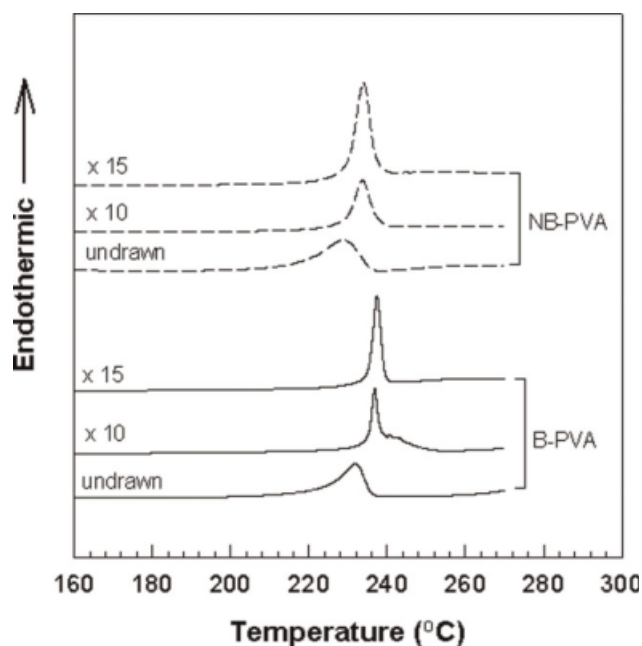


Figure 4 DSC thermograms of the NB-PVA fibers and B-PVA fibers containing boric acid (0.3 wt % based on PVA) with draw ratios.

higher than those of NB-PVA fibers. Wang et al.²³ published that an increase of the boric acid content can result in a higher degree of cross-linking because the average distance between the nearest cross-linked points become shorter. The molecular chain of gel behaves less mobile. Thus a higher temperature of endothermic transition of PVA gel is the result.

Generally, atactic PVA, when pyrolysed in the absence of oxygen, undergoes dehydration and elimination of side groups (over 200°C), dehydration of

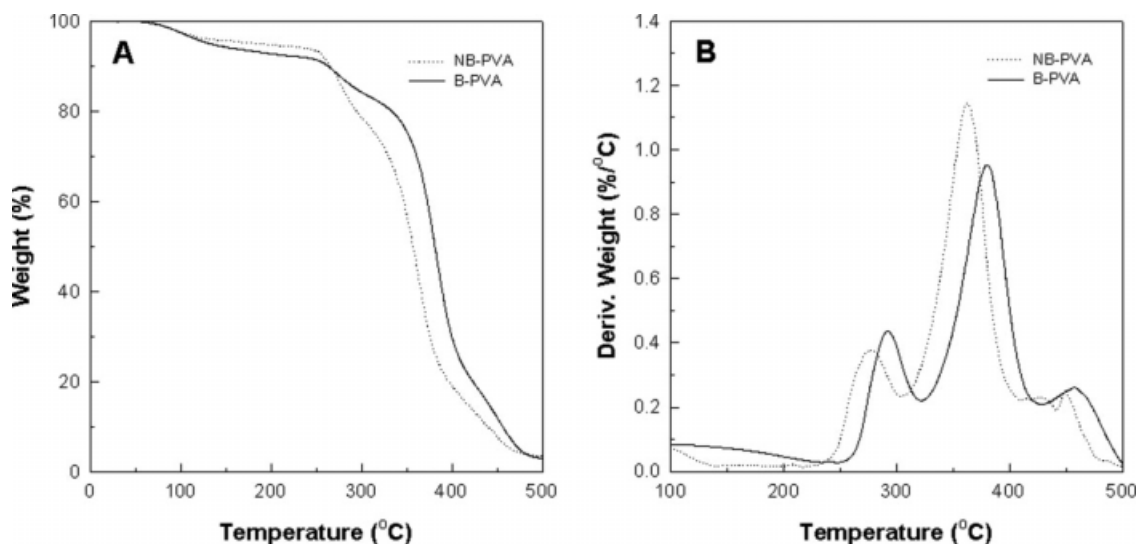


Figure 5 TGA thermograms (A) and the derived weight curves (B) of the NB-PVA fibers and the B-PVA fibers containing boric acid (0.3 wt % based on PVA).

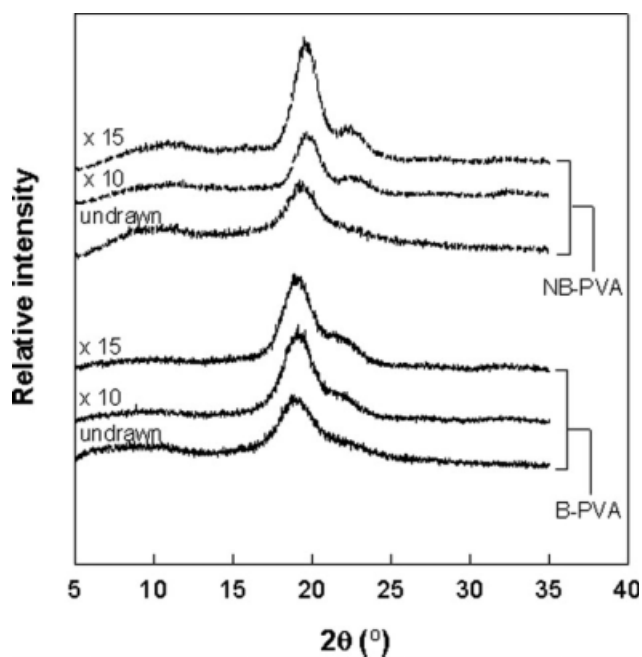


Figure 6 X-ray diffractograms of the NB-PVA fibers and the B-PVA fibers containing boric acid (0.3 wt % based on PVA).

main polymer backbone (over 300°C), and depolymerization (over 400°C).^{24–26} In this study, thermal degradation of B-PVA fiber was compared with that of NB-PVA fiber. Figure 6 shows the weight [Fig. 5(A)] and the derived weight [Fig. 5(B)] as functions of the temperatures for the NB-PVA and B-PVA fibers, respectively. The first weight loss of NB-PVA fiber happened between 240 and 300°C, followed by second weight loss from 300 to 420°C, and then the last weight loss from 420 to 470°C, then leaving a residue of 2.55 wt % at this temperature. The results

were consistent with the elimination of partial side groups at the first stage, followed by weight loss of the residue side groups and partial polymer backbone at the second stage, and the remaining polymer backbone was eliminated at the last stage, as denoted in previous literature.^{24–26} However, for the B-PVA fiber, similar ranges of the weight loss were observed, the first from 260 to 320°C, followed by a further weight loss between 320 and 450°C, and the last weight loss from 450 to 500°C, then leaving a residue of 3.5 wt %. Consequently, the start of temperature of each stage of B-PVA fiber 20–30°C higher than those of NB-PVA fiber is presented, and B-PVA fibers have a better thermal stability than NB-PVA fiber. This may be the result of a special cross-linking by boric acid associated to the better thermal resistance.

Figure 6 shows X-ray diffractometer scans of NB-PVA fiber along the equatorial direction through the 100, 001, 10 $\bar{1}$, 101, and 200 reflections. 2 θ s at all reflections coincide with those, as reported by Bunn²⁷ as unit cell parameters of atactic PVA. On the other hand, in the case of B-PVA fiber, all peaks shifted to lower scattering angle, which might result from the some broadening of the original PVA unit cell, owing to intrusion of -B between PVA chains by cross-linking.^{28,29}

The effect of draw ratio on the tensile strength [Fig. 7(A)] and Young's modulus [Fig. 7(B)] of the NB-PVA fiber and B-PVA fibers are presented in Figure 7, respectively. The tensile strength and Young's modulus also increased with an increase in the zone draw ratio. The B-PVA fiber with cross-linking from boric acid had greater tensile strength and modulus than NB-PVA fiber without cross-linking. The value of tensile strength and Young's

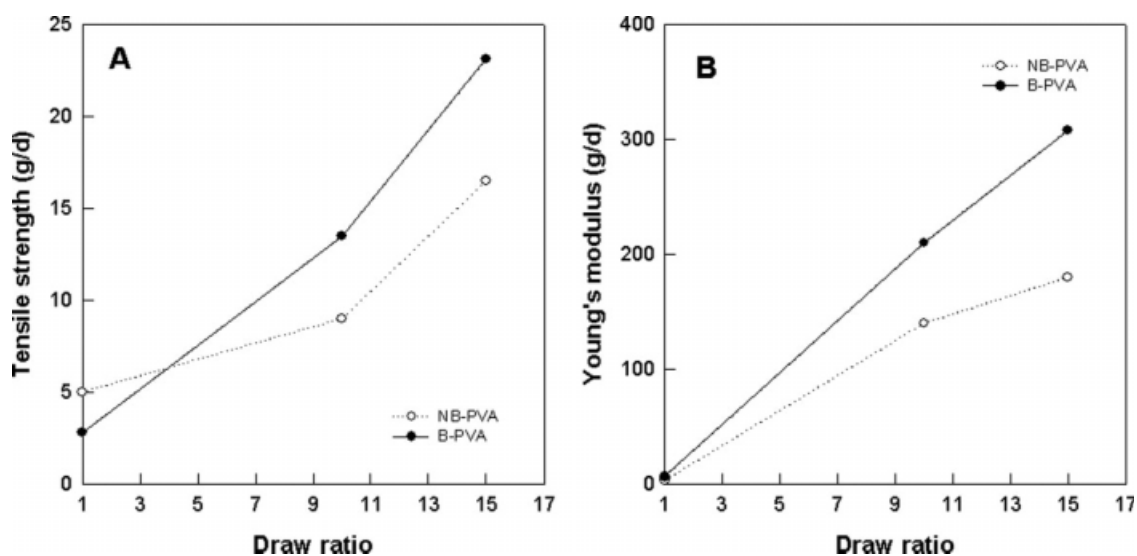


Figure 7 Tensile strength (A) and Young's modulus (B) of the NB-PVA fiber and B-PVA fiber containing boric acid (0.3 wt % based on PVA) with draw ratio.

modulus of B-PVA fiber with draw ratio of 15 are 23.1 and 308.3 g/d, respectively.

CONCLUSIONS

Considering the cross-linking effects by boric acid on the structure and properties of gel-spun and zone-drawn HMW PVA fiber, we may conclude the following. The cross-linking using an optimum amount of boric acid and zone drawing varied the structure and properties of HMW PVA gel-spun fiber. Cross-linking improved thermal properties of the HMW PVA fiber, resulting from increases of both degradation temperature and amount of final residue. In the case of B-PVA fiber, it was found that the unit cell broadening occurred, which was caused by the intrusion of -B into PVA chains. The tensile properties of the B-PVA fiber are superior to those of the NB-PVA fiber. The tensile strength and Young's modulus of B-PVA fiber with draw ratio of 15 are 23.1 and 308.3 g/d, respectively. In the near future, we will report on the gel spinning of HMW syndiotactic PVA accompanied with cross-linking by using boric acid.

References

- Smith, P.; Lemstra, P. J. *J Mater Sci* 1980, 15, 505.
- Cha, W. I.; Hyon, S. H.; Ikada, Y. *J Polym Sci Part B: Polym Phys* 1994, 32, 297.
- Sakurada, I. *Polyvinyl Alcohol Fibers*; Marcel Dekker: New York, 1985; p 147.
- Martin, F. L. *Encyclopedia of Polymer Science and Technology*; Wiley: New York, 1985.
- Cebe, P.; Grubb, D. T. *J Mater Sci* 1985, 20, 4465.
- Grubb, D. T.; Kearney, F. T. *J Appl Polym Sci* 1990, 39, 695.
- Fujiwara, H.; Shibayama, M.; Chen, J. H.; Nomura, J. *J Appl Polym Sci* 1989, 37, 1403.
- Hwang, K. S.; Lin, C. A.; Lin, C. H. *J Appl Polym Sci* 1994, 52, 1181.
- Garrett, P. D.; Grubb, D. T. *Polym Commun* 1988, 29, 60.
- Kunugi, T.; Kawasumi, T.; Ito, T. *J Appl Polym Sci* 1990, 40, 2101.
- Carraher, C. *Modification of Polymer*; Plenum: New York, 1983.
- Maréchal, E. *Chemical Modification of Synthetic Polymers*; *Comprehensive Polymer Science*: Oxford, 1989; Vol 6, pp 1-47.
- Caro, V.; Sung, C.; Merrill, E. *J Appl Polym Sci* 1976, 20, 3241.
- Korsmeyer, R.; Peppas, N. *J Membr Sci* 1981, 9, 211.
- Shibayama, M.; Sato, M.; Kimura, Y.; Fujiwara, H.; Nomura, S. *Polymer* 1988, 29, 336.
- Lyoo, W. S.; Lee, S. G.; Kim, J. P.; Han, S. S.; Lee, C. J. *Colloid Polym Sci* 1998, 276, 951.
- Lyoo, W. S.; Lee, H. W. *Colloid Polym Sci* 2002, 280, 835.
- Lyoo, W. S.; Kwak, Y. J.; Ha, W. S. *J Korean Fiber Soc* 1996, 33, 321.
- Kim, S. G.; Lee, W. S.; Jo, S. M.; Kim, B. C.; Lyoo, W. S.; Han, J. R. *J Korean Fiber Soc* 1999, 36, 354.
- Lyoo, W. S.; Kim, J. H.; Koo, K.; Lee, J. S.; Kim, S. S.; Yoon, W. S.; Ji, B. C.; Kwon, I. C.; Lee, C. J. *J Polym Sci Part B: Polym Phys* 2001, 39, 1263.
- Kim, S. S.; Seo, I. S.; Yeum, J. H.; Ji, B. C.; Kim, J. H.; Kwak, J. W.; Yoon, W. S.; Noh, S. K.; Lyoo, W. S. *J Appl Polym Sci* 2003, 92, 1426.
- Lyoo, W. S.; Lee, S. J.; Kim, J. H.; Noh, S. K.; Ji, B. C.; Kim, B. C. *J Appl Polym Sci* 2004, 93, 41.
- Wang, H. H.; Shyr, T. W.; Hu, M. S. *J Appl Polym Sci* 1999, 73, 2219.
- Tsushiya, Y.; Sumi, K. *J Polym Sci Part A-1: Polym Chem* 1969, 7, 3151.
- Gao, J.; Liu, Y.; Yang, L. *Polym Degrad Stab* 1999, 63, 19.
- Holland, B. J.; Hay, J. N. *Polymer* 2001, 42, 6775.
- Bunn, C. W. *Nature* 1948, 161, 929.
- Cho, J. D.; Lyoo, W. S.; Chvalun, S. N.; Blackwell, J. *Macromolecules* 1999, 32, 6236.
- Lyoo, W. S.; Chvalun, S.; Ghim, H. D.; Kim, J. P.; Blackwell, J. *Macromolecules* 2001, 34, 2615.