

Gel-Spinning of Partially Saponificated Poly(vinyl alcohol)

KAZUO YAMAURA, RIE KUMAKURA

Faculty of Textile Science and Technology, Shinshu University, Tokida 3-15-1, Ueda-city, Nagano-prefecture 386-8567, Japan

Received March 1999; accepted September 1999

ABSTRACT: DMSO/water (80/20 volume ratio) solutions of commercial poly(vinyl alcohol)s (α -PVA₉₉, α -PVA₈₈) with degrees of saponification of 99.3 and 88 mol % were gel-spun into methanol (-20 and -70°C). The dry filaments obtained were drawn at 200°C (α -PVA₉₉) and 150 – 180°C (α -PVA₈₈). The maximum draw ratio and Young's modulus were 26 and 34 GPa for α -PVA₉₉ and 21 and 24 GPa for α -PVA₈₈ (drawing temperature: 160°C). So, at first, the dry filaments obtained for α -PVA₈₈ were drawn at 150 – 180°C until 10 times their original length. Moreover, the predrawn α -PVA₈₈ filaments were perfectly saponificated under fixing at the both ends and then the filaments were redrawn at 200°C . The maximum draw ratio and Young's modulus for the filaments (α -PVA_{88 \rightarrow 99}) predrawn at 150°C were 28 and 39 GPa, respectively. The α -PVA_{88 \rightarrow 99} filaments had two melting peaks (228 and 236°C). © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2872–2876, 2000

Key words: poly(vinyl alcohol); partial saponification; drawing, gel-spinning; high modulus; high strength

INTRODUCTION

The preparation of ultrahigh modulus polyethylene (PE) fibers and films from the ultradrawing of dried gels, produced by gelation from a semidilute solution, has been extensively studied in recent years.^{1–5} Matsuo and Sawatari produced ultrahigh drawn PE with a Young's modulus at 20°C of 216 GPa.⁵ Poly(vinyl alcohol) (PVA) with a planar zigzag structure, such as PE, has the potential to induce a high modulus and high strength. The crystal modulus of PVA and the strength of perfectly oriented PVA fiber are high; they are estimated to be 250–300 GPa.^{6,7} To this day, despite various attempts, the limited values have not been obtained experimentally for PVA.⁸ A

Young's modulus of 115 GPa is the highest value reached so far.⁹ It does not reach the theoretical values. This is considered to be caused by intermolecular hydrogen bonding, which interferes with the drawing.

Poly(vinyl acetate) is an amorphous polymer. Therefore, the acetic acid groups in the polymer chains of PVA interfere with the crystallization of PVA. The existence of acetic acid groups in the polymer chains of PVA is expected to support the ultradrawing of fibers and films of PVA.

In this article, we carried out gel-spinning and drawing of the filaments obtained and examined the effect of acetic acid groups on the drawing. Moreover, we tried postdrawing the filaments saponificated perfectly after predrawing the partially saponificated filaments.

EXPERIMENTAL

Samples and Solutions

Three samples of PVA (atactic PVA, α -PVA) derived from vinyl acetate, supplied from Unichica

Correspondence to: K. Yamaura.

Contract grant sponsor: Ministry of Education, Science, Sports and Culture of Japan; contract grant number: 10CE2003.

Journal of Applied Polymer Science, Vol. 77, 2872–2876 (2000)
© 2000 John Wiley & Sons, Inc.

Table I PVA Samples Used

Sample Names	Degree of Saponification	Degree of Polymerization
UP-180	88	1850
UF-170M	96.5	1780
UV4HM	99.34	1720

Chemical Co. Ltd. (Japan), were used and the properties are shown in Table I. The tacticity measured by $^1\text{H-NMR}$ revealed the atactic nature of PVA_{99} [0.208 (mm), 0.528 (mr), 0.264 (rr)]. The PVA solutions were prepared in a sealed tube at 120°C . Mixed solutions of dimethyl sulfoxide (DMSO) and water were used as a solvent.

Gelation

The sealed tubes with the solutions (polymer concentration $C = 7.0$ g/dL) were placed in a methanol bath maintained at room temperature and cooled at a rate of $1^\circ\text{C}/\text{min}$. During cooling, the gelation or freezing temperatures of the solutions were measured. We assumed the gelation temperature at which the fluidity of PVA solutions in a test tube stopped.

Gel-spinning

PVA_{88} was dissolved in an 80 vol % DMSO and 20 vol % water mixture in a sealed test tube at about 120°C . The spinning apparatus shown in the previous article¹⁰ was used for the gel spinning. The solutions (about 20°C) were extruded into a methanol bath of -20°C (PVA_{99}) or -70°C (PVA_{88}). The gel filaments were kept in the bath for 2–3 h, then wound around on a reel in air and dried. The dry filaments were drawn in an oven.

Saponification

The drawn PVA_{88} filaments fixed at both sides were perfectly saponificated in methanol with 3% NaOH at 30°C for 24 h, then washed in methanol for 24 h and dried ($\text{PVA}_{88 \rightarrow 99}$). PVA_{88} was perfectly saponificated for 3 h. The dry filaments were redrawn in an oven.

Measurements of Properties of Filaments

Tensile properties of the filaments were measured using a tensile tester of a TOM/5 type of Shinko Tsushin Kogyo at the temperature of 20 – 22°C and the relative humidity of about 50%. The

birefringence was measured using a Nihon Kohgaku polarizing microscope equipped with a Wetzer compensator. The thermal properties of the filaments were tested at a heating rate of $20^\circ\text{C}/\text{min}$ using a differential scanning calorimeter (DSC3200) made by Mac Science Co. (Japan). The melting points of the filaments were taken as the maximum of the melting curves. The density of the filaments was determined by a floating method in a benzene–carbon tetrachloride mixture.

RESULTS AND DISCUSSION

Gelation and Freezing Temperatures of Solutions

To study the gelation and freezing behaviors of PVA_{99} , PVA_{96} , and PVA_{88} in $\text{H}_2\text{O}/\text{DMSO}$ mixtures, the systems with a polymer concentration of 7 g/dL were used. Figure 1 shows the relations between the gelation or freezing temperatures and the DMSO content for the three samples. In the case of the three samples with DMSO contents of 0–30 and 90–100 vol %, the solutions froze before gelation except PVA_{99} with DMSO contents of 10–30 vol %. The gelation temperature decreased with decrease in the degree of

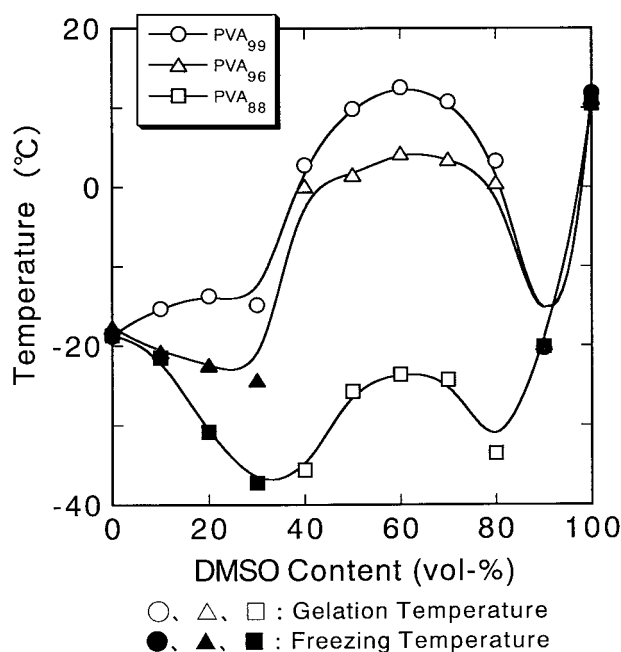


Figure 1 Relations between gelation or freezing temperatures and DMSO content for three α -PVA samples with different degrees of saponification (PVA_{99} , PVA_{96} , PVA_{88}).

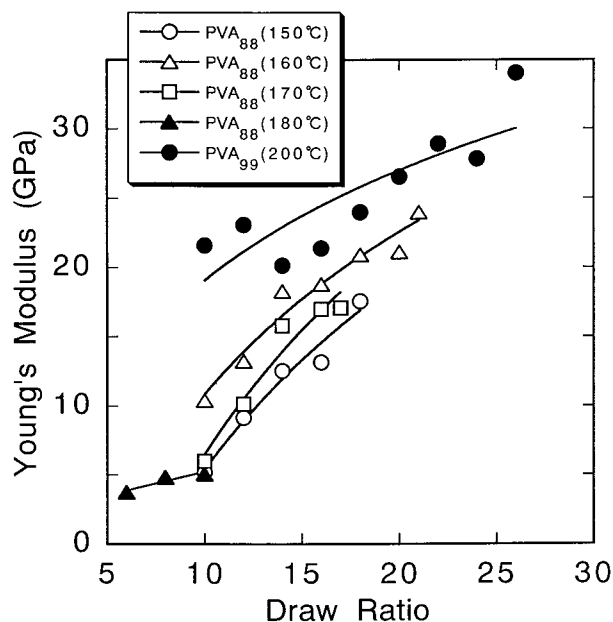


Figure 2 Relations between Young's modulus and draw ratio for PVA₉₉ and PVA₈₈ filaments obtained by gel-spinning.

saponification, that is, the gelation decreased with the decrease in the degree of saponification. The gelation of PVA solutions was considered to be brought about by the formation of many crystallites in the solutions. The existence of acetic acid groups in the PVA chain weakens the intermolecular hydrogen bonds and interferes with the formation of crystallites. Therefore, the existence of acetic acid groups in the PVA chain is expected in that the drawability of filaments obtained from PVA with a low degree of saponification is heightened.

As shown in Figure 1, the PVA₉₉ and PVA₈₈ solutions with a DMSO content of 80 vol % gelled at about 0 and -35°C , respectively. Therefore, the gel-spinning of the PVA₉₉ and PVA₈₈ solutions with the DMSO content of 80 vol % were carried out in methanol at about -20 and -70°C , respectively.

Drawability and Mechanical Properties of Filaments

Figures 2 and 3 show the relations between the Young's modulus or the strength at break and the draw ratio for PVA₉₉ and PVA₈₈ filaments obtained by gel-spinning. Figure 4(a,c) shows the DSC curves of the undrawn PVA₉₉ and PVA₈₈ filaments. The melting points were 226 and

196°C , respectively. For the PVA₈₈ filaments, the optimum drawing temperature was 160°C . The temperature is the starting point of melting. The maximum draw ratio was about 21. The value was lower than that (about 26) of the PVA₉₉ filaments drawn at 200°C . This result was not up to the described expectation that the drawability of the filaments obtained from PVA with a low degree of saponification is heightened. The Young's modulus and the strength at break of the PVA₉₉ filaments drawn at 200°C were also higher those that of the PVA₈₈ filaments drawn at 150 – 180°C . The drawability at 180°C of the PVA₈₈ filaments was very low and the maximum draw ratio was only 10, that is, the crystallites with acetic acid groups cannot resist the drawing force. So, we tried postdrawing (termed drawing at first stage) the filaments saponificated perfectly after pre-drawing (termed drawing at second stage) the partially saponification filaments.

Postdrawing of Filaments Saponificated Perfectly After Predrawing

The PVA₈₈ dry filaments obtained by gel-spinning were first drawn until 10 times their original length at 150, 160, 170, and 180°C (drawing at first stage). The melting point and the birefringence of the drawn PVA₈₈ filaments were 196 – 203°C (Fig. 4) and 2.4×10^{-2} – 2.8×10^{-2} , respec-

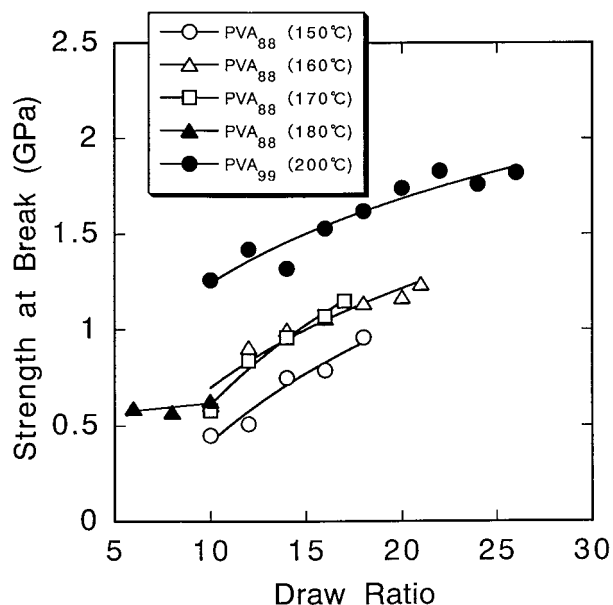


Figure 3 Relations between strength at break and draw ratio for PVA₉₉ and PVA₈₈ filaments obtained by gel-spinning.

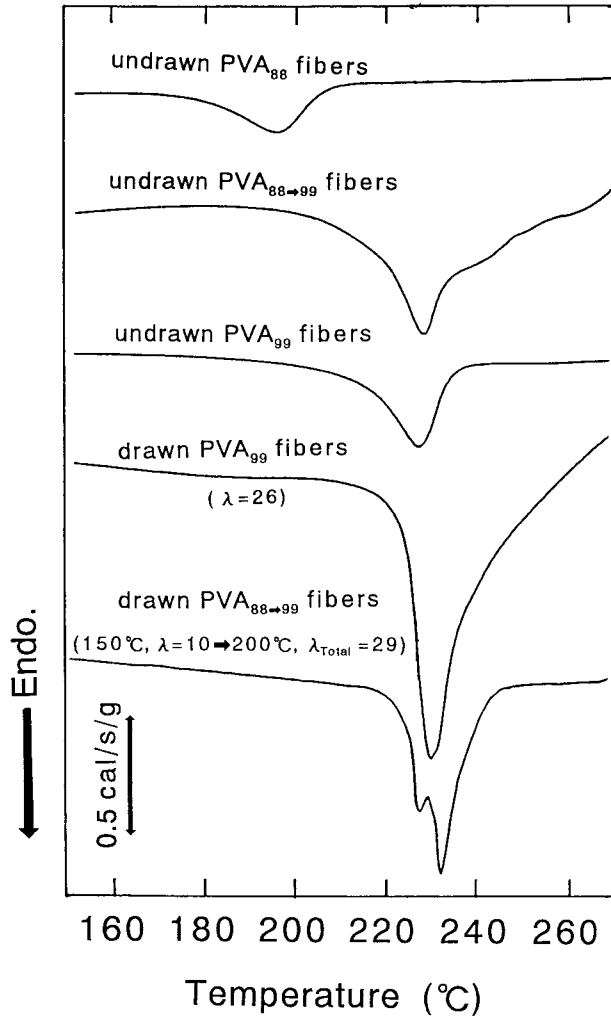


Figure 4 DSC thermographs for undrawn PVA₈₈, undrawn PVA₉₉, undrawn PVA_{88→99}, drawn PVA₉₉, and drawn PVA_{88→99}.

tively, and increased with increase of the drawing temperature. As the drawing at higher temperatures was smooth, it was considered that the orientation of molecular chains was high and the size of the crystallites at the junction point was large. The pre-drawing filaments fixed at the both sides were perfectly saponificated and then the washed/dried filaments were redrawn until just before breakage at 200°C (drawing at second stage).

Figure 5 shows the relation between the draw ratio of the postdrawing filaments (PVA_{88→99}) and the pre-drawing temperature. The maximum draw ratio of PVA_{88→99} was about 28 for the filament pre-drawn at 150°C and the draw ratio of PVA_{88→99} decreased with increase of the drawing temperature at the first stage. This is considered

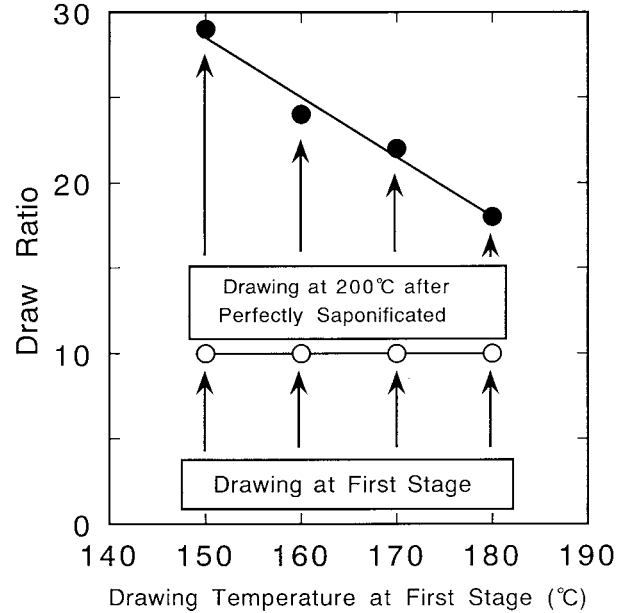


Figure 5 Relation between total draw ratio after postdrawing at 200°C for PVA_{88→99} and pre-drawing temperature for PVA₈₈.

to be due to the high orientation of molecular chains and the propagation of crystallites to a large size.

Figure 6 shows the relation between the Young's modulus of the postdrawing filaments (PVA_{88→99}) and the pre-drawing temperature. The

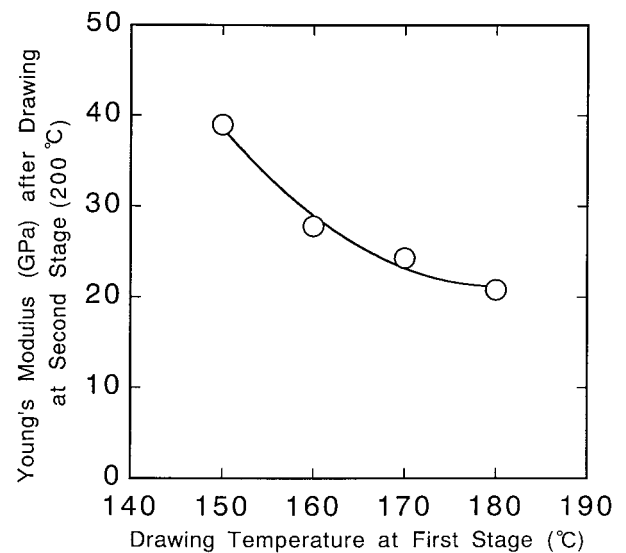


Figure 6 Relation between Young's modulus after postdrawing at 200°C for PVA_{88→99} saponificated perfectly under fixing at the both ends for pre-drawn PVA₈₈ filaments and pre-drawing temperature for PVA₈₈.

maximum Young's modulus of PVA_{88→99} was about 39 GPa for the filament predrawn at 150°C and higher than that (about 34 GPa) of the drawn filaments of PVA₉₉ (see Fig. 2; draw ratio = 26). As the stabilization of the junction points in the filaments was attained by saponification, the redrawing of PVA_{88→99} at 200°C is considered to proceed until a higher draw ratio is achieved. As shown in Figure 4, two melting peaks (228 and 236°C) appeared in the DSC thermograph of the redrawn PVA_{88→99} filaments and the crystallinity was 63.0%. This shows that new, larger, stable crystallites propagated during drawing at the second stage. For the PVA₉₉ filament drawn at 200°C, the melting point was single (230°C) and the crystallinity was 58.7%, that is, the redrawing after perfect saponification is considered to be effective to obtain a high modulus. However, it was restricted to the PVA₈₈ filaments predrawn at 150°C.

The commercial partial saponified *α*-PVA is well known in that acetic acid groups exist blocky in the polymer chains, that is, it is a block copolymer with vinyl alcohol and vinyl acetate. Therefore, the crystallites that consisted of a vinyl alcohol sequence with hydrogen bonds are considered to be mechanically stable yet.

CONCLUSIONS

The DMSO/water (80/20 volume ratio) solution of commercial *α*-PVA₈₈ with a degree of saponification of 88 mol % was gel-spun into methanol (−70°C); the dry-filaments obtained were drawn at 150–180°C until 10 times their original length. Moreover, the predrawn *α*-PVA₈₈ filaments were perfectly saponified and then the filaments

were redrawn at 200°C. The maximum draw ratio and Young's modulus were 28 and 39 GPa, respectively. Their values were very low compared to our expectations. As the commercial partial saponified *α*-PVA is a block copolymer with vinyl alcohol and vinyl acetate, it was considered that the drawability of the filaments was low. Therefore, the partially saponified *α*-PVA that introduced randomly acetic acid groups into polymer chains was considered to be possibly high drawing. This study will be included in our next work.

A part of this work was supported by a Grant-in-Aid for COE Research (10CE2003) by the Ministry of Education, Science, Sports and Culture of Japan.

REFERENCES

1. Smith, P.; Lemstra, P. J. *J Mater Sci* 1980, 15, 505.
2. Smith, P.; Lemstra, P. J.; Pippers, J. P. L.; Kiel, A. M. *Colloid Polym Sci* 1980, 258, 1070.
3. Smith, P.; Lemstra, P. J.; Booi, H. C. *J Polym Sci Polym Phys Ed* 1981, 19, 877.
4. Sawatari, C.; Matsuo, M. *Colloid Polym Sci* 1985, 263, 783.
5. Matsuo, M.; Sawatari, C. *Macromolecules* 1986, 19, 2036.
6. Sakurada, I.; Itoh, T.; Nakamae, K. *J Polym Sci C* 1966, 15, 75.
7. Tashiro, K.; Kobayashi, M.; Tadokoro, H. *J Macromol Sci* 1977, 10, 731.
8. For example, Yamaura, K. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC: Boca Raton, FL, 1996; Vol. 9, p 6998.
9. Kunugi, T.; Kawasumi, T.; Itoh, T. *J Appl Polym Sci* 40, 2101, 1990.
10. Matsuzawa, S.; Sun, L.; Yamaura, K. *Kobunshi Ronbunshu* 1991, 48, 691.