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Studies on the Gel-Spun Poly(vinyl Alcohol) Fiber (I)
- Gel Spinning of High Molecular Weight Atactic Poly(vinyl Alcohol)/ Dimethyl Sulfoxide and Zone Drawing -

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1. Introduction

Poly(vinyl alcohol) (PVA) is a linear flexible chain polymer having a high limit strength of 236g/d and maximum crystal modulus of 2,251g/d. PVA fibers have high tensile and compressive strengths, high tensile modulus, high abrasion resistance, excellent alkali resistance, oxygen barrier property and adhesiveness[1-3] than polyamide, polyester, and polyacrylonitrile fibers. So PVA fiber has developed unique uses mostly in industrial field. In recent years the fiber has caught much attention as reinforcement fiber for cement (best replacement material for natural carcinogenic asbestos fiber or iron rod of ferro-concrete) owing to its excellent alkali resistance.

If a PVA fiber having high resistance to hot water and high resistance to dry heat, as well as still higher tensile strength and modulus, is developed, rubber and plastics reinforced with such fiber for tire cord and rope, fishing net, tent and the like comprising such fiber would become usable under severe conditions of high temperature or high wet temperature, thereby being superior materials excellent in safety, durability, light weight and the like features. To have such properties, PVA must retain high molecular weight (HMW) and high syndiotacticity. Recently, researches for the synthesis of HMW PVA and for the acquirement of high strength fiber from HMW PVA are in progress actively.[4-15]

Up to now, PVA fibers produced by wet spinning from aqueous solution have been widely used in industry, but are quite low in both strength and modulus in comparison with aromatic polyamide fibers. Therefore, to enhance the strength and modulus, organic solutions have been proposed as spinning dope instead of aqueous solutions. These organic solvent systems are as follows: 1, ethylene glycol (EG) or glycerin (GC) from which dry spinning was carried out;[16] 2, dimethyl sulfoxide (DMSO) solution, which was used for wet spinning into

organic coagulants such as methanol, ethanol and benzene;[17] 3, DMSO or DMSO/water mixture solutions from which dry-wet spinning was performed;[15, 18] 4, GC, EG or GC/EG/water solutions, which were employed as the dope for gel spinning of PVA.[7, 9, 19] The fibers obtained from these dopes, however, exhibit in all cases strength lower than 25g/d (3GPa) and modulus lower than 700g/d (85GPa) despite of PVA having limit strength of 236g/d and maximum crystal modulus of 2,251g/d. This reason might be explained by the existence of the hydroxyl group and the hardness of the crystals in PVA. The hydroxyl groups cause steric hindrance and prevent slippages and alignments of molecular chains during drawing or annealing. Moreover, hydrogen bonds are formed between adjacent hydroxyl groups. The intra and inter molecular hydrogen bonds are very numerious and complex. The crystal of PVA has high melting temperature of 225-265°C and is harder in plastic deformation. The crystal act as points that bundle the molecular chains and inhibit the free movement of amorphous chains. From the facts described above, it can be supposed that the hydrogen bonds and hard crystals rather than molecular chain entanglements are more important for superdrawing to enhance the tensile strength and modulus of PVA.

This paper will describe gel spinning of high molecular weight atactic PVA from DMSO. PVA samples were prepared by low temperature bulk and solution polymerizations of vinyl acetate and saponification to produce HMW PVA.[20] In order to effectively orient molecular chains of gel-spun PVA fiber, those prepared were drawn under various hot and zone drawing conditions. Also, the tensile properties of the PVA fiber were investigated.

2. Experimental

Linear HMW (PVA)s (number average degree of polymerization (P_n) of 3,000-5,000) were obtained by saponifying HMW poly(vinyl acetate)s ((PVAc)s). (PVAc)s were prepared by using a low temperature bulk and solution polymerization of vinyl acetate to obtain HMW and good linearity.[20] The PVA/DMSO spinning dope was prepared at 80°C. Dry-wet spinning was performed by extruding the dope from a nozzle having a hole size of 1mm. The dope was extruded into open air at 30°C, and then immediately coagulated in methanol kept at various temperatures to obtain undrawn PVA gel fibers. The dried fibers were hot- and zone-drawn at 220°C. The tensile strength and tensile modulus of the fibers were measured at a cross-head speed of 10mm/min, a gauge length 25mm, and 25°C.

3. Result and Discussion

Figure 1 shows the tensile strength of PVA (P_n of 3,200, syndiotactic diad content of 52.7%, and degree of saponification of 99.9%) fiber prepared by hot drawing at 220°C as a function of draw ratio. Draw ratio up to 15.5 times was achieved. Tensile strength increased with increasing draw ratio of the fiber and the maximun value could reach to 3.01GPa. Figure 2 shows the tensile modulus of PVA fiber described in Figure 1. Tensile modulus increased with increasing draw ratio of the fiber and the maximun value could reach to 83.28GPa.

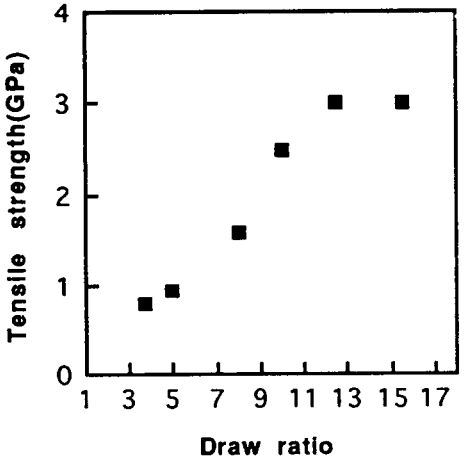

Figure 1. Tensile strength of hot-drawn PVA fiber with draw ratio.

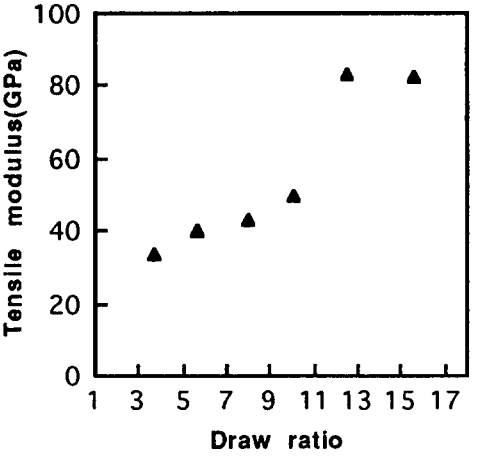

Figure 2. Tensile modulus of hot-drawn PVA fiber with draw ratio.

These data were well coincident with strength data in Figure 1. The tensile properties of PVA (P_n of 3,200, syndiotactic diad content of 52.7%, and degree of saponification of 99.9%) fibers prepared by hot and zone drawings at 220°C are listed in Table 1. The tensile properties of the fiber prepared by zone drawing were superior to those by hot drawing. In case of the zone drawn fiber, ultrahigh modulus of over 100GPa could be obtained.

Table 1. Comparison of tensile properties between zone-drawn and hot-drawn PVA fibers

	Maximum tensile strength (GPa)	Maximum tensile modulus (GPa)
Zone-drawn	3.17	101.47
Hot-drawn	3.01	83.28

4. Conclusion

This study is mainly focused on the preparation of high strength and high modulus PVA fibers by gel spinning and high-temperature zone drawing. Gel spinning of HMW atactic PVA was conducted from the PVA/DMSO dope. Ultrahigh modulus as well as high strength could be achieved by using simple zone drawing method. The maximum tensile strength and modulus of the drawn fiber were approximated to 3.17 and 101.47GPa, respectively.

5. References

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