

Preparation of High-Strength Poly(vinyl Alcohol) Fibers by Crosslinking Wet Spinning

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Synopsis

High-strength poly(vinyl alcohol) (PVA) fiber was obtained by the crosslinking wet-spinning technique, which is an improved technique of the conventional non-crosslinked type wet-spinning of PVA. High tensile strength as well as high Young's modulus was achieved by introduction of the borate ion-aided crosslinks during the coagulation process. The drawability of the as-spun fiber greatly depends on the fiber thickness. The thinner the fiber, the higher the drawability. Since thinner fiber is subject to a very high shear rate on extrusion, the crosslinks introduced are believed to maintain topological memory of the oriented chains, which have a low density of entanglements. This allows drawing the fiber to a higher draw ratio. The strength and Young's modulus of the resultant highly drawn PVA fiber were achieved to be 22 g/d (2.3 GPa) and 430 g/d (50 GPa), respectively. The mechanism of the spinning was discussed and the spinning condition was carefully examined in order to optimize the final mechanical properties of the PVA fibers.

INTRODUCTION

Technical developments of ultrahigh strength fiber production is based on the concept of the perfect chain orientation by unfolding of flexible polymer chains or designing rigid rod molecules. Discovery of the gel spinning of ultrahigh molecular weight polyethylene, which is one of the most flexible polymers, has prompted investigations of ultradrawing of many kinds of flexible polymers.¹⁻⁵

Poly(vinyl alcohol) (PVA) has high potential as a candidate of ultrahigh strength fibers because of its superior qualities of crystalline modulus, impact strength, weather durability, antialkaline resistance, and so on.⁶ The crosslinking wet-spinning technique was originally employed to produce uniform PVA fibers.^{7,8} Recently this technique has been used to produce a high strength fiber.⁹ Although many studies have been reported in patents,⁹⁻¹⁷ for the above reasons, little attention has been paid to the spinning mechanism. In this article, we discuss the mechanism of the crosslinking wet-spinning with respect to both the chain orientation and the effects of crosslinks, and show the spinning conditions which optimize the final mechanical properties.

EXPERIMENTAL

Material

Commercially available atactic poly(vinyl alcohol) was resaponified in a mixture of methanol and water (80/20 wt%) containing NaOH and was

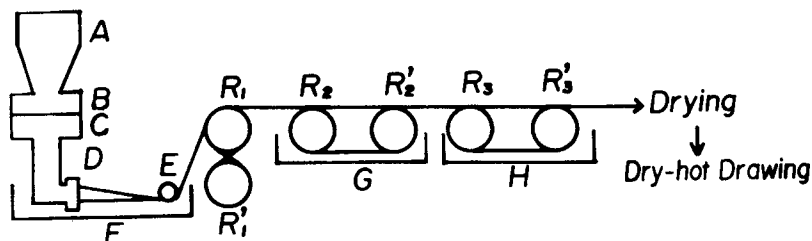


Fig. 1. Schematic diagram of the apparatus of the crosslinking wet-spinning of PVA: spinneret, A; gear pump, B; filter, C; nozzle, D; guide E; coagulation bath, F; neutralization bath, G; washing bath, H.

purified by dialysis. The final saponification value was higher than 99.5 mol%. The degree of polymerization, P , was determined to be 1780 by viscometry. Purified PVA was dissolved in boiling water. The concentrations of PVA and boric acid in the spinning solution were varied between 2 and 20 wt% and between 0 and a few percent, respectively.

Spinning

The spinning apparatus employed in this study is shown in Figure 1, which is composed of four parts, the spinneret (Solution tank A, Gear pump B, Filter C, and Nozzle D), the coagulation bath F, the neutralization and wet curing bath G, and the washing bath H. The spinning speed at the nozzle was between 10 and 20 m/min and the diameter of the nozzle was chosen from among 0.06, 0.08, 0.09, 0.04, and 0.8 mm. Several kinds of inorganic salt solutions were examined for the coagulation bath (F). Wet drawing was conducted between roller R_1 and R_2 . Then the fiber was sent to the neutralization bath (G) where the crystallinity of the fiber was raised by crosslinking scission and wet curing. Successive washing with water was carried out in the washing bath (H) followed by drying and dry-hot drawing up to the maximum draw ratio at ca. 235°C.

Viscometry

Viscosities of the spinning solutions were measured with a viscometer, Coolninc Circulator CTE-22A, Yamato Kagaku Co. at 60°C.

Electron Microscopy

Scanning electron micrographs of the cross section of the spun fibers shadowed with platinum were taken with a JSM-T100, Japan Electron Co., Ltd.

RESULTS AND DISCUSSION

Optimization of the Spinning Conditions

Viscosity and stability of the boric acid-added PVA spinning solution. Figure 2 shows the viscosity of the PVA spinning solutions in the existence of NaOH (A), $\text{Na}_2\text{B}_4\text{O}_7$ (B), and the blank (C), as a function of boric

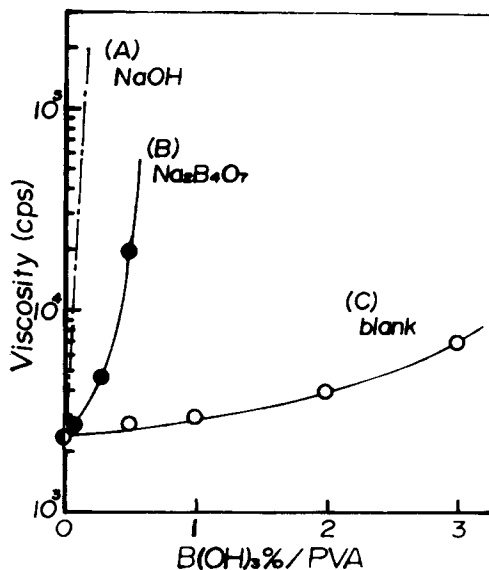


Fig. 2. Boric acid concentration dependence of the viscosity of the spinning solutions with either NaOH (A) or Na₂B₄O₇ (B) and the blank (C).

acid concentration. For Case (B) boric acid concentration was calculated by assuming perfect dissociation of Na₂B₄O₇. In the case of (C), this is an acidic solution, the viscosity gradually increases with boric acid content which is accounted for by an increase in hydrogen bonding. On the other hand, viscosity steeply increases with the boric acid concentration in the existence of alkaline reagent [sodium hydroxide (A) or alkaline salt such as Na₂B₄O₇ (B)]. This is due to crosslinking between PVA chains. The mechanism of the crosslinking formation of PVA in the existence of boric acid, which was investigated in a previous report,¹⁸ is a borate-ion-aided crosslink based on the monodiol complex as shown in Figure 3. The stability of the spinning solution was monitored by measuring the viscosity at 60°C for more than 10 days. There was no significant change in viscosity for either solutions with or without boric acid.

Effects of coagulants on the fiber. Several alkaline salts and/or alkaline reagents were examined as coagulants. Table I shows the reagents, those concentrations in g/L, pH, total draw ratio, and tenacity. Na₂SO₄, listed at the bottom (No. 5), is the coagulating reagent normally used in the wet-spinning. In this case the cross section is flattened and there exists so-called skin-core structure. This is a result of coagulation taking place from the surface of the fiber where a coagulated shell is formed. This shell cannot be shrunk and, therefore, makes the fiber flat due to further solidification. On the contrary, the other coagulants (marked 1 to 4) provide a round cross section. This is due to crosslinking of PVA chains in alkaline condition. Boric acid in the spinning solution plays an important role in the coagulation process. It is believed that prior to coagulation the PVA solution gels maintaining the high permeability of the crosslinking reagent and the solvent. Successive coagulation occurs by squeezing water rather homogeneously, giving rise to a circular

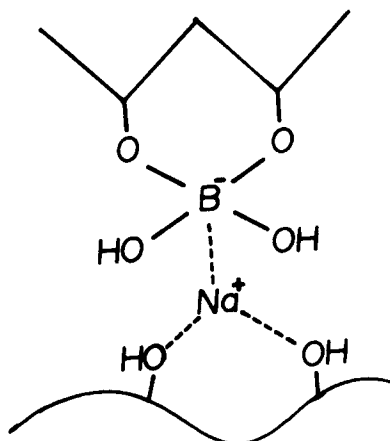


Fig. 3. Chemical structure of the borate-ion-aided crosslink based on the monodiol complex proposed from a ^{11}B -NMR study. The crosslink is formed by an ionic bonding between the PVA-bound borate ion and the PVA-chelated sodium ion.

shaped cross section. From among several reagents, a sodium hydroxide and sodium sulfate mixture gives the highest drawability and tenacity. Taking into account that sodium sulfate is a salting reagent and sodium hydroxide is a crosslink-aiding reagent, both reagents are necessary to obtain crosslinked coagulated fibers. We chose the NaOH and Na_2SO_4 mixture as one of the best coagulants. Concentration dependence of the final mechanical properties of PVA fiber was then studied and the combination of 20 to 40 g/L of NaOH, and 400 g/L of Na_2SO_4 was determined as one of the best compositions of coagulant. The effect of boric acid concentration on the spinning solution as well as the PVA concentration on the final properties of the fiber was also examined and found to be best when 1 wt% of boric acid ratio was added to a 15–18 wt% of PVA aqueous solution. This boric acid concentration corresponds to ca. 1/70 to the PVA monomeric units.

Fiber-thickness dependence of the maximum wet-draw ratio. Fibers were spun with several spinnerets having different hole diameters so as to clarify the relationship between the fiber thickness and the maximum wet-draw

TABLE I
Effects of the Composition of the Alkaline Coagulants on the Properties
of the PVA Fiber

No.	Coagulants	(g/L)	pH	Total draw ratio (times)	Tenacity (g/d)
1	CH_3COONa	100	9.0	13.0	11.2
2	Na_2CO_3	100	11.0	15.0	10.3
3	NaOH	400	13.7	16.2	14.6
4	Na_2SO_4	400	13.0	20.5	17.1
5 ^a	NaOH	10			
	Na_2SO_4	400	7.0	13.5	12.5

Spinning condition: $\text{B}(\text{OH})_3$ concentration; 1 wt%/PVA; Nozzle; 100 H \times 0.09 mm ϕ .

^a One of the conditions of conventional noncrosslinking spinning.

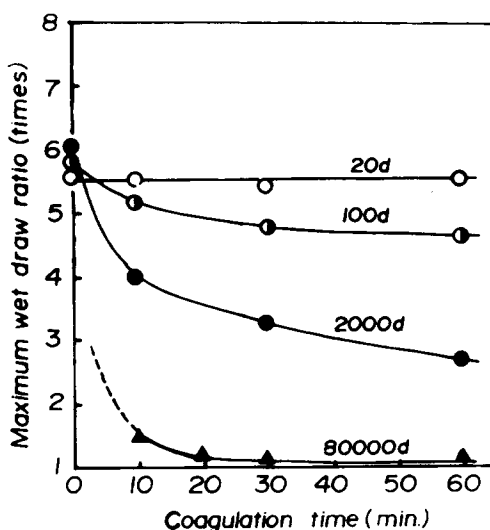


Fig. 4. Coagulation time dependence of the maximum draw ratio for several fibers having different fiber thicknesses.

ratio. The rate of extrusion at the nozzle was kept constant (20 m/min). Figure 4 shows the coagulation time dependence of the maximum wet-draw ratio for fibers spun with different fiber thickness. Several interesting points are disclosed from this figure: (1) The thinner the fiber, the more drawable it is. (2) For the fibers having 20 d, there is no coagulation time dependence of the wet-draw ratio in this time scale. (3) A PVA lump made between parallel filtering papers, which is corresponding to about 80000 d, has almost no drawability if it is coagulated longer than 20 min.

Two kinds of crosslinks: drawable and nondrawable, are obtained by changing the nozzle diameter. In the case of thin fibers, coagulation takes place instantly when the fiber is extruded. With increasing fiber thickness coagulation time dependence appears. In addition, the spun fibers lose the drawability with time. Crosslinking takes place quickly just after the spinning solution is extruded, where the PVA chains might be highly oriented particularly when the nozzle diameter is small and the extrusion rate is fast enough. This is the case of the fiber of 20 d. The crosslinks may keep the topological memory of the original PVA chains. Otherwise, it is difficult to explain the nozzle thickness dependence of drawability. These findings strongly indicate that the shear induced on extrusion plays an important role in drawability.

Spinning-draft dependence. The spinning-draft dependence of the fiber properties was studied by changing the roller (R_1) speed under the constant spinning quantity, 10 g/min and the size and number of the nozzle, 0.08 mm ϕ \times 100 holes. Figure 5 shows the spinning-draft dependence of maximum draw ratio and tenacity. The total draw ratio is obtained by multiplying the wet-draw ratio by the hot-draw ratio. This shows that the lower the spinning draft, the higher the maximum draw ratio of the wet drawing, which results in the higher total drawability and tenacity. This indicates that extruded chains, which are crosslinked just after the nozzle and are spontaneously relaxed due

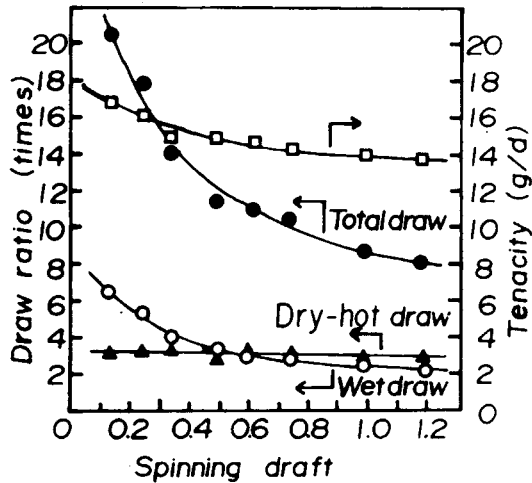


Fig. 5. Spinning draft dependence of the maximum draw ratio and the tenacity.

to the low spinning draft, have a memory of a high orientation and low entanglement density when they are spun.

Neutralization bath. The neutralization bath process is used for neutralization, crosslink scission, and crystallization process of the alkaline spun fibers. It is well known that anti-hot water resistance depends largely on the degree of crystallinity which is partially controlled in this process. Owing to the swelling experiments of the fibers after treatment in this process, we found that salt concentration and temperature are two of the major factors in controlling the final properties. We chose 250–300 g/L of Na_2SO_4 , 5–10 g/L of H_2SO_4 as a neutralization reagent and 85–95°C for the processing temperature.

Residual boric acid concentration. Although the greatest amount of boric acid is removed at the neutralization and washing processes, there is some residue, which is believed to be important to heat resistance of the

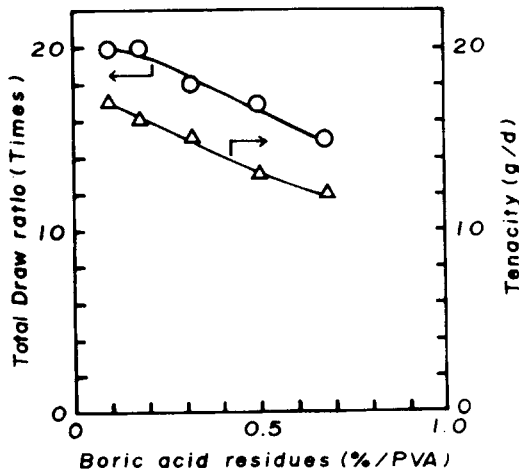


Fig. 6. Boric acid content dependence of the final properties of the fiber.

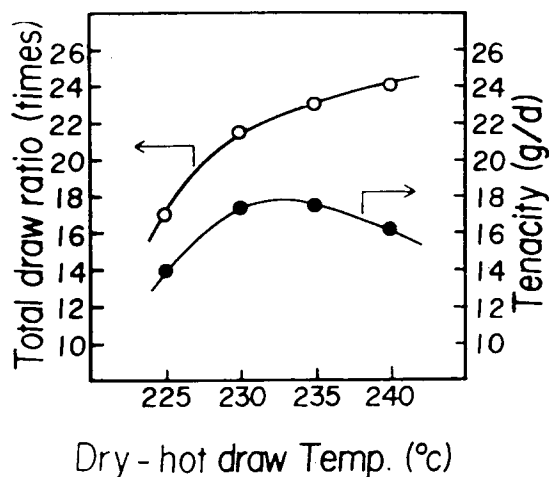


Fig. 7. Dry-hot drawing temperature dependence of the total draw ratio and the tenacity.

fiber.¹³ Figure 6 shows the boric acid content dependence of the total draw ratio and tenacity of the fiber. From this figure one may conclude that 0.1% of residual boric acid content is best for the final properties, although experiments for lower residues are uncertain.

Dry-hot drawing condition. Figure 7 shows the dry-hot drawing temperature dependence of the total draw ratio and tenacity. Total draw ratio increases with drawing temperature, whereas tenacity does not. Tenacity reaches a maximum around 235°C. Considering that the melting temperature of the spun PVA fibers is around 235°C, (to be discussed in a forthcoming report¹⁹), this may be due to slippage between the chains.

Comparison of the Morphology and Mechanical Properties Between the Fibers Prepared with This Method and with the Conventional Noncrosslinking Method

In this section we compare the morphology and mechanical properties of the fibers prepared by the crosslinking wet-spinning and the conventional noncrosslinking method. The samples were obtained at several stages of the spinning process; (a) as extruded, (b) after washing, and (c) after dry-hot drawing. Although the details will be discussed elsewhere,¹⁹ Table II shows the sample specification used for the comparison. N-5 and B-5 are fibers drawn three times, wet-heat-treated and washed. N-7 was obtained by dry-hot drawing of N-5 4.0 times (the maximum draw ratio) at 235°C. The total draw was 12.0. B-7 was drawn 3.5 times before the wet-heat treatment and 6.3 times (the maximum draw ratio) in the dry-hot drawing process. The total draw was 22.1.

Cross section of the fibers. Figure 8 shows micrographs of the cross sections of the fibers prepared with this method (B series) and those with the conventional noncrosslinking method (N series). In the case of N series, coagulation takes place first at the skin of the fiber, which delays further coagulation of the inner parts. The hard skin, which is hardly shrunk, leads

TABLE II
Fiber Sample Specification

Sample code	Draw ratios (times)			Remarks
	Wet	Dry-hot	Total	
B-1	1	—	1	As extruded
B-5	3	—	3	After washing
B-7	3.5	6.3	22.1	After dry-hot drawing
N-1	1	—	1	As extruded
N-5	3	—	3	After washing
N-7	ca.3	ca.4	ca.12	After dry-hot drawing

the flattened cross section and so-called “skin-core” structure. In the case of B series, on the contrary, the micrographs suggest that the PVA is crosslinked prior to being coagulated. That is, the gelled PVA keeps its round shape at the cross section during solidification. The skin-core two-phase structure is not so clear.

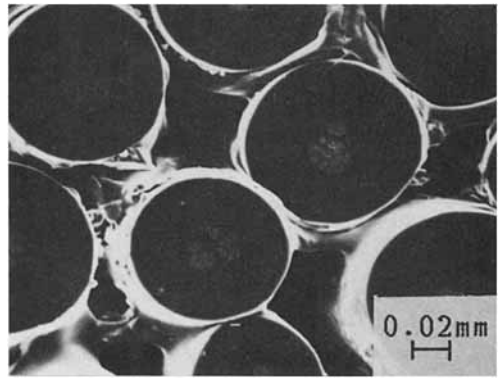
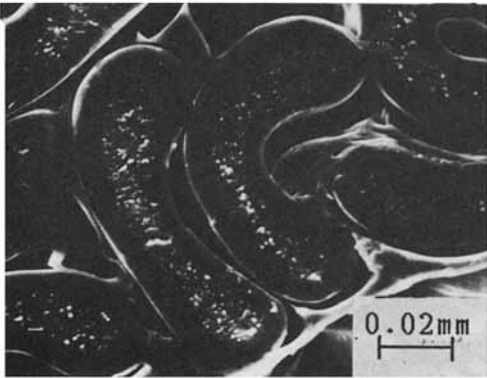
Tensile properties of the fibers. Tensile properties of B series were compared with those of N series. The results are shown in Figure 9. As can be seen, the dry-hot drawing plays an important role in improving the tensile properties of the fibers for both N and B series. B series, having a history of crosslinks, has higher maximum drawability at the hot-drawing process. This results in the higher tensile strength, 22 g/d, compared with that of N-7 (13 g/d). The higher tensile strength of B-7 (22 g/d) than that discussed in the previous section (about 17 g/d as shown in Fig. 4) results from the reduction of the wet-draw ratio to 3.5 times and the increase of the dry-hot draw ratio. The wet-draw ratio in Figure 4 is the maximum wet-draw ratio at which the fiber is broken. Since the final tensile strength depends greatly on the combination of the spinning draft, the wet-draw ratio, and the dry-hot draw ratio, we saved the drawability of the fiber at the wet-draw stage so as to maximize the dry-hot draw effect.

Crosslinks and Drawability

As discussed in the preceding sections, the fibers prepared with the crosslinking wet-spinning have high drawability. In this section we discuss the origin of that high drawability on the basis of the chain orientation and summarize the spinning process. Figure 10 shows the schematic diagram of the molecular orientations of PVA chains in the process of the crosslinking wet-spinning. PVA chains are oriented along the extruding direction when they are extruded through the nozzle. Just after extrusion, the chains are crosslinked as shown in Figure 10(b). In this process the entanglement density should be relatively low because a high shear rate is applied. This is partially supported by electron micrographs (Fig. 8) and fiber thickness dependence of the maximum draw ratio (Fig. 4). Although the fibers are relaxed as shown in (c), their memory of the low entanglement density is topologically reserved. This enables one to draw the fibers without slippage or breakdown (d). The crosslinks are then cut in the acidic bath, because the crosslinks prevent the

Non-crosslinked Type

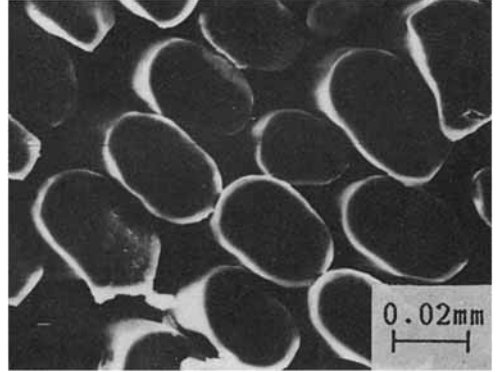
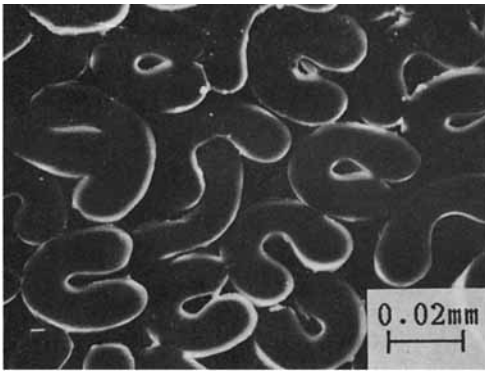
Crosslinked Type



N-1

Sampled after
Coagulation Bath

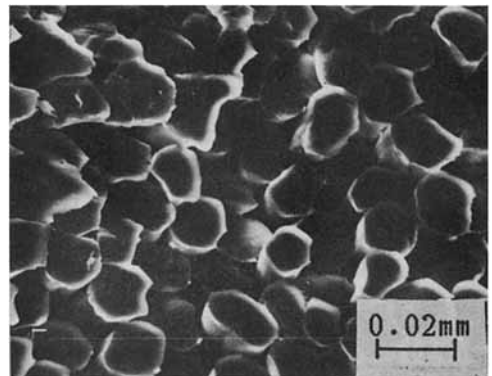
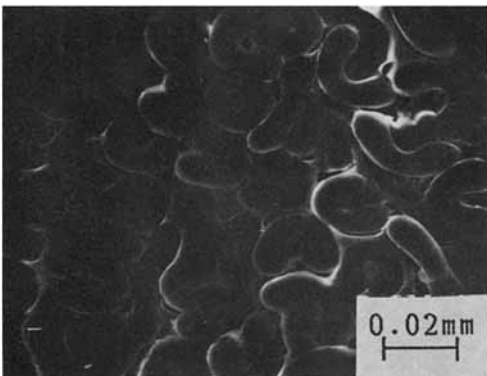
B-1



N-5

Sampled after
Washing Bath

B-5



N-7

Sampled after
Dry-hot Drawing

B-7

Fig. 8. Electron micrographs of the cross sections of the fibers of N series (noncrosslinked type) and B series (crosslinked type).

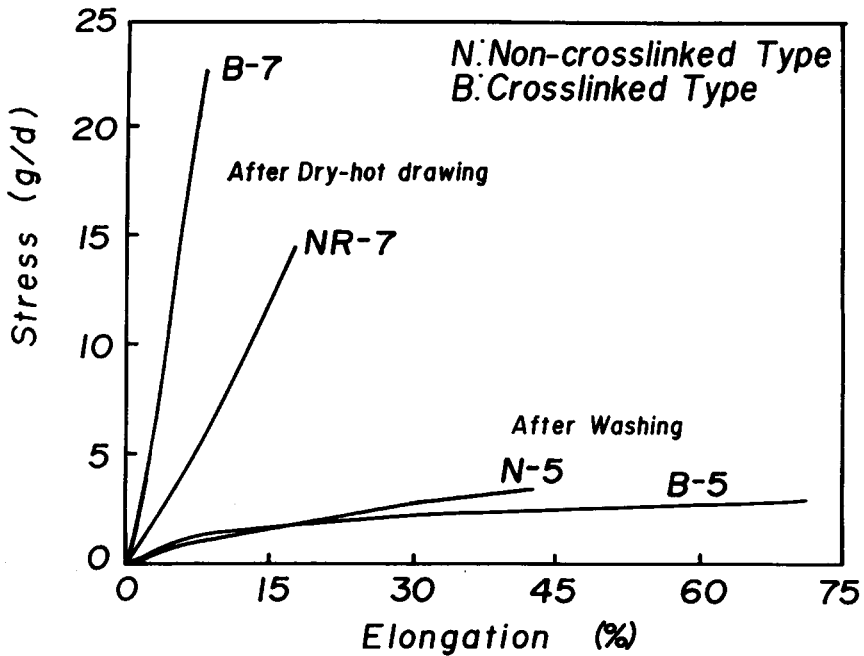


Fig. 9. Stress-strain curves of N and B series.

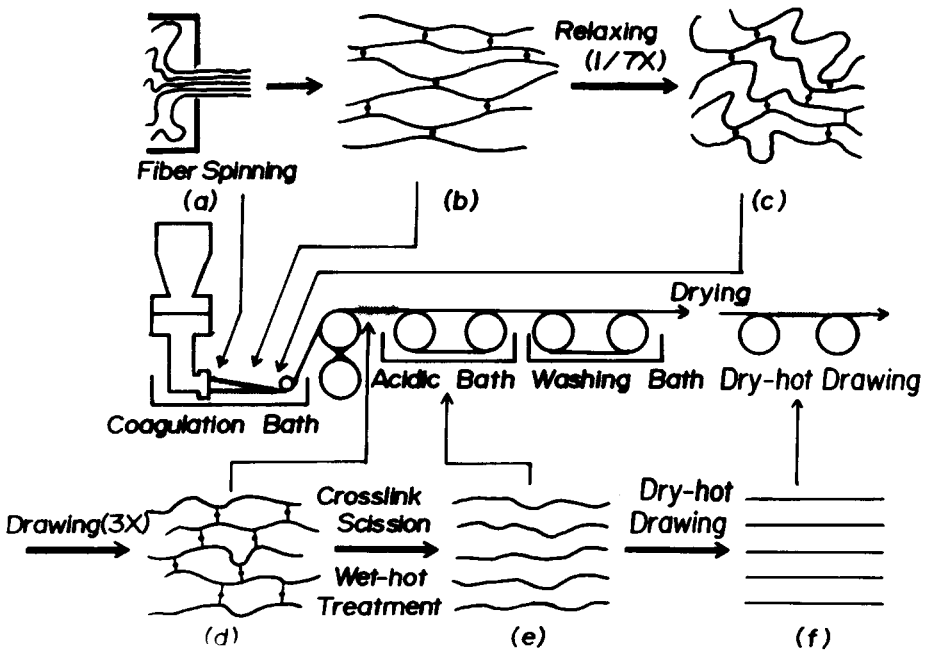


Fig. 10. Schematic diagram showing the molecular orientation during the spinning process. The solid lines and circles denote the PVA chains and the crosslinking points, respectively. The shaded areas show where the fibers are drawn.

fiber from being highly drawn. In addition to this, the wet-hot acidic bath treatment promotes crystallization of PVA. Successive hot drawing increases the crystallinity and improves the mechanical properties.

The most important process of this technique is (b), namely the introduction of crosslinks into the oriented chains. Although this process has not been directly examined in light of the chain orientation by any experimental methods, indirect observations, say, the fiber thickness dependence and the spinning draft dependence of drawability, as well as the shapes of the cross sections support the above mechanism.

CONCLUSION

Conditions for crosslinking wet-spinning of PVA were carefully examined to provide high tenacity fibers. It is concluded that the following is one of the best conditions for this technique:

Coagulation bath	350–400 g/L of Na ₂ SO ₄ and 20–40 g/L of NaOH, temperature 40°C
Boric acid concentration	1 wt% with respect to PVA
Spinning draft	around 1/5 to 1/7 (spontaneous relaxing)
Neutralization bath	250–300 g/L of Na ₂ SO ₄ and 5–10 g/L of H ₂ SO ₄ , temperature 85–95°C
Dry-hot drawing temperature	230–235°C

These conditions provide a high strength PVA of 22 g/d (~ 2.3 GPa) tenacity, 430 g/d (~ 50 GPa) Young's modulus and a round-shaped cross section with this little inhomogeneity along the radial direction. Mechanical properties of the fiber were remarkably improved by employment of the crosslinking wet-spinning.

The origin of the high tenacity of the fibers prepared with the crosslinking wet-spinning technique was discussed on the basis of the chain orientation during the spinning: (1) The introduction of the crosslinks into the oriented chains is very important to reduce entanglement density and slippage between chains. (2) Stretching of the fibers in the existence of crosslinks is effective to chain orientation. (3) Crosslink scission is necessary for higher stretching and further crystallization in the dry-hot draw process.

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