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Structure and properties of microfibrillar poly(vinyl alcohol) fibres prepared by saponification under shearing force of poly(vinyl pivalate)

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Novel, high-strength, microfibrillar poly(vinyl alcohol) fibres (PVA fibrils) having a number-average degree of polymerization (P_n) of 4500–20 000, a degree of saponification (*DS*) of 85.0–99.9% and a syndiotactic dyad (S-dyad) content of 57–64% could be prepared successfully by saponifying under shearing force poly(vinyl pivalate) having a P_n of 11 300–33 000. The saponifying agent used was a mixture of potassium hydroxide, water and methanol. The PVA fibrils had dimensions of 1–50 μm in diameter, 0.5–200 mm in length, irregular cross-sections and needle-point-like ends. The high-strength PVA fibrils prepared by the fibrillation method had an orientation index of over 0.88, a crystallinity of over 48%, a crystal melting temperature of higher than 260°C and an accumulated ultrafine microfibril structure. The PVA fibrils having a P_n of over 10 000 exhibited higher than 12 g den^{-1} of maximum tensile strength and their resistance to hot water was excellent. Moreover, these properties were enhanced by increases in the P_n, S-dyad content and *DS* of the PVA fibrils. Copyright © 1996 Elsevier Science Ltd.

(Keywords: high-strength PVA fibrils; S-dyad content; fibrillation method)

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a linear, flexible-chain polymer having a high-limit strength of 236 g den^{-1} and a maximum crystal modulus of 2251 g den^{-1}. PVA fibres are employed profitably as a high-performance substance and the best replacement material for natural, carcinogenic asbestos fibres or iron rods in ferroconcrete because they have high tensile and impact strengths, high tensile modulus, high abrasion resistance, excellent alkali resistance, oxygen barrier properties and good binding properties[1-3]. For the fibres to have such properties, the PVA must have a high molecular weight (HMW)[4,5] and high syndiotacticity. Research is active in the synthesis of syndiotacticity-rich, ultrahigh-molecular-weight (UHMW) PVA and the acquirement of high-strength fibre from UHMW PVA. Yamaura *et al.*[6] obtained a syndiotacticity-rich, UHMW PVA having a maximum number-average degree of polymerization (P_n) of over 12 000 and a syndiotactic dyad (S-dyad) content of 57% by the bulk polymerization of vinyl trifluoroacetate. Yamamoto *et al.*[7,8] synthesized a syndiotacticity-rich, UHMW PVA having a maximum P_n of 18 000 and an S-dyad content of 62.8% via the ultra-violet (u.v.) ray initiated, low-temperature emulsion polymerization of vinyl pivalate (VPi). Fukunishi *et al.*[9] prepared high-performance PVA fibres having a tensile strength of over 25 g den^{-1} and a tensile modulus of over 640 g den^{-1} by spinning and drawing a syndiotacticity-rich, HMW PVA from a solution in dimethyl sulfoxide (DMSO). Nakamae *et al.*[10] made fibres using PVAs with different tacticities and found that the higher the syndiotacticity of PVA, the more excellent the physical properties of the fibres.

Since the first invention of PVA fibres by Herrmann and Haehnel in 1931[11], the preparation of high-strength and high-modulus PVA fibres has been achieved via zone drawing[12,13], crosslinking and wet spinning[14-16], crystal mat drawing[17] and gel drawing[18-22], concomitant with complex steps such as spinning, drawing and heat treatment. Yoon and Son[23,24] found that poly(p-phenylene terephthalamide), a rigid-rod polymer forming a lyotropic liquid crystal in a certain concentration range, could form a microfibrillar structure during its synthesis. However, in the case of fibre-forming flexible-chain polymers such as PVA, polyethylene, polyacrylonitrile, poly(vinyl chloride) and polystyrene, the fibrillation of polymers has depended entirely on the immiscible polymer blend procedure involving extrusion, orientation and extraction[25-30].

In this study, to obtain syndiotacticity-rich, UHMW PVA, we synthesized HMW poly(vinyl pivalate) (PVPi) and directly prepared high-strength microfibrillar PVA fibre (PVA fibril) via the saponification under shearing force of the resultant HMW PVPi. The effects of the molecular weights (*MWs*) of PVPi and PVA, the syndiotacticity of PVA and the degree of saponification (*DS*) of PVA on the structure and properties of the PVA fibrils were also investigated.

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EXPERIMENTAL

Materials

VPi from Shin-Etsu was washed with an aqueous solution of $NaHSO_3$ and water and dried over anhydrous $CaCl_2$, then distilled under reduced pressure and an atmosphere of nitrogen. 2,2-Azobis(2,4-dimethylvaleronitrile) (ADMVN) from Wako was dissolved in methanol and purified by crystallization. Other reagents were used as received from Aldrich.

Photo-bulk and solution polymerization of VPi

VPi and VPi–DMSO were added separately to a pyrex tube in a low-temperature methanol bath. The tube was flushed with nitrogen for 3 h. Once the polymerization temperature had been reached and ADMVN added, the mixture was irradiated with a high-pressure mercury lamp. The polymer was purified by reprecipitation from benzene–methanol[31] and dried in a vacuum oven at 60°C.

Saponification and in situ *fibrillation*

In a flask equipped with a reflux condenser, a thermocouple, a dropping funnel and a stirrer, 3 g of PVPi was dissolved in 300 ml of tetrahydrofuran (THF). The PVPi solution was flushed with nitrogen, as was an optimal amount of a potassium hydroxide–methanol–water mixture in a dropping funnel. The alkali solution was added to the PVPi solution with stirring and the mixture was kept at a fixed temperature. Once the saponification reaction was complete, the fibrillar reaction mixture in methanol was shaken mechanically or treated with an ultrasonic generator. The fibres thus produced were filtered and washed several times with methanol. A quantitative yield of bright-yellow, high-strength PVA fibrils was obtained (*Figure 1*).

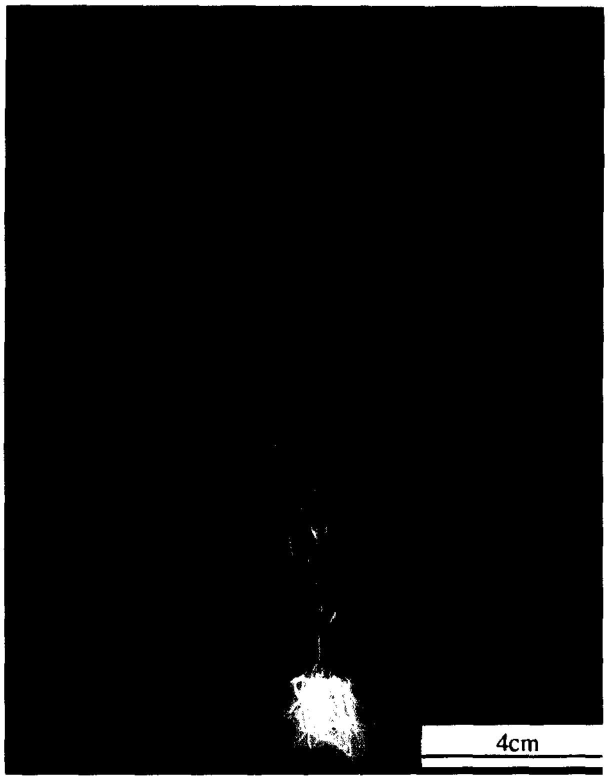


Figure 1 Photograph of microfibrillar PVA fibres

Acetylation of PVA fibrils

To a three-necked flask were added 1 g of PVA fibrils, 2 ml of pyridine, 20 ml of acetic anhydride and 20 ml of acetic acid, and the mixture was stirred for 100 h under an atmosphere of nitrogen. Then the mixture was poured into cold water to precipitate poly(vinyl acetate) (PVAc). The PVAc thus produced was filtered and purified by repeated reprecipitation from a mixture of methanol and water.

Determination of the MW

The *MW* of PVPi was calculated using[32]

$$[\eta] = 2.88 \times 10^{-5} M_n^{0.77} \quad \text{(in acetone at 25°C)} \qquad (1)$$

where $[\eta]$ is the intrinsic viscosity of PVPi and M_n is the number-average *MW* of PVPi. Alternatively, the *MW* of PVA could be determined from the viscosity of the PVAc produced by acetylating PVA using[33]

$$[\eta] = 8.91 \times 10^{-3} P_n^{0.62} \quad \text{(in benzene at 30°C)} \qquad (2)$$

where P_n is the number-average degree of polymerization of PVAc.

Determination of syndiotacticity and the DS

The S-dyad content of the PVA fibrils was determined using a proton nuclear magnetic resonance (^1H n.m.r.) spectrometer (Varian, Sun Unity 300). The *DS* of the PVA fibrils was determined from the weight loss after saponification and from the ratio of t-butyl proton and methylene proton peaks in the ^1H n.m.r. spectrum.

Wide-angle X-ray diffraction analysis

Wide-angle X-ray diffractograms were obtained with nickel-filtered CuKα radiation (40 kV, 200 mA) and diffraction patterns were obtained with a Laue camera (Mac Science, MXP-18). The degree of orientation π was calculated from

$$\pi = (180 - H^\circ)/180 \qquad (3)$$

where H° is the half-width of the intensity distribution curve for the 101 reflection of the PVA fibril. The crystallite size $D_{(101)}$ was estimated using Scherrer's equation

$$D_{(101)} = \lambda/\beta\cos\theta \qquad (4)$$

where λ is the X-ray wavelength, θ is the Bragg angle of the reflection and β is the pure integral width of the reflection.

Degree of crystallinity

The density of the PVA fibrils (d) was determined by a density-gradient tube method (in benzene–carbon tetrachloride) at 30°C. The degree of crystallinity (X_c) was calculated from

$$1/d = X_c/1.345 + (1 - X_c)/1.269 \qquad (5)$$

where 1.345 (g ml^{-1}) and 1.269 (g ml^{-1}) are the crystal[34] and amorphous[35] densities of PVA, respectively.

Crystal melting temperature

The crystal melting temperature (T_m) of the PVA fibrils was measured on a differential scanning calorimeter (Perkin–Elmer, DSC 7) with a sample weight of 10 mg and a heating rate of 10°C min^{-1}.

Surface structure observation

Polarizing micrographs of the PVA fibrils were obtained using a polarizing microscope with a Senarmont compensator (Nikon, Optiphot-Pol 104). Scanning electron micrographs of the PVA fibrils were taken on a Cambridge S-360 scanning electron microscope at an acceleration voltage of 10 kV.

Tensile strength

Load–elongation curves were recorded on an Instron 4201 using a sample length of 2 cm and a crosshead speed of 10 mm min^{-1}. The reported tensile strength of the PVA fibril was the average value of 20 samples.

Degree of solubility and swelling

The degree of solubility of the PVA fibrils in hot water at 105°C after 3 h was calculated using[36]

$$\text{degree of solubility} = 1 - (W_a/W_b) \qquad (6)$$

where W_a is the weight of dried fibrils after treatment and W_b is the weight of dried fibrils before treatment. The degree of swelling of the PVA fibrils in water at 30°C after 50 h was derived from[36]

$$\text{degree of swelling} = (W_s/W_d) - 1 \qquad (7)$$

where W_s is the weight of swollen fibrils and W_d is the weight of dried fibrils after swelling.

Alkali resistance

To test the alkali resistance of the PVA fibrils, we soaked the PVA fibrils in 0.1% (g l^{-1}) aqueous calcium hydroxide solution at a pH of 13.4 for 20 days.

RESULTS AND DISCUSSION

Preparation of PVA fibrils

High-strength PVA fibrils having a P_n of 4500–20 000, a *DS* of 85.0–99.9% and an S-dyad content of 57–64% were obtained by saponifying PVPi dissolved in THF[37]. To improve the properties of the PVA fibrils, we utilized five combinations of shear speeds and stirring devices, as listed in *Table 1*.

The fibres formed by our fibrillation method had dimensions of 1–50 μm in diameter, 0.5–200 mm in length, irregular cross-sections, needle-point-like ends and an accumulated ultrafine microfibril structure. In terms of the optimal combination of complex fibrillation factors, it was possible to control the thickness and length of the PVA fibrils to some extent. The fibres prepared with an H-shaped anchor-type stirrer were finer and longer than those prepared with a simple anchor-type stirrer owing to the more regular propagation of shear force to the inner part of the reaction mixture. In the case of the higher shear speeds, finer and longer fibres were obtained by fixing a housing onto the stirrer for the suppression of the Weissenberg effect. For the same stirring device, the higher the syndiotacticity, shear speed and reaction temperature, the finer and longer the fibrils. Also, the mechanical shaking and ultrasonic treatment of the fibrils after the saponification affected the length and thickness of the fibrils.

Table 1 Methods used for the fibrillation of PVA

Method	Agitation speed (rev min^{-1})	Stirring device
A	10 000	H-shaped anchor-type stainless steel stirrer with housing
B	5000	H-shaped anchor-type stainless steel stirrer with housing
C	5000	Anchor-type stainless steel stirrer
D	1000	Anchor-type Teflon stirrer
E	500	Egg-shaped magnetic stirrer bar

Crystal structure and degree of orientation of the fibrils

It is known that the volume taken up by the hydroxy groups in PVA is so small that the polymer can crystallize despite the stereoirregular arrangement of the hydroxy groups[38,39]. *Figure 2* shows the crystal structures of atactic and syndiotactic PVAs constructed on the basis of Bunn and Peiser's model[38]. The higher the syndiotacticity of PVA, the more regular the distribution of hydroxy groups, and the packing of PVA chains becomes compact and dense[40].

There have been many X-ray diffraction studies made of atactic and syndiotactic PVA fibres[10,41], films[42], gels[43] and crystal mats[17]. The wide-angle X-ray diffractograms of the PVA fibrils showed typical fibre reflection patterns (*Figure 3*). The two kinds of PVA fibrils in *Figure 3* had similar P_n values, but there was a difference of about 5% between the S-dyad contents. Strong arcs for the (100) and (101) planes in the equatorial direction are present, but the reflection for the (020) plane in the meridional direction in *Figure 3a* is stronger than the corresponding reflection in *Figure 3b*. It was considered that if the S-dyad content was increased, the number of hydroxy groups irregularly distributed would decrease, and the regularity of the (020) plane would increase owing to the presence of strong intermolecular hydrogen bonds in

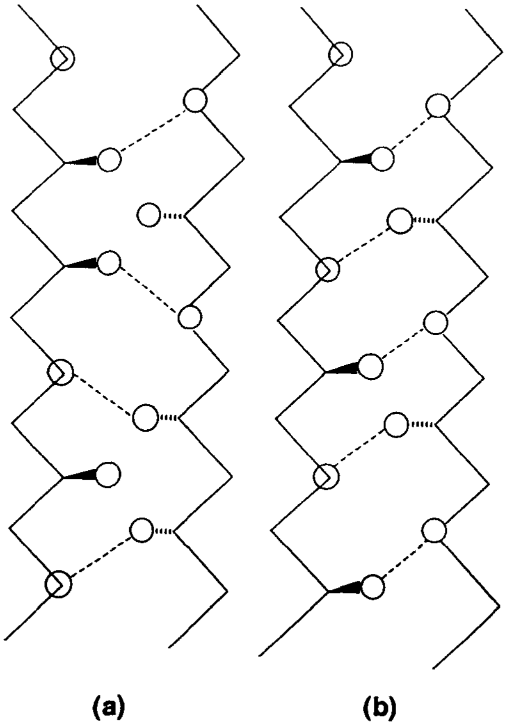


Figure 2 Crystal structures of (a) atactic and (b) syndiotactic PVA (c projection): (. . .) hydrogen bonds; (○) hydroxy groups (⊃, downward; ⊂, upward)

Table 2 Characteristics of PVA fibrils having a P_n of 16700, an S-dyad content of 63.9% and a DS of 99.4%

Parameter	Method of fibrillation				
	A	B	C	D	E
Orientation index	0.881	0.867	0.832	0.804	0.767
Crystallinity (%)	48.6	47.3	43.3	39.5	37.9
T_m from the first heating (°C)	261.2	258.4	256.7	254.2	253.8
T_m from the second heating (°C)	248.2	248.7	248.8	248.0	248.5
Maximum tensile strength (g den^{-1})	15.4	14.1	12.9	9.1	8.8
Degree of solubility (%)	0.00	0.00	0.00	0.51	4.60
Degree of swelling (%)	0.04	0.09	0.17	0.42	0.89

highly syndiotactic PVA. Nakamae *et al.*[10] have reported that the reflection for the (020) plane of a PVA fibre having an S-dyad content of 63.0% prepared via spinning and drawing is stronger than the same reflection of a PVA fibre having an S-dyad content of 55.2%, and this is consistent with our results.

The orientation indices of the PVA fibrils prepared by the five different fibrillation methods listed in *Table 1* are shown in *Table 2*. The higher the shear speed, the more highly oriented the PVA fibrils, and the orientation index of the fibrils prepared by method A was 0.881. Because the usual preparation steps of high-performance PVA fibres such as spinning, drawing and heating were not conducted, an orientation index of over 0.9 could not be obtained.

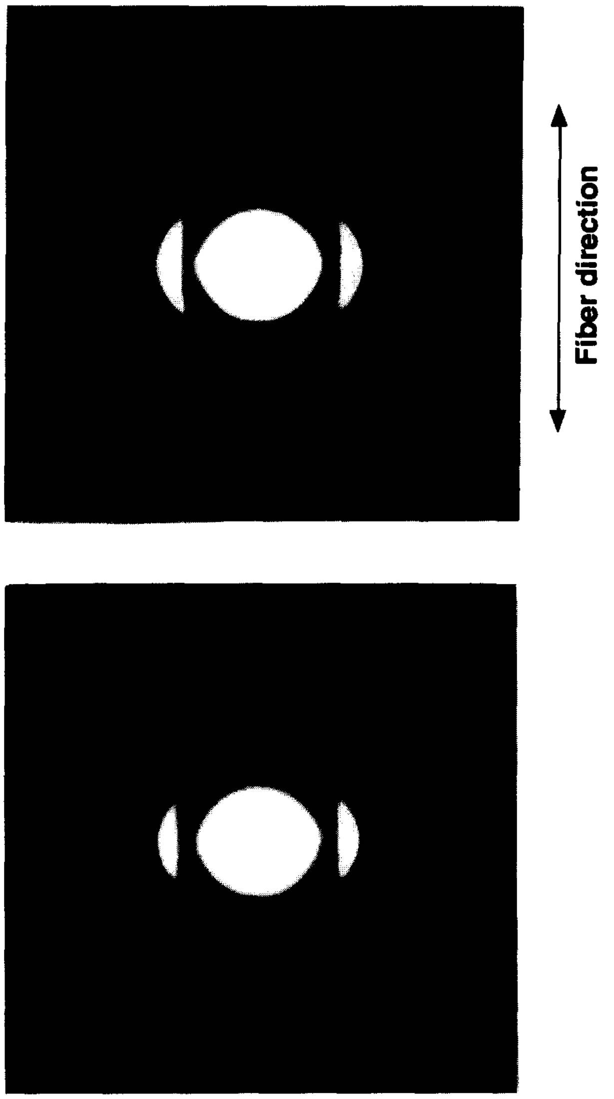


Figure 3 The X-ray photographs of PVA fibrils prepared by method A (*Table 1*): (a) P_n of 15 100 and S-dyad content of 63.4%; (b) P_n of 15 400 and S-dyad content of 58.5%

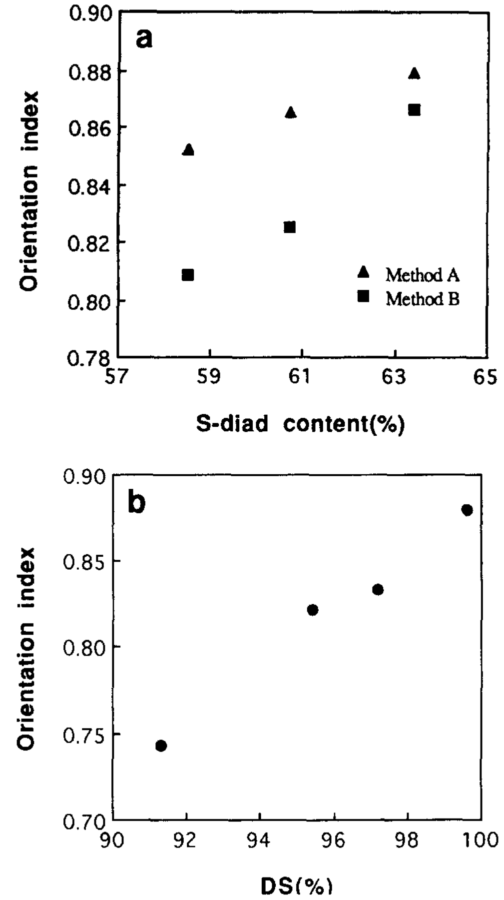


Figure 4 (a) Changes in orientation index with S-dyad content for PVA fibrils having a P_n of about 15000. (b) Changes in orientation index with DS for PVA fibrils having an S-dyad content of about 63% and prepared by method A

Figure 4a shows how the orientation index of the PVA fibrils changes with the S-dyad content. Particularly noteworthy are two points. Firstly, the orientation index increases with increasing S-dyad content. Secondly, the differences in the orientation index between method A and method B decrease with increasing S-dyad content. These facts strongly suggest that the self-preoriented effect of the highly syndiotactic PVA chain resulting from the stereoregular molecular structure is a more dominant factor relative to the posterior mechanical shear force in leading to the most effective orientation. *Figure 4b* shows how the orientation index of the PVA

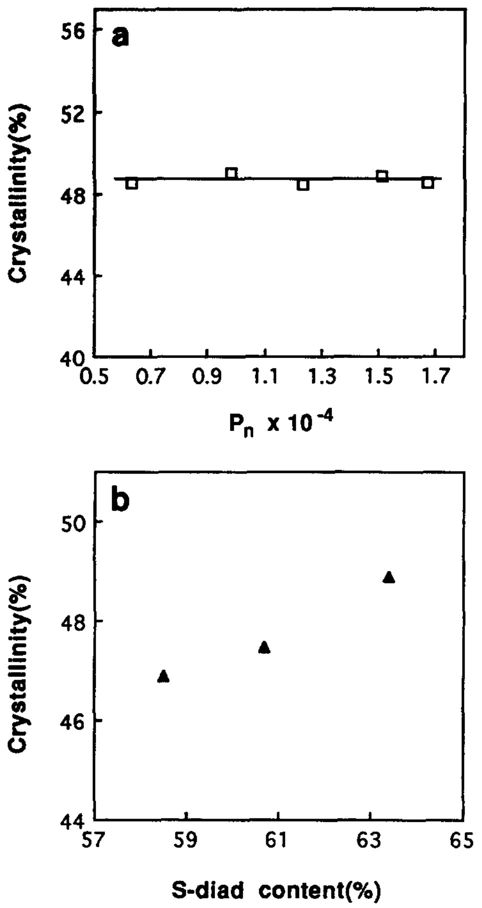


Figure 5 (a) Changes in crystallinity with P_n for PVA fibrils having an S-dyad content of about 63%. (b) Changes in crystallinity with S-dyad content for PVA fibrils having a P_n of about 15000. The fibrils were prepared by method A

fibrils prepared by method A changes with the *DS*. The higher the *DS*, the larger the orientation index. This result can be explained in terms of the fact that bulky pivaloyl groups impede the molecular self-orientation of the syndiotactic PVA. That is, this implies that a syndiotacticity-rich PVA with a higher *DS* develops molecular orientation more easily.

The crystallite sizes $D_{(101)}$ of the PVA fibrils with a P_n of 16700, an S-dyad content of 63.9% and a *DS* of 99.4% were calculated using equation (4). All values were about 40–45 Å (1 Å = 0.1 nm). In the case of method A, the highest value of about 45 Å was obtained.

The crystallinities of the PVA fibrils prepared by the five fibrillation methods shown in *Table 1* are listed in *Table 2*. A crystallinity of over 40% was obtained by all of the fibrillation methods except methods D and E, and the crystallinity of the fibrils prepared by method A was over 48%. The PVA fibres or film would have to be heat treated or hot drawn to achieve such a crystallinity in the conventional process. A reason for this fairly high crystallinity of the fibril might be that there occurred a self-oriented and shear-induced crystallization through a special attraction[37] between the syndiotactic PVA and the saponifying agent and through a powerful shear force during the saponification reaction.

Figures 5a and *5b* show the effect of the P_n and syndiotacticity of the PVA fibrils on crystallinity. The crystallinity was nearly constant irrespective of changes in P_n, as shown in *Figure 5a*. However the crystallinity increased with increasing S-dyad content (*Figure 5b*). This implies that the syndiotacticity has a marked influence on the crystallization of the PVA fibrils during the saponification and *in situ* fibrillation.

Factors affecting the T_m *of the fibrils*

It is known[44] that the T_m of completely saponified atactic PVA having an S-dyad content of about 50% is about 230°C. For fibrous PVA having an S-dyad content of over 60%, the relationship between T_m and the *MW* and stereoregularity of the PVA fibril has been investigated.

The T_m values from the first and second heatings of the

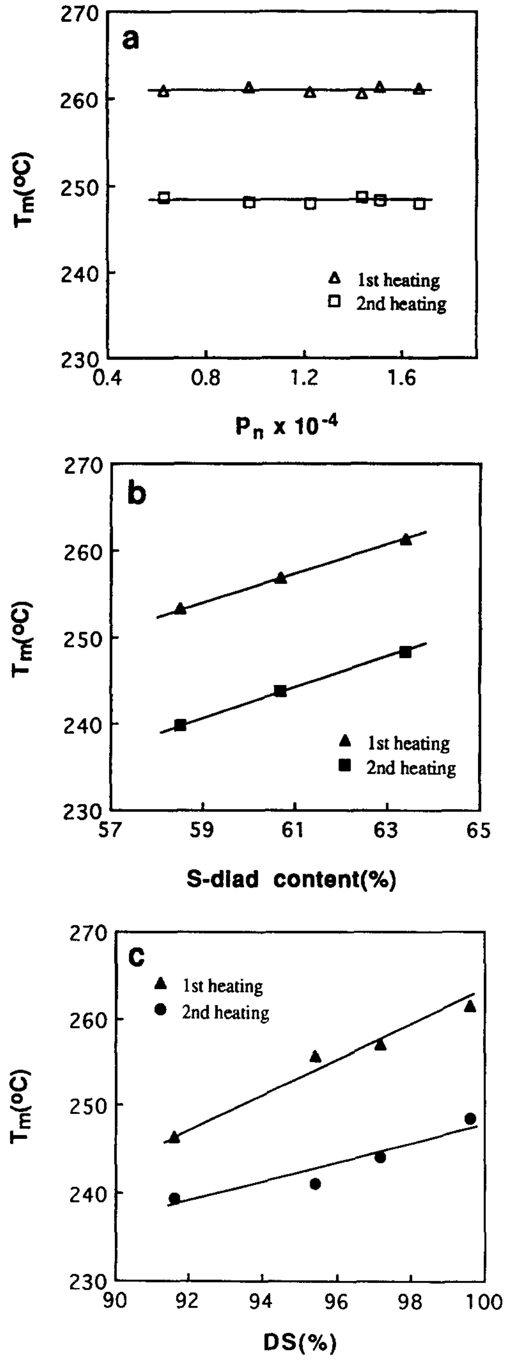


Figure 6 (a) Plot of T_m against P_n for PVA fibrils having an S-dyad content of about 63%. (b) Plot of T_m against S-dyad content for PVA fibrils having a P_n of about 15000. (c) Plot of T_m against *DS* for PVA fibrils having an S-dyad content of about 63%. The fibrils were prepared by method A

PVA fibrils for a P_n of 16 700 and an S-dyad content of 63.9% are shown in *Table 2*. On the first heating, various T_m values in the range 253–261°C were obtained. However, on the second heating, T_m was a nearly constant value of about 248°C. From this result, it is evident that by the second heating, the syndiotacticity-rich PVA with an S-dyad content of 63.9% has lost its structural history previously induced by fibrillation. The T_m values of the fibrils obtained by methods A and B in the first heating were 261.2°C and 258.4°C, respectively. In fact, these values are slightly lower than the T_m value[9] of the high-strength and high-modulus PVA filament obtained via spinning of the syndiotacticity-rich, HMW PVA solution in DMSO and subsequent drawing with a high draw ratio of over 10. However, it is quite apparent that PVA fibrils having a high T_m could be prepared by direct saponification of PVPi and *in situ* fibrillation without additional treatment.

The T_m values of the PVA fibrils from the first and second heatings are plotted against P_n in *Figure 6a*. All the samples exhibited similar T_m values in the first and second heatings. A negligible effect of the *MW* on the T_m of the PVA fibrils suggests that the shape and size of the crystals produced by the self-oriented and shear-induced crystallization are identical to some extent in the *MW* range of the samples used in this study. To examine the effect of molecular parameters such as the syndiotacticity and the *DS* on the T_m values of the PVA fibrils, we plotted the T_m values against the S-dyad content and the *DS* (*Figures 6b* and *6c*). Linear relationships between these molecular parameters and the T_m can be seen. That is, the T_m values in the first and second heatings of fibrils with a higher S-dyad content were higher than those of fibrils with a lower S-dyad content, as shown in *Figure 6b*, and this result corresponds fairly well to the previous crystallinity data. It is obvious that the syndiotacticity greatly affects the morphology of the self-oriented and shear-induced crystals formed by

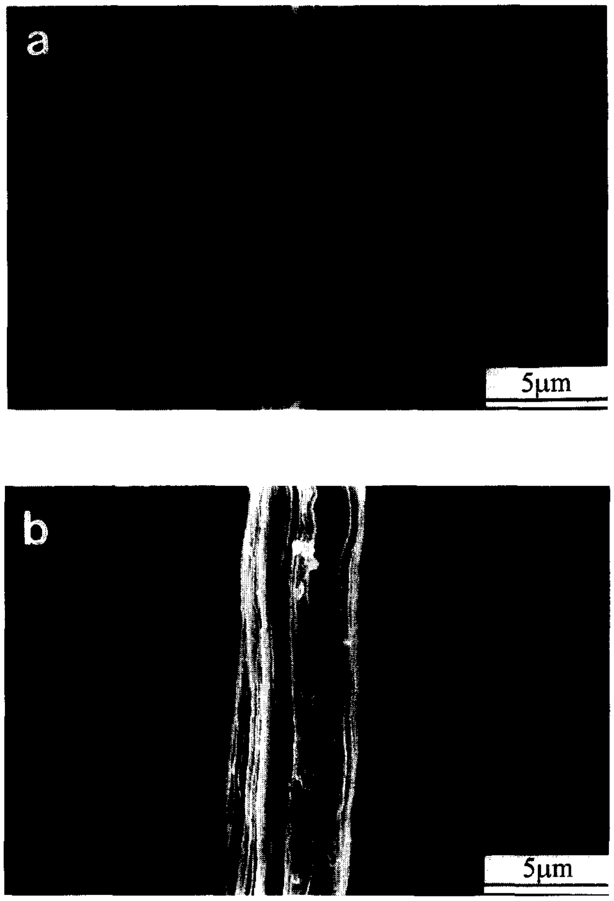


Figure 8 Scanning electron micrographs of PVA fibrils with a P_n of 16 700 and an S-dyad content of 63.9% prepared by method A (a) and method B (b)

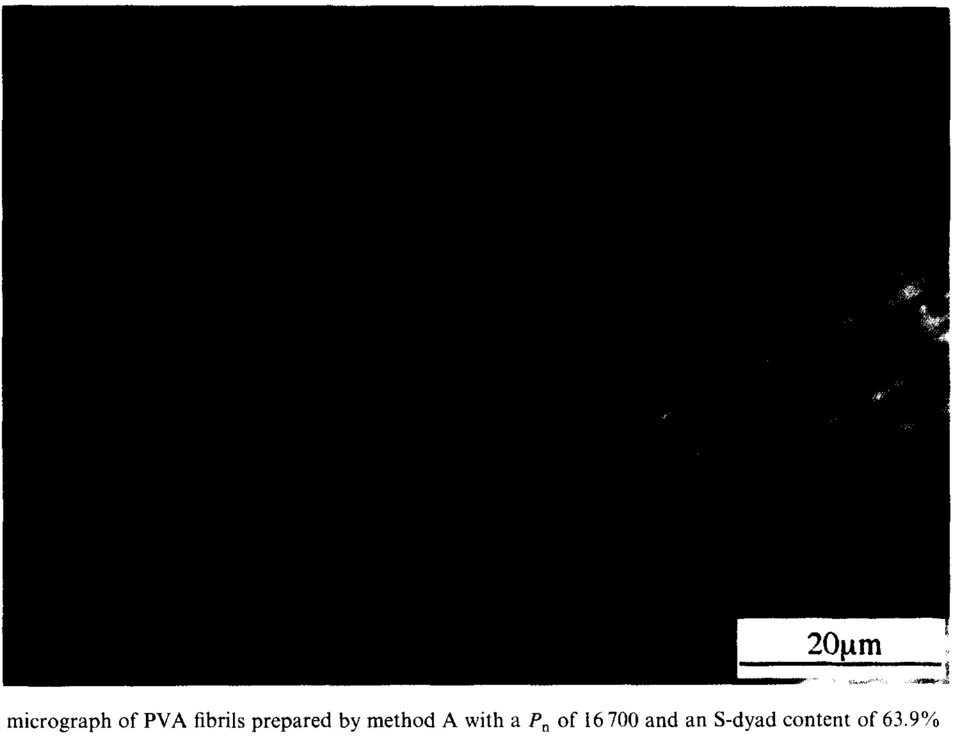
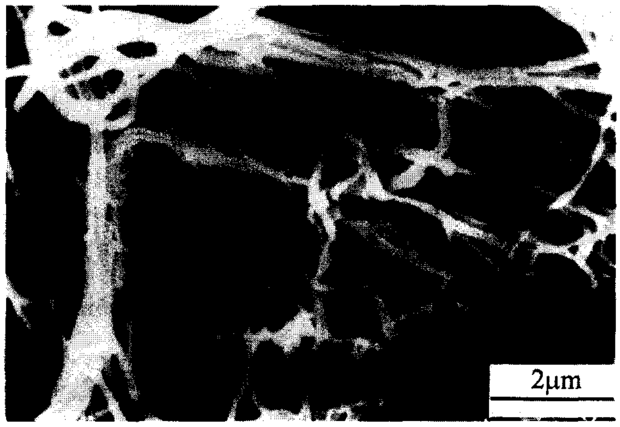
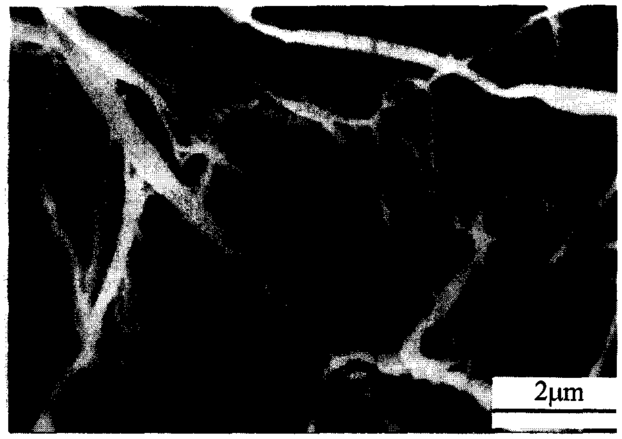


Figure 7 Polarizing micrograph of PVA fibrils prepared by method A with a P_n of 16 700 and an S-dyad content of 63.9%



method A



method C

Figure 9 Difference in fineness of PVA fibrils prepared by different fibrillation methods with a P_n of 16700 and an S-dyad content of 63.9%

fibrillation. The T_m values in the first and second heatings decreased with a decrease in the *DS* of PVA. This can be explained in terms of a melting point depression of the copolymer composed of crystalline and non-crystalline units.

Observation of the surface structure of the fibrils

Figure 7 shows the polarizing micrograph of some PVA fibrils. It is clear that the microfibrils are bundled like natural cotton, linen, ramie and jute fibres[45].

Figure 8 shows scanning electron micrographs of PVA fibrils. The fibrils are fairly well aligned (*Figure 8b*). In general, the minimum thickness of all commercial spun PVA fibres is 4 μm. However, fine PVA fibrils having a thickness of below 4 μm could be prepared by control of the fibrillation conditions (*Figure 8a*). *Figure 9* shows the cracked end surfaces of the fibrils. The PVA fibrils prepared by method A using a housing to prevent the Weissenberg effect and a higher shear speed were finer than those prepared by method C.

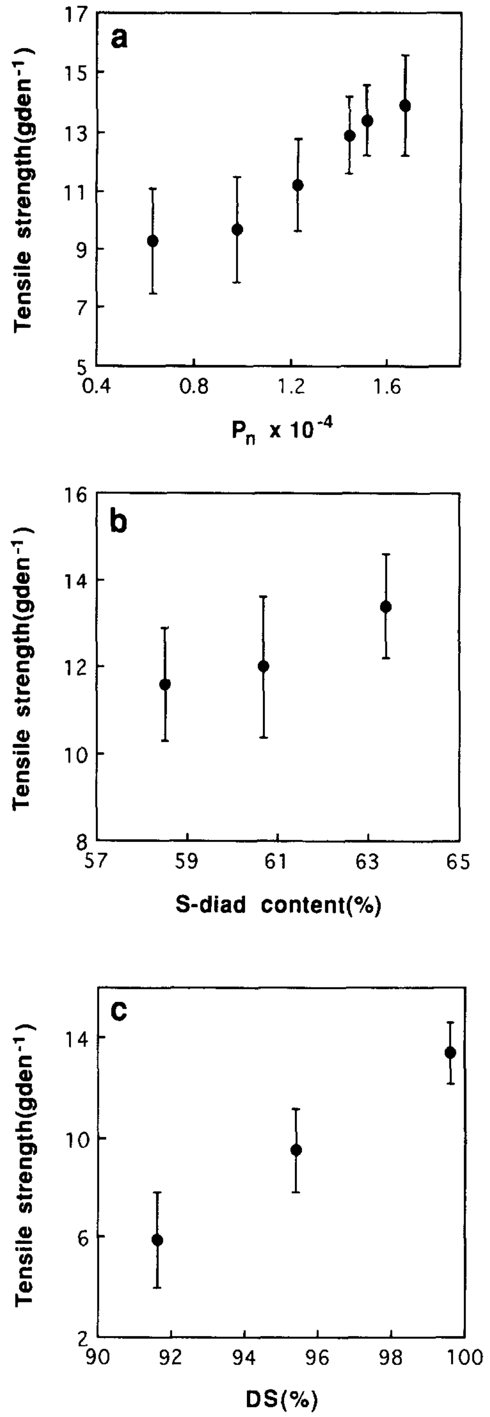


Figure 10 (a) Changes in tensile strength with P_n for PVA fibrils having an S-dyad content of about 63%. (b) Changes in tensile strength with S-dyad content for PVA fibrils having a P_n of about 15000. (c) Changes in tensile strength with *DS* for PVA fibrils having an S-dyad content of about 63%. The fibrils were prepared by method A

Tensile properties of the fibrils

The P_n values of the PVA fibril were very high, being in the range 4500–20000. The relationship between the tensile strength of HMW PVA fibres prepared by the conventional spinning method and the *MW* of PVA is[9]

$$\text{tensile strength (gden}^{-1}) \geqslant 12P_v^{0.1} - 7.5 \qquad (8)$$

where P_v is the viscosity-average degree of polymerization of PVA. From equation (8), it may be expected that the tensile strength of the fibrils, having the maximum P_n in this work would be over 25 g den^{-1}. However, the maximum tensile strength was only just over 15 g den^{-1}. The reason for this unfavourable result is that the PVA fibrils were irregular in shape and had needle-point-like ends, and breakage at the thinnest ends of the fibrils occurred.

By methods A, B, and C, a tensile strength of over 10 g den^{-1} was obtained (*Table 2*). In particular, the strength of the fibrils prepared by method A reached the highest value of 15.4 g den^{-1}. The reason for this fairly high strength of these fibrils, despite the low orientation index of below 0.9, is that the fibrils had a high *MW*, high syndiotacticity and a well-packed,ultrafine microfibril structure.

Figure 10a shows the tensile strength of PVA fibrils as a function of P_n. The tensile strength increased with an increase in the P_n of PVA, and the tensile strength of the PVA fibrils with a P_n of 6300 prepared by method A was over 9 g den^{-1}. *Figures 10b* and *10c* show the changes in tensile strength of the PVA fibrils prepared by method A with changes in S-dyad content and *DS*, respectively. The tensile strength of the PVA fibrils increased with increasing S-dyad content and *DS*. As shown in these figures, the tensile strength slightly increased with an increase in the S-dyad content, and steeply increased with an increase in the *DS*, suggesting that both a high *DS* and high S-dyad content are requisite factors to achieve high tensile strength.

Resistance to water of the fibrils

PVA is soluble in highly polar and hydrophilic solvents such as water. Therefore, to obtain good water resistance for use as a fibre, PVA should be acetalized with formaldehyde. PVA with a fairly high P_n is water resistant to some extent, but atactic, HMW PVA has poor hot-water resistance. Thus, for improved water resistance of PVA, the crystallinity of the PVA fibre should be increased by high-temperature heat treatment. Although the crystallinity of atactic PVA fibres or films increases upon high-temperature heat treatment or stretching, the hot-water resistance of atactic PVA is lower than that of syndiotactic PVA for the same crystallinity, probably owing to the different crystal compactness of the PVA.

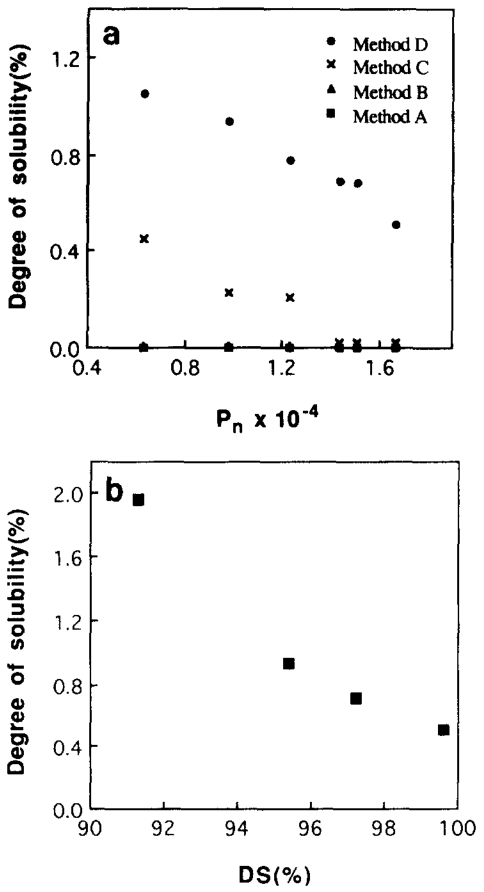


Figure 11 (a) Changes in degree of solubility with P_n for PVA fibrils having an S-dyad content of about 63%. (b) Changes in degree of solubility with *DS* fibrils prepared by method D and having an S-dyad content of about 63%

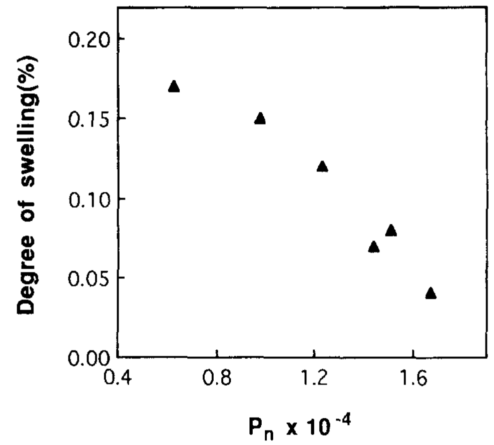


Figure 12 Changes in degree of swelling with P_n for PVA fibrils prepared by method A and having an S-dyad content of about 63%

The relationship between the breaking temperature in hot water and the *MW* of syndiotacticity-rich, HMW PVA fibre prepared via spinning and subsequent drawing is[9]

$$T_b \geqslant 1.2P_v^{0.35} + 117 \qquad (9)$$

where T_b (degrees Celsius) is the breaking temperature in hot water under a 2 mg den^{-1} load.

The degrees of solubility of the PVA fibrils prepared by the five fibrillation methods listed in *Table 1* are presented in *Table 2* and *Figure 11a*. The degree of solubility decreased with increasing P_n and reached 0% for a P_n of over 14 000 (methods A, B and C). From these results, it is clear that the PVA fibrils can have excellent stability to hot water under severe conditions, as described earlier. In addition, the hot-water resistance of the fibrils increased with an increase in the *DS* (*Figure 11b*), and the PVA fibrils with the larger S-dyad contents had the higher hot water resistances. These results agree with the results of Matsuzawa *et al.*[36].

By soaking the PVA fibrils in water at 30°C for 50 h, we determined the degree of swelling of the fibrils. *Figure 12* shows the effect of P_n on the degree of swelling of the fibrils: the higher the P_n, the lower the degree of swelling.

Finally, to examine the usability of the PVA fibrils as a profitable replacement material for carcinogenic asbestos fibres, we tested the alkali resistance of the PVA fibrils. It was found that the PVA fibrils prepared by methods A, B and C remained in their original states.

CONCLUSIONS

Novel, high-performance PVA fibrils could be prepared by controlling the *MWs* of PVPi and PVA, the syndiotacticity and *DS* of PVA, the type and concentration of the saponifying agent, and the shearing device and shear speeds used in the fibrillation of PVA.

In preparing the high-strength PVA fibrils using only chemical reaction and a powerful shear force, it was a prerequisite that to form more complete crystals having tight, intermolecular hydrogen bonds, we would have to use highly syndiotactic PVA. The high orientation of the PVA fibrils was achieved through an optimal combination of special saponifying agents. A reduction in affinity to water was achieved by control of the *DS*, hydrophobicity and syndiotacticity.

The high-strength PVA fibrils prepared by the most effective fibrillation method had an orientation index of over 0.88, a crystallinity of over 48%, a T_m of higher than 260°C and an accumulated ultrafine microfibril structure. The PVA fibrils having a P_n of over 10 000 exhibited a maximum tensile strength higher than $12\,\mathrm{g\,den^{-1}}$ and their resistance to hot water was excellent. Moreover, these properties were enhanced by increases in the P_n, S-dyad content and *DS* of the PVA fibrils.

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