

# Effects of Heat Treatment on Tensile Properties of High-Strength Poly(vinyl alcohol) Fibers

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**ABSTRACT:** The tensile properties of high-strength poly(vinyl alcohol) (PVA) fibers after heat treatment in air, water, and engine oil were studied. The results show that heat treatment in air, water, and engine oil have a different influence on the tensile properties of high-strength PVA fibers. After heat treatment in air, the fibers possess excellent heat stability of the tensile properties. But in water, especially in hot water, the tenacity, Young's modulus, and specific work of rupture of the fibers decrease, while the elongation at break of the fibers increases. Similarly, engine oil has a significant influence on the tensile properties of the fibers. When the temperature of engine oil is above 120°C, the tensile properties of the fibers decrease drastically. We also discuss the influence of heat, water, and engine oil on the tensile properties of high-strength PVA fibers in relation to the structure of the fibers. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 237–242, 2000

**Key words:** high-strength PVA fiber; tensile properties; heat treatment; microstructure

## INTRODUCTION

Poly(vinyl alcohol) (PVA) fibers were first manufactured and used in Japan in 1939. At that time, the major application of PVA fibers was for apparel fabric. In the latter 1970s, due to the revival of natural fibers and the impact of other new synthetic fibers in the area of apparel fabric, world production of PVA fibers decreased, and its market also changed from apparel fabric to industrial materials.<sup>1</sup>

Due to the diversified use of PVA fibers for industrial application, there is a need to improve the properties of PVA fibers. At the end of the 1970s, the gel-spinning process was developed by DSM Corp., and great success was made in the development of high-strength fibers. This kind of spinning process was first applied in the manufacture of high-strength polyethylene fibers by

improving the molecular orientation and chain extension. In the past decade, this spinning process was also applied to other polar, flexible polymers, such as polyamides, polyacrylonitrile, and PVA. Among these polymers, PVA fibers were proved to be the most successful. The tensile properties of several high-strength fibers are listed in Table I.

Table I shows that the tensile properties of high-strength PVA fibers are not so superior among the high-strength fibers. However, high-strength PVA fiber possesses other advantages, such as excellent creep characteristics, weatherability, chemical resistance, and adhesion to matrices.<sup>5</sup> In addition, compared with other high-strength fibers, the price of high-strength PVA fibers is much lower. Therefore, in those circumstances where high strength is not so important, but excellent creep characteristics, weatherability, chemical resistance, and adhesion to matrices are necessary, the application of high-strength PVA fibers is practical. Today, high-strength PVA fibers are used in building materials instead of

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**Table I** Tensile Properties of High-strength Fibers

Fibers	Tenacity (g/d)	Elongation at Break (%)	Young's Modulus (g/d)
High-strength PVA fiber <sup>2-4</sup>	12-20	4.5-6.0	450-500
PAN-based carbon fiber	30	1.5	2080
Glass fiber			
Type E	30	4.8	635
Type S	40	5.4	750
High-strength PE Fiber (Spectra 900)	26	2.7	1470
Kevlar 49	23	2.8	950

asbestos (e.g., asbestos tile, reinforced cement), coating materials, reinforced rubber, and other kinds of composites.<sup>6-8</sup>

For industrial application, mechanical properties are one of the important factors in determining the total properties of a material. However, it is known that one of the major disadvantages of PVA fiber is its poor mechanical properties at high temperature and in hot water, especially the sensitivity to moisture.<sup>1</sup> From the literature,<sup>9-11</sup> it is observed that work on the tensile properties of high-strength PVA fibers after heat treatment in air, water, and engine oil has not been reported. Hence, considering the importance of the industrial application of the fibers, a study on the tensile properties of high-strength PVA fibers after heat treatment in air, water, and engine oil was carried out.

## EXPERIMENTAL

### Materials

The material used in this study was high-strength PVA fibers of 1800den/1000F, supplied by the Kuraray Corp. (Japan).

### Measurement of Melting Point

The melting point of high-strength PVA fibers was measured using a DuPont 9900 differential scanning calorimeter (DSC). The weight of the fibers was about 4 mg. The DSC curve was drawn for a temperature range of 0-300°C at a heating rate of 10°C/min. The experiment was performed in a N<sub>2</sub> atmosphere.

### Tensile Tests

Tensile tests were performed on a DCS-500 tensile tester, using a gauge length of 100 mm and a crosshead speed of 500 mm/min. To investigate the effects of heat treatment on the tensile prop-

erties of high-strength PVA fibers, three different treatments were followed:

- (i) Heat treatment in air: High-strength PVA fibers were heated in an oven without tension at temperatures of 80, 120, 160, 200, and 225°C for 30 min;
- (ii) Heat treatment in water: High-strength PVA fibers were saturated in water without tension at temperatures of 20, 40, 60, 80, and 100°C for 30 min; and
- (iii) Heat treatment in engine oil: High-strength PVA fibers were heated in engine oil without tension at temperatures of 80, 120, 160, and 200°C for 30 min.

In addition, untreated high-strength PVA fibers (control) were tested on the tensile tester under standard conditions (20 ± 2°C and 65 ± 2% RH).

### Measurement of Birefringence

The birefringence of four samples—untreated fibers (no. 1), fibers treated in air at 225°C (no. 2), fibers treated in water at 100°C (no. 3), and fibers treated in engine oil at 200°C (no. 4)—were measured by a ZEISS polarizing microscope. The testing condition used was  $t = 20^\circ\text{C}$  and lighting with a Na-ray ( $\lambda = 589 \times 10^{-9}$  m).

### Measurement of Crystallinity

The crystallinity of sample nos. 1-4 were estimated using an X-ray diffractometer and the crystallinity of the samples was calculated using peak separating.

### Scanning Electron Microscopy (SEM)

A Cam Scan-4 SEM was used to examine the changes on the surface of samples nos. 1-4.

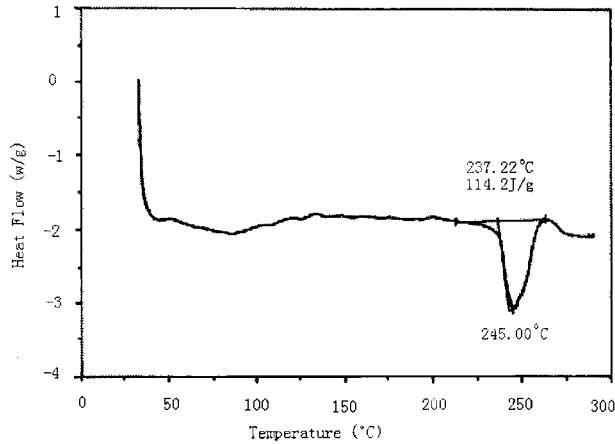


Figure 1 DSC curve of high-strength PVA fibers.

## RESULTS AND DISCUSSION

### Melting Point of Fibers

Figure 1 shows the DSC curve of the high-strength PVA fibers. Figure 1 shows that in the range of 50–120°C and 225–265°C two peaks appear, and the value of second peak is greater than that of the first peak. The first peak is caused by water or other volatile materials in the fibers, while the second peak is caused by phase transition in the crystalline region of the fibers. There-

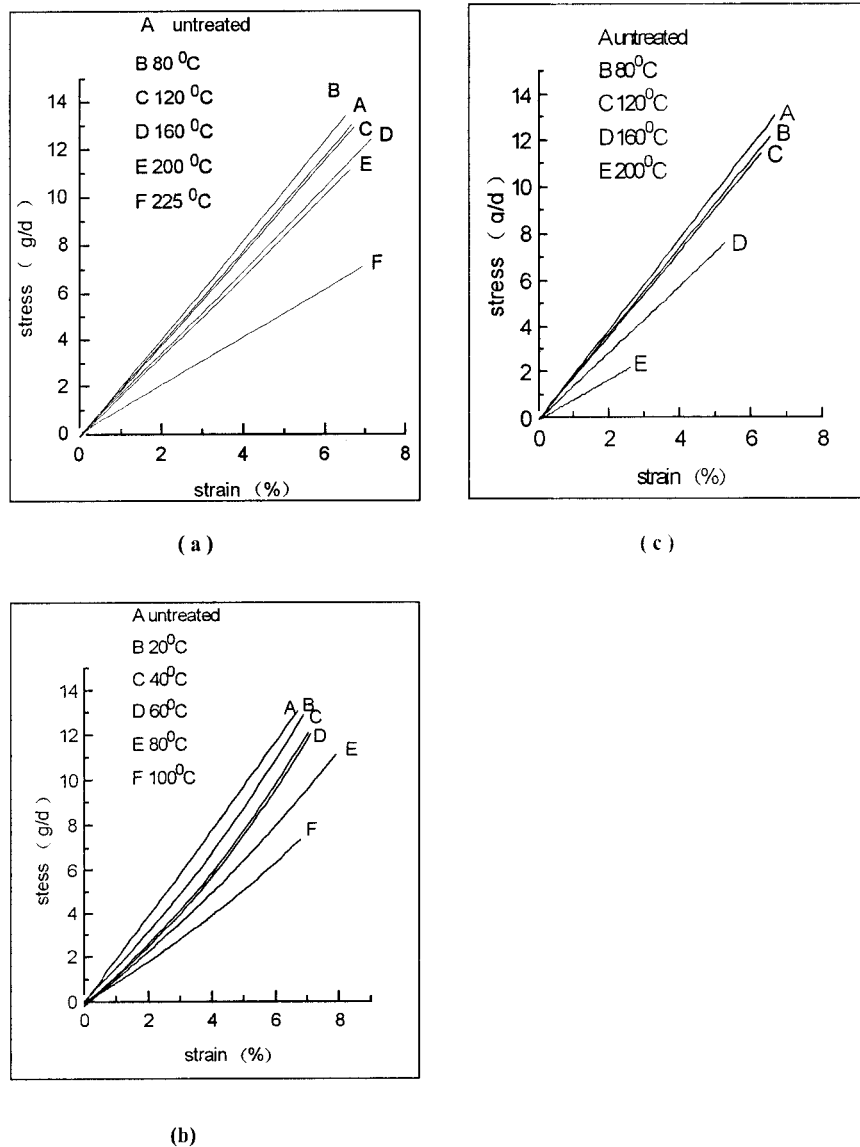
fore, 245°C is taken as the melting point of the high-strength PVA fibers.

### Tensile Properties of Fibers

Tensile test results for high-strength PVA fibers after different treatments are listed in Table II and the stress-strain curves are given in Figure 2(a–c). From Figure 2 and Table II, it is observed that (1) all stress-strain curves after treatments have no yield points, and the shapes of the curves are linear with the character of brittle materials. Compared with the stress-strain curve of untreated fibers, the shape of the curves did not change after heat treatment in air and in engine oil, but changed after heat treatment in water. (2) The stress-strain curves of the fibers after heat treatment in air, water, and engine oil are all below those of the untreated fibers (except for the curve of the heat treatment in air at 80°C). (3) The tenacity, Young's modulus, and specific work of rupture of the fibers decrease significantly at temperatures above 200°C in air, 80°C in water, and 120°C in engine oil, but the change is little when the temperatures are below 200°C in air, 80°C in water, and 120°C in engine oil. There is no significant change in the elongation at break of the fibers after treatment except for the fibers treated in engine oil.

Table II Tensile Properties of High-strength PVA Fibers After Treatment

Treatment	Tenacity (g/d)	Elongation at Break (%)	Young's Modulus (g/d)	Specific Rupture Work (J/g)
Untreated	13.07	6.67	181.67	38.35
Heat treatment in air				
80°C	13.47	6.52	186.11	38.73
120°C	12.98	6.72	179.45	38.21
160°C	12.44	7.15	167.78	37.66
200°C	11.19	6.63	145.83	31.41
225°C	7.12	6.93	114.58	20.89
Heat treatment in water				
20°C	12.70	6.87	180.06	37.71
40°C	11.85	7.00	138.00	35.85
60°C	11.71	7.10	123.19	35.73
80°C	10.91	7.90	100.05	35.70
100°C	7.32	6.77	83.91	20.54
Heat treatment in engine oil				
80°C	12.17	6.54	175.28	35.10
120°C	11.47	6.30	165.56	31.87
160°C	7.63	5.27	128.06	17.73
200°C	2.23	2.60	62.28	2.56



**Figure 2** Stress-strain curves of high-strength PVA fibers: (a) heat treatment in air; (b) heat treatment in water; (c) heat treatment in engine oil.

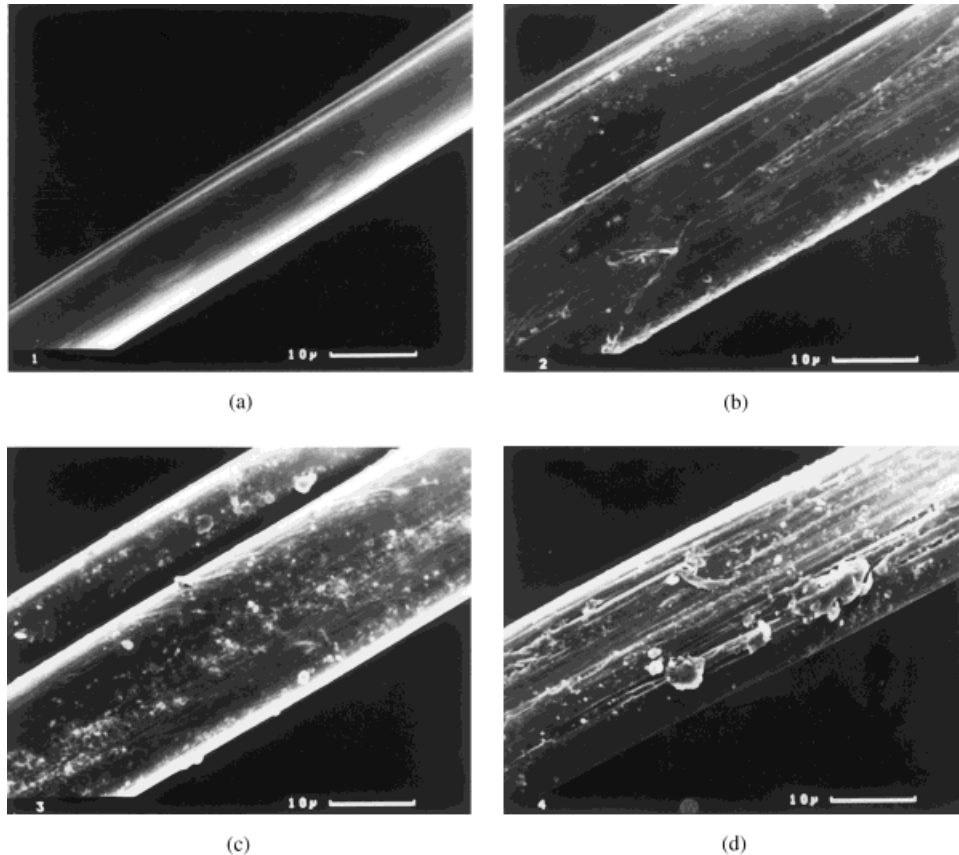
### Birefringence and Crystallinity of Fibers

The results of the birefringence and crystallinity of high-strength PVA fibers are listed in Table III. Table III shows that (1) the values of the birefringence and crystallinity of the fibers are all high, and (2) after treatment, the values

of the birefringence and crystallinity all decrease, but different changes correspond to different treatments: The most significant decreases of the birefringence and crystallinity occur with engine oil treatment, followed by water treatment and the least with heat treatment in air.

**Table III** Birefringence and Crystallinity of High-strength PVA Fibers After Treatment

Treatment	Untreated (No. 1)	Treatment in Air at 225°C (No. 2)	Treatment in Water at 100°C (No. 3)	Treatment in Engine Oil at 200°C (No. 4)
Birefringence $\Delta n$	0.0673	0.0649	0.0484	0.0164
Crystallinity $\alpha$ (%)	71.7	55.9	52.4	49.7



**Figure 3** SEM of high-strength PVA fibers: (a) sample no. 1: untreated; (b) sample no. 2: treated in air at 225°C; (c) sample no. 3: treated in water at 100°C; (d) sample no. 4: treated in engine oil at 200°C.

### SEM

Figure 3 shows the SEM of samples nos. 1–4. The SEM shows that the surface of the untreated fibers is smooth and even [Fig. 3(a)]; after heat treatment in air, there are slight cracks along the surface of fibers [Fig. 3(b)]; after heat treatment in water, the fibers appear to have a rugged surface [Fig. 3(c)]; and after heat treatment in hot engine oil, there are long cracks and a rugged surface on the fibers [Fig. 3(d)].

### CONCLUSIONS

From the results of our study, we can see that the heat treatments in air, water, and engine oil have a different influence on the tensile properties of high-strength PVA fibers as well as on the structure of the fibers. The PVA fibers used in this study are drawn at high speed during fiber processing and possess high orientation and high crystallinity. Therefore, the birefringence and

crystallinity of the fibers are high, and the fibers possess high tenacity, low elongation at break, high Young's modulus, and absence of a yield point on the stress–strain curves. Under heat treatment in air, as long as the temperature of the heat treatment is below the melting point of the fibers (245°C), the changes of the fiber structure are caused mainly by the motion of the chain in amorphous regions. So, in the present study, heat treatment in air at different temperatures has no significant effect on the birefringence, crystallinity, and tensile properties of the fibers.

The improvement of the tensile properties of the fibers under heat treatment in air at 80°C [curve B in Fig. 2(a)] is probably caused by the removal of water or other volatilizable materials, which leads to a more regular arrangement of the fiber molecules. This result is also consistent with the appearance of the first peak in Figure 1. At the same time, we found that when the temperature of the heat treatment in air exceeded 200°C the color of the fibers turned yellow, which indicates that the



chemical structure of the fibers has changed and the chemical reactions such as thermolysis, resulting in the aging of the fibers, might have occurred. So, the birefringence, crystallinity, and tensile properties of the fibers obviously decrease.

Water had a significant effect on the microstructure and tensile properties of the fibers at high temperature in present study. It is well known that PVA is a water-soluble polymer. After being spun, drawn, and heat-treated, PVA fibers become insoluble in water below 80°C, but they still absorb a large amount of water and swell due to the presence of a number of free —(OH) groups on the PVA molecules. These —(OH) groups could combine with H<sub>2</sub>O through a hydrogen bond which disturbs the arrangement of the fiber molecules, resulting in the swelling of PVA fibers. Lin et al.<sup>12</sup> studied the effects of water on high-strength PVA fibers at normal temperature, and their results indicated that the presence of water in the fibers damaged the structure of the fibers and disturbed the orientation of the molecular chains. In our study, the fibers did not dissolve even in water at 100°C, and the tensile properties of the fibers did not change significantly until temperature of the water was above 80°C, which is attributed to the regular molecular structure of the fibers with high crystallinity. Water cannot enter into the crystalline regions at low temperature and swelling occurs only in the amorphous regions, so the structure of the fibers cannot have been damaged seriously. When the temperature of water exceeded 80°C (glass transition temperature of PVA is in the range of 70–80°C<sup>1</sup>), the swelling of the fibers becomes more serious due to the motion of the molecular chains in the amorphous regions of the fibers and the more severe motion of the water. Some water even enters into the crystalline regions to result in a more serious disturbance of the fiber microstructure. So, the crystallinity and orientation of the fibers decrease, and the same tendency for the tensile properties of the fibers treated in high-temperature water was observed.

Under heat treatment in engine oil, the tensile properties of the fibers change little unless the temperature of the engine oil is above 120°C. Because the size of the engine oil molecule is much larger than that of water and the engine oil is not a solvent for PVA, oil molecules could not enter into amorphous regions of the fibers, nor could strong links be formed between PVA molecules and oil molecules at low temperature. When the temperature of the engine oil treatment is increased, the motion of the engine oil molecules

becomes more severe and the oil will enter into voids of the fibers, which leads to break of the crosslinks between the fiber molecules. So, the birefringence, crystallinity, and tensile properties of the fibers decrease drastically.

From the SEM of samples nos. 1–4, we can see that the heat treatment in air has a slight effect on the fibers' surface, while water damages the fibers to some extent with a rugged surface, which is characteristic of swelling; hot engine oil damages the fibers seriously, with long and deep cracks observed on the fibers. These changes of the fiber surface can also explain the change of the tensile properties of the fibers after heat treatment in air, water, and engine oil.

From the present study, it was shown that

1. High-strength PVA fibers possess excellent tensile properties at normal temperature. After heat treatment in air, water, and engine oil, the changes of the tensile properties of the fibers are different: after heat treatment in air, fibers have excellent heat stability of tensile properties below 200°C, but in water, especially in hot water, the tensile properties the fibers obviously decrease. Engine oil has a significant influence on the tensile properties of the fibers: Especially, when the temperature of the engine oil is above 120°C, the tensile properties of the fibers decrease drastically.
2. Changes of the tensile properties of high-strength PVA fibers after heat, water, and engine oil treatment are related to structural changes of the fibers.

## REFERENCES

1. Sakurada, I. *Polyvinyl Alcohol Fibers*; Marcel Dekker: NewYork, 1985; Chapter 1.
2. Kuraray Co. Jpn. Patent J4–18 113, 1992.
3. Toray Co. Jpn. Patent J6–235 117, 1994.
4. Huang, K. S. *J Appl Polym Sci* 1994, 52, 1181.
5. Maoqing, *China Text Leader* 1997, 3, 14.
6. Kuraray Co. Jpn. Patent J4- 289 215, 1994.
7. Toray Industries Inc. *High Perform Text* 1990, 10, 6.
8. Kuraray Co. Jpn. Patent J4–126 829, 1992.
9. Govaert, L. E.; Peijs, T. *Polymer* 1995, 36, 3589.
10. Shibyama, M.; Hayasaki, T.; Chen, J. H. *Sen-i Gakkaishi* 1990, 46, 15.
11. Peijs, T.; Van Vught, R. J. M.; Govaert, L. E. *Composites* 1995, 26(2), 83.
12. Lin, C.-A.; Hwang, K.; Lin, Ch. H. *Text Res J* 1995, 65(5), 278.