북한에서 생산된 폴리비닐알코올 (비날론) 섬유의 구조와 성질

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Structure and Properties of Poly(vinyl alcohol) (Vinalon) Fiber Produced in North Korea

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1. Introduction

Poly(vinyl alcohol) (PVA) is a linear flexible chain polymer having a high limit strength of 236 g/d and maximum crystal modulus of 2,251 g/d. PVA fibers have high tensile and compressive strength, high tensile modulus, high abrasion resistance, excellent alkali resistance, oxygen barrier property, and adhesiveness [1-8]. Thus, PVA fiber has developed unique uses mostly in industrial field. In recent years the fiber 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. In addition, more recently, PVA fiber has been used as an environmental-friendly water soluble fiber for industrial non-woven fabric owing to its nice biocompatibility.

Vinalon, trade name of PVA, is most extensively produced synthetic fiber in North Korea, about 50,000 t per year. North Korea is the second largest manufacturer of PVA. Due to the political specialities, however, Vinalon has not been commercialized elsewhere but North Korea. Therefore, characteristics and usabilities of Vinalon have not been evaluated until now.

In this paper, the structure and properties of Vinalon fiber were examined to evaluate the characteristics of Vinalon for various industrial applications.

2. Experimental

2.1 Determination of the MW

The molecular weight of PVA could be determined from the viscosity of the PVAc produced by acetylating PVA using eq. (1)[2]

$$[\eta] = 8.91 \times 10^{-3} P_n^{0.62} \text{ (in benzene at 30 ℃)} \quad (1)$$

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

2.2 Determination of syndiotacticity and degree of saponification[1,2]

The syndiotactic diad (S-diad) content of Vinalon fiber was determined using a proton nuclear magnetic resonance (^{1}H NMR) spectrometer (Varian, Sun Unity 300). The degree of saponification (DS) of Vinalon fiber was determined from the weight loss after saponification and from the ratio of methyl proton and methylene proton peaks in the ^{1}H NMR spectrum.

2.3 Wide-angle X-ray diffraction[1,6]

The degree of orientation of the crystallite regions was determined using the Hermans equation, based on the azimuthal halfwidth of the meridional reflection on the second layer line measured using an optical densitometer. $\theta/2\theta$ diffractometer scans were recorded using a Rigaku D/MAX-2200H diffractometer with scintillation counter in the transmission mode. CuK radiation was used in all measurements. The apparent crystallite size $D_{(hkl)}$ was estimated using Scherrers eq. (2):

$$D_{(hkl)} = \lambda / \beta \cos\theta \quad (2)$$

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

2.4 Degree of crystallinity

The density of Vinalon fiber (d) was determined by a density-gradient tube method (in benzene-carbon tetrachloride) at 30 ℃. The degree of crystallinity (X_c) was calculated from

$$1/d = X_c/1.345 + (1-X_c)/1.269 \quad (3)$$

where 1.345 (gml^{-1}) and 1.269 (gml^{-1}) are the crystal and amorphous density of PVA, respectively.

2.5 Crystal melting temperature

The crystal melting temperature (T_m) of Vinalon fiber was measured on a differential scanning calorimeter (Perkin-Elmer, DSC 7).

2.6 Surface structure observation

Polarizing and Scanning electron microscopes were used to observe surface structure of Vinalon fiber.

2.7 Tensile property

Load-elongation curves were recorded on an Instron 4201. The reported tensile strength and modulus of Vinalon fiber was the average value of 20 samples.

2.8 Degree of solubility and swelling[3]

The degree of solubility of the Vinalon fiber in hot water was calculated using

$$\text{degree of solubility} = 1 - (W_a/W_b) \quad (4)$$

where W_a is the weight of dried Vinalon fiber after treatment and W_b is the weight of dried fiber before treatment. The degree of swelling of Vinalon fibers in water at 30 ℃ after 50 h was derived from

$$\text{degree of swelling} = (W_s/W_d)-1 \quad (5)$$

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

2.9 Alkali resistance

To test the alkali resistance of Vinalon fiber, we soaked Vinalon fibers in 0.1% (gl^{-1}) aqueous calcium hydroxide solution at a pH of 13.4.

3. Results and Discussion

To study a structure and properties of Vinalon fiber produced in North Korea, we conducted various experiments. *Figure* 1 shows a ^1H NMR spectrum of Vinalon fiber. From the absence of the methyl proton peak at 1.7 ppm and area ratio of the three OH peak at 4.1-4.7 ppm, we can know that *DS* and *S*-diad content of Vinalon fiber are 99.9% and 54%, respectively. Equatorial diffractometer scan of Vinalon fiber is shown in *Figure* 2. On the whole, the crystals in lateral direction were developed. But, the peak for ($10\bar{1}$) plane at 19° was overlapped with that for (101) plane around 20°. Thus, this implies that higher oriented crystals found in high strength and modulus PVA fiber or syndiotactic PVA fibril[6] were not formed in Vinalon fiber. Generally, tacticity, *DS*, degree of branching, and 1,2-glycol content have a marked influence on the T_m and glass transition temperature of PVA. The T_m of Vinalon fiber from the 1st and 2nd heatings are presented in *Figure* 3. On the 1st heating, T_m of 235.3 °C was obtained. However, on the 2nd heating, T_m was 230.9 °C. From this result, it is evident that by 2nd heating, Vinalon fiber lost its structural history preciously induced by spinning and drawing. Water solubility of Vinalon fiber was examined. Vinalon fiber was completely soluble in hot water over 100 °C. Conclusively, it is expected that Vinalon fiber is a powerful candidate as a water soluble fiber for various industrial and biomedical applications.

4. References

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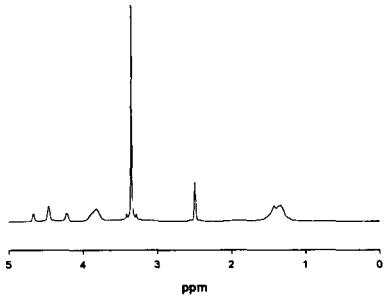


Figure 1. ^{1}H NMR spectrum of Vinalon fiber.

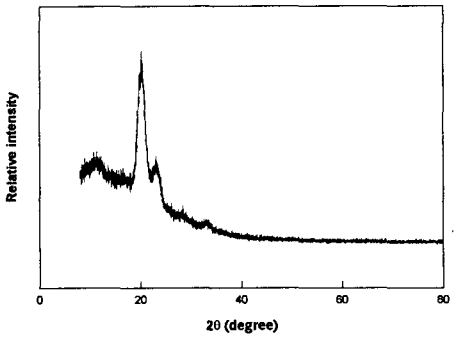
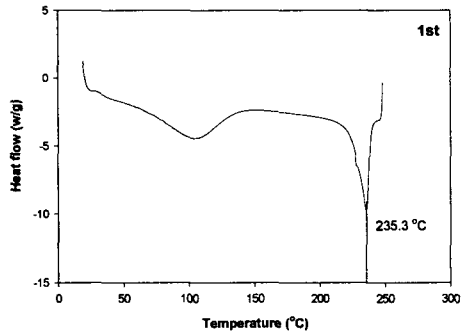


Figure 2. X-ray diffractometer-equatorial scan of Vinalon fiber.



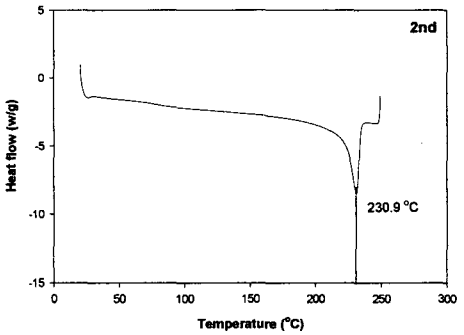


Figure 3. DSC thermogram of Vinalon fiber.