Poly(vinyl alcohol)/Milk Casein Blend Fiber의 제조와 물성

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A Study on the Properties of Poly(vinyl alcohol)/Milk Casein Blend Fibers

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1. Introduction

Casein, a milk protein is used in food, paper, leather and textile industries. The milk casein fiber was developed 1935 first. The strong point of milk casein fiber, the contraction is fewer the wool when washing and damage of harmful insect is smaller than wool.[1] But proteins are the major category of natural polymers that are difficult to be processed into fibrous forms. This is because of their complex macromolecular and three-dimensional structures as well as strong inter- and/or intra molecular forces.[2] Attempts to improve these characteristics of casein proteins have been reported via side-chain modification or grafting of acrylic, methacrylic, and acrylonitrile, monomers. Graft copolymerization of acrylonitrile on casein has also been processed into silk-like fibers. They have been reported to have superior elasticity than silk and cellulose triacetate, and superior electric static property than nylons and polyesters.[3] Currently, the commercialization of casein fiber does not become accomplished not to be, it is a condition where the production is discontinued.

Poly(vinyl alcohol)(PVA) has high potential as a candidate of ultrahigh strength, weather durability, antialkaline resistance, and so on.[4] And PVA is a nontoxic, water-soluble, biocompatible, and biodegradable crystalline polymer, which is widely used in biomedical and biochemical applications. PVA has good fiber-forming, highly hydrophilic properties, and its fibers have been commercialized since the 1950s, and are used in textiles as a silk substitute.[4] Polymer blends have received increasing attention from both the scientific and industrial community. Many improvements have been considered to develop a polymer blend.

Polymer blends are one of the most investigated catagories in the polymer sciences from both theoretical and practical points of view, because of the technical advantages to obtain a specified portfolio of physical properties, without the need to synthesize specialized polymer system. It is well known that blending is an effective and convenient method to improve the performance of polymer materials. Our approach to interrupt the three-dimensional structure and to dissociate the protein molecule was adding another polymer that has a dissimilar structure and capacity to form secondary bonding with proteins. The mechanical properties of casein fibers may also be improved by mixed-component spinning solutions with other water-soluble polymer.

Thus, in the present study, PVA blend fibers, containing casein (0~30wt%) were prepared

using wet spinning. The objective of this study is to incorporate the good properties of milk protein casein into PVA by blending method. We investigated the effect of blend compositions on physical properties, thermal properties, mechanical properties, and morphology of PVA/milk casein bled fibers.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) (PVA, DC Chemical Co., Ltd, DP=1700, DS=99.5%) and PVA (DC Chemical Co., Ltd, DP=1700, DS=85%), milk casein (Fluka), sodium sulfate(Na_2SO_4, Shimakyu's Pure Chemicals), sulfaric acid(H_2SO_4, Junsei), formaldehyde(38%, Junsei), and sodium hydroxide (NaOH, Aldrich Chemical) were used without further purification.

2.2. Preparation

Two kinds of PVA with different degrees of saponification (99.5%, 85%) were used in this study. PVAs (DP=1700) were dissolved in distilled water; the solid contents were 15wt%, 25wt% with stirring respectively. And milk casein was dissolved in 0.1M aqueous solution of NaOH. Three series of PVA/milk casein blends with variable weight ratios (100/0, 85/15, 70/30 w/w%) were prepared by solution blending at room temperature for hours.

To prepare the spinning solution dopes, PVA/milk casein blending solutions were filtered through a 200 mesh filter under pressure. The clear filtrate as a spinning solution was poured into the spinning tank, and degassed under diminished pressure for an hour. After that, the spinning solution was extruded at an extruding rate of 3m/min from a 314-hole (0.08-mm diameter) viscose-type spinneret into a coagulating bath containing an 48% aqueous solution of sodium sulfate(Na_2SO_4) at 40℃ to form fibers. The winding speed was 7.4m/min.

In spite of the fact that PVA has good mechanical properties in the dry state, its applications were limited by its high hydrophilicity. PVA fiber can be readily crosslinked to improved mechanical properties and anti-water solubility. PVA/milk casein blend fiber was placed in H_2SO_4 250㎖, Na_2SO_4 300g, formaldehyde(38%) 250㎖ and H_2O 1000㎖ at 50℃ for 5min. Then the fiber was washed with acetone and water and dried at 50℃.

2.3. Measurements

IR spectra was acquired by using a Fourier Transform Infrared Spectrometer(Nicolet Impact 400D). The viscosity of PVA/milk casein blend solution was measured using a Brookfield viscometer (Model LVDV II+). The thermal behavior of PVA/milk casein bend fibers were examined by using a DSC 220C (Seiko) at a heating rate of 10℃/min under a nitrogen atmosphere. The measurement of thermal stabilities were performed on Perkin Elimer LTD (U.S.A.) TGA7 in the temperature rage of 25~700℃ at a heating rate of 10℃/min in the presence of a nitrogen atmosphere. The dynamic mechanical properties of film samples were measured at 5Hz using DMTA MK III (Rheometric scientific) with heating rate of 2℃/min in the temperature range of -50~150℃. The dimension of PVA/milk casein bend films was a 5/5/0.5(mm/mm/mm) for DMTA measurement. A wide-angle X-ray diffractometer (Rigaku D/MAX-2400) was used to determine the structure of fibers and crystallinities. Birefringence($\Delta n=r/d$) was determined from the retardation(r, nm) and diameter(d, ㎛) of the sample with a polarizing microscope(Zeiss,

Germany). Strain-stress measurement was made in a sample extension on dumbbell specimens using a tensile tester (Tensile AGS 500D, Simazu) at a cross-head of 20mm/min. The structure and morphology of PVA/milk casein bend fibers were observed by Scanning Electron Microscope(SEM) (HITACH S-4200).

4. Results and Discussion

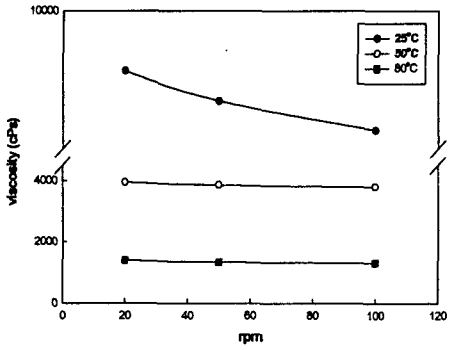
The sample designation, composition, solid content, and birefringence of the PVA/milk casein blend fibers prepared in this study are shown in Table 1. The viscosity(cPs) of spin dope solution was 9350~290 with temperature and rpm. The viscosity was significantly decreased with increasing temperature and rpm.

The birefringences of PVA/ casein blend fiber were significantly decreased with increasing casein content(see Table 1). This indicates that the orientation of PVA was reduced by incorporation casein in PVA matrix. This may be due to the compatible blending of PVA and casein.

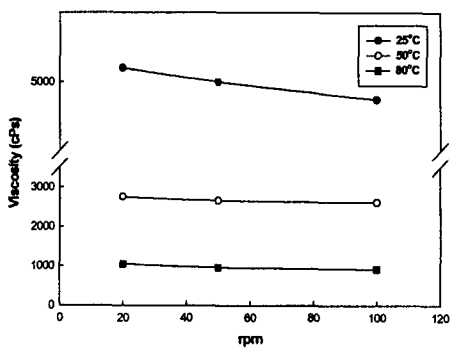
Table 1. Sample designation, the birefringences of the PVA/milk casein blend fibers.

Sample Designation	PVA/casein (wt%)	total solid content	Birefringence X100
*$P_{99.5}$/C 100/0(15)	100/0		2.528
$P_{99.5}$/C 85/15(15)	85/15	15wt%	2.507
$P_{99.5}$/C 70/30(15)	70/30		2.443
$P_{99.5}$/C 100/0(25)	100/0		2.193
$P_{99.5}$/C 85/15(25)	85/15	25wt%	2.158
$P_{99.5}$/C 70/30(25)	70/30		1.736
**P_{85}/C 100/0(15)	100/0		2.259
P_{85}/C 85/15(15)	85/15	15wt%	1.914
P_{85}/C 70/30(15)	70/30		1.879
P_{85}/C 100/0(25)	100/0		2.278
P_{85}/C 85/15(25)	85/15	25wt%	1.692
P_{85}/C 70/30(25)	70/30		1.418

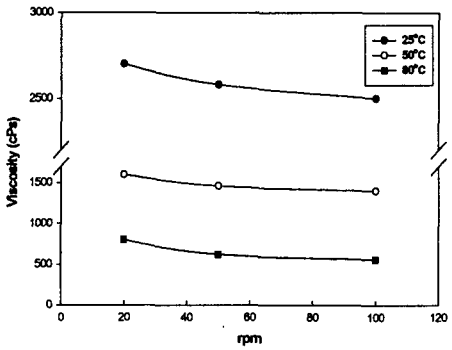
* PVA degree of saponification 99.5%, **PVA degree of saponification 85%



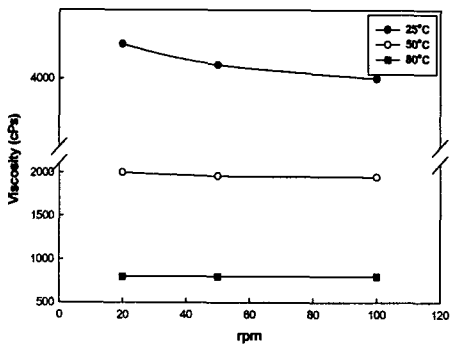
(a) $P_{99.5}$/C 100/0(15)



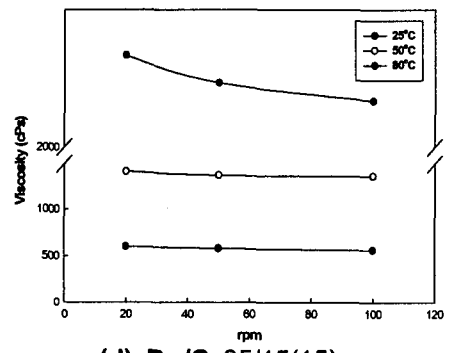
(b) $P_{99.5}$/C 85/15(15)



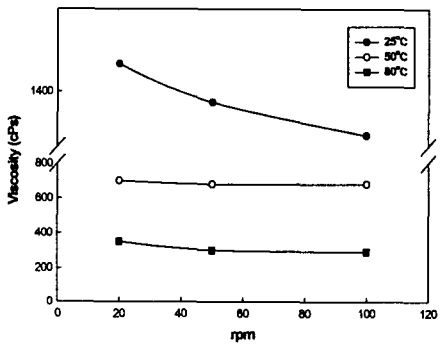
(c) $P_{99.5}$/C 70/30(15)



(d) P_{85}/C 100/0(15)



(d) P_{85}/C 85/15(15)



(d) P_{85}/C 70/30(15)

Figure 1. The changes in the viscosity (cPs) of the PVA/milk casein blend fibers.

5. References

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