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The Effect of Coagulant on the Post Drawing and Morphology of Wet Spun Regenerated SF/Nylon 6 Blend Filaments

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In this paper, the regenerated silk fibroin (SF)/nylon 6 blend filaments were fabricated using wet spinning technique and the effect of coagulant on the post drawing and morphology of blend filaments was investigated. In the result of wet spinnability, methanol, acetone, DMF, and THF showed relatively good coagulation strength and fiber formation for the regenerated SF. On the contrary, they did not exhibit strong enough to produce a uniform nylon 6 filament due to the lack of coagulation strength. In the examination of post drawing performance, methanol showed the highest maximum draw ratio of the blend filament over all blend ratios. The maximum draw ratio of SF/nylon 6 blend filaments decreased with the reduction of SF content regardless of type of coagulant. SEM observation showed the consistent result with that of post-drawing performance. As SF content decreased, the uniform and regular structure was changed to irregular one. In particular, the severe macro-phase separation between SF and nylon 6 could be detected in the 50/50 SF/nylon 6 blend filaments coagulated in methanol and THF.

Key words: Regenerated silk fibroin, nylon 6, Blend filament, Wet spinning, Coagulant, Post-drawing, Morphology.

Introduction

The regenerated silk fibroin (SF) filament prepared by wet spinning technique has received a lot of interests due to its biomedical and biotechnological applications (Ki *et al.*, 2007; Marsano *et al.*, 2005; Mathur *et al.*, 1997; Trabbic and Yager, 1998). Because the structure and properties of SF filament could be controlled diversely, the SF filament might be a high performance fiber for biotechnological application fields.

The author (Um *et al.*, 2004a; Um *et al.*, 2004b) could prepare successfully the wet spun SF filament using formic acid and methanol as a solvent and a coagulant, respectively and elucidated the effect of coagulation conditions and post drawing on their morphologies and structural characteristics. In the studies, it was found that the morphology of wet spun SF filament could be varied by changing coagulation conditions such as coagulants and the temperature of coagulation bath. Furthermore, the mechanical properties could be enhanced significantly by post drawing though it could not reach those of natural silk.

Considering the mechanical properties of wet spun SF filament are not good enough to industrialize until now, it is still necessary to make an effort to enhance its physical properties. Furthermore, a relatively expensive price of SF restricts its application to various industrial areas except biotechnological fields. Polymer blend technique has been utilized as a simple and easy way to improve drawbacks of a polymer by just mixing more than two polymers. In also case of SF, lots of studies on the SF blends have been reported for film (Kweon *et al.*, 2001; Park *et al.*, 1999; Um *et al*, 2002; Freddi *et al*, 1995) and wet spun filament (Hirano *et al.*, 2002; Lee *et al.*, 2007) indicating a blending can also be one of effective ways to enhance drawbacks of SF.

In the meanwhile, nylon 6 has been used in various industrial fields from biomedical fields including surgical suture (Shimamura *et al.*, 2006) to textile industry (Collier and Tortora, 2001). In addition, nylon 6 is a cheap material and it has a structural similarity with silk polymer because the chemical structure of nylon was designed by

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getting inspiration from that of silk.

As revealed in the previous studies (Um *et al.*, 2004a; Um *et al.*, 2004b), a good solvent / coagulant system is the key factor determining physical properties of wet spun filaments. The mechanical properties of wet spun fiber can be significantly improved by the post drawing which is mainly influenced by the solvent / coagulant system. That is, the highly post drawn filament can be produced when the wet spun filament has the uniform and well developed structure resulted from a good solvent / coagulant system. Therefore, to find out a good solvent / coagulant system is one of important things in wet spinning, however, it is the most difficult thing in the process at the same time.

In the case of wet spinning of polymer blend, the work to have a good solvent / coagulant system becomes more important and difficult since it needs co-solvent / co-coagulant system for two polymers. Because formic acid is the good solvent for SF and nylon 6, to obtain co-coagulant system for both polymers can be said to be a crucial issue in the preparation of wet spun SF / nylon 6 blend filament.

In this paper, the regenerated SF / nylon 6 blend filaments were fabricated by wet spinning and the effects of coagulant on the post-drawing and morphology of the blend filaments were investigated to find out a optimum coagulant for the wet pinning of SF / nylon 6 blends and to have a better understanding of the behavior of post drawing and morphological change of the blend filament.

Material and Methods

Preparation

To obtain the SF polymer, *Bombyx mori* cocoons were degummed twice with a marseillus soap 0.5% (o.w.f.) and sodium carbonate 0.3% (o.w.f.) solution at boiling temperature for 1 hr, and then rinsed thoroughly in warm water. SF was first dissolved in a tertiary solvent system of $CaCl_2$ / H_2O / EtOH solution (1 / 8 / 2 mole ratio) for 30 min at 70°C.

The aqueous SF solution was obtained through the dialysis of the dissolved SF solution in a cellulose tube (molecular cutoff= 12,000 ~ 14,000) against a circulating water for 4 days at room temperature. The solution was then dried to obtain regenerated SF film. The SF film was dissolved in 98% formic acid to produce 12% (w / v) SF / formic acid solution. Nylon 6 pellets (2.45 viscosity grade) were kindly provided by Hyosung. The pellet was dissolved in 98% formic acid to produce 35% (w / v) nylon 6 / formic acid solution. The two concentrated polymer solutions were filtered through a nonwoven fabric to remove insoluble particles. Then, the blend dope solutions were prepared by mixing the two dope solutions with a certain blend ratio and then filtered again to produce blend dope solutions for wet spinning.

Regenerated SF / nylon 6 blend filaments were spun using a syringe and syringe pump by extruding the dope solution through 22-gauge needle into a coagulation bath. The flow rate of fiber extrusion was controlled to 20 ml / hr. The blend filaments were left in the coagulants overnight to allow the solvent (formic acid) to diffuse out completely from the filament before drying. Finally, the as-spun filaments were dried under tension to prevent the contraction which can occur during the drying process.

5 different coagulants (methanol, acetone, dimethylformamide (DMF), tetrahydrofuran (THF), and water) were considered for the fabrication of the blend filament. In the previous study (Um *et al.*, 2004a), 9 organic solvents were tested as the coagulant for wet spinning of regenerated SF. Among them, methanol was chosen for wet spinning of SF / nylon 6 solutions because it is the most powerful coagulant for SF among the alcoholic coagulants. Acetone, DMF, and THF were also chosen since they showed relatively good coagulation performance compared to others. In case of nylon 6, it has usually been fabricated by melt spinning rather than wet spinning due to its simple process and economical advantage. Therefore, the study on the wet spinning of nylon 6 has not been performed extensively. However, Hancock et al. (Hancock *et al.*, 1977) has studied the wet spun nylon 6 filament using water as a coagulant. Therefore, water, the coagulant for nylon 6, was also tested as a candidate for co-coagulant for wet spinning of the SF / nylon blends.

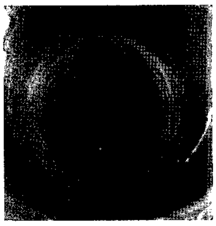
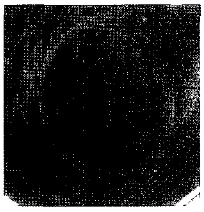
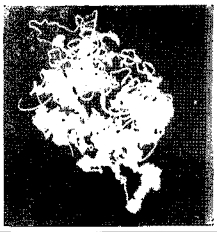
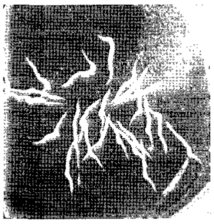
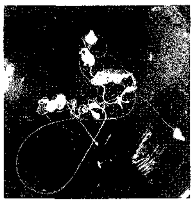
Measurement

The wet spinnability was evaluated by the continuity of spinning and uniformity of spun filament. And the results were obtained by taking the pictures of spun filament in coagulants by digital camera. The maximum draw ratio was calculated by the ratio of maximum drawn length of fiber and the length of as spun fiber in wet state. The measurement of fiber length was performed for 30 different parts of each filament sample and the maximum draw ratio for different coagulants and blend ratios was determined by averaging the 30 results of measurement. The cross-section and surface of SF / nylon 6 blend filaments were examined using a Field Emission Scanning Electron Microscope (FE-SEM) (S-4300, Hitachi, Japan) after a gold coating.

Results and Discussions

It is generally known that the coagulation behavior and wet spinnability strongly influence the physical properties

Table 1. The wet spinnability of regenerated SF and nylon 6 in the various coagulants

	Methanol	Acetone	DMF	THF	Water
SF					
Nylon 6					

of wet spun filament. Furthermore, the coagulation behavior and wet spinnability of blend filament are determined by those of original components. With these backgrounds, the author examined the coagulation behavior and the wet spinnability of SF and nylon 6 in various coagulants by taking the picture of as spun fiber in coagulant and the results were depicted in table 1.

As it can be seen in the table, all coagulants except water showed good coagulation behavior and wet spinnability for SF dope resulting in continuous fiber formations. On the contrary, in case of nylon 6, a good wet spinnability was not observed in any coagulants tested. Methanol and acetone produced thin nylon filaments implying the coagulation strength is weak. DMF and THF yielded thicker filaments indicating that the coagulation strength is a little bit stronger than methanol and acetone though they did not result in continuous fiber formation. A slightly higher coagulation strength of DMF and THF could also be verified by observing the coagulating time of them. When nylon dope solution was dropped in the coagulant, the droplets of DMF and THF were coagulated faster than those of methanol and acetone showing that their color was changed from transparent to opaque and white. Water also did not show good coagulation behavior neither wet spinnability for nylon 6. On the whole, most coagulants except water had the good coagulation strength and the wet spinnability for the regenerated SF dope while all coagulants did not show them for nylon 6 dope.

The maximum draw ratio is known to have a strong relationship with mechanical properties. In also the previous study regarding to wet spinning of SF (Um *et al.*, 2004b), the breaking strength could be increased by rising draw ratio. Based on this reason, the maximum draw ratio has been utilized as a barometer for fiber spinnability. In this study, to find out the optimum coagulant for wet spinning of SF/nylon blend filaments, the maximum draw ratio of blend filament with various blend ratios was measured for different coagulants and the results were shown in Fig. 1.

The several features for the results of maximum draw ratio were observed. First, as SF content decreased, the maximum draw ratio was decreased and finally, the filaments could not be drawn at 50% SF content regardless of coagulant type. That can be easily understood considering that those coagulants tested are good coagulants only for SF while they are not strong enough to coagulate nylon 6 as illustrated in table 1.

Second, the order of maximum draw ratio for coagulants was nearly unchanged at more than 50% SF content exhibiting methanol and acetone yielded higher maximum draw ratios. This means that the coagulation behavior of the coagulant against SF has a decisive role in determin-

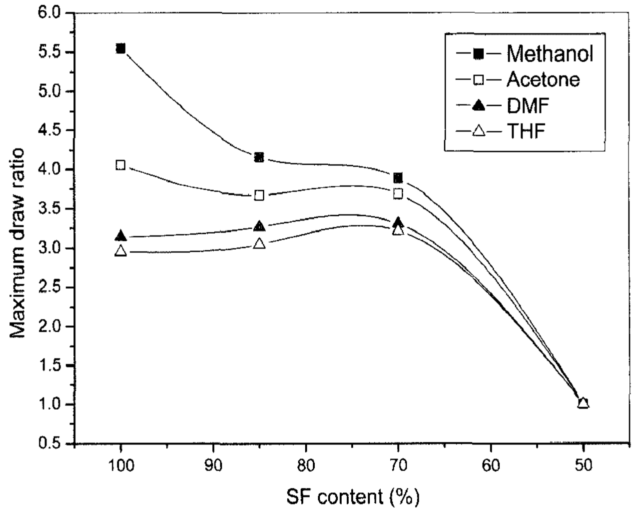


Fig. 1. The effect of coagulant on maximum draw ratio of wet spun SF/nylon 6 filaments with various SF contents.

ing the maximum draw ratio of SF/nylon 6 filaments when the SF content is higher than 50%. That is, the effect of coagulation power against nylon 6 seems to be minimal in this region. This result is also due to the fact that the coagulants have a strong coagulation power for SF, not nylon 6.

Third, the maximum draw ratios of DMF and THF increased a little bit until 70% SF content and decreased abruptly at 50% SF content, while those of methanol and acetone decreased constantly. This might be due to the difference of coagulation strength of coagulants against SF and nylon 6. Firstly, methanol and acetone had a stronger coagulation power than DMF and THF against SF showing the higher maximum draw ratio at the higher SF content regions. On the contrary, DMF and THF had a slightly stronger coagulation strength for nylon 6 than methanol and acetone. Therefore, due to this adverse trend of coagulants for SF and nylon, the difference of maximum draw ratio between the coagulants became minimized when SF and nylon 6 compositions were equal.

It is generally known that the fiber morphology strongly influences physical properties of wet spun filament such as mechanical properties, luster, etc. Especially, in the study on the polymer blend, the morphology is one of key issues because it gives the information whether macrophase separation occurs or not (Hobbs and Watkins, 2000). When the phase separation occurs in the polymer blend, the mechanical properties of blend are deteriorated. Based on this background, the morphology of blend has been observed to characterize the miscibility and phase behavior of SF blend (Um and Park, 2007; Tanaka *et al.*, 1998). In this paper, the phase behavior of blend filaments was observed by FE-SEM and the results are illustrated in

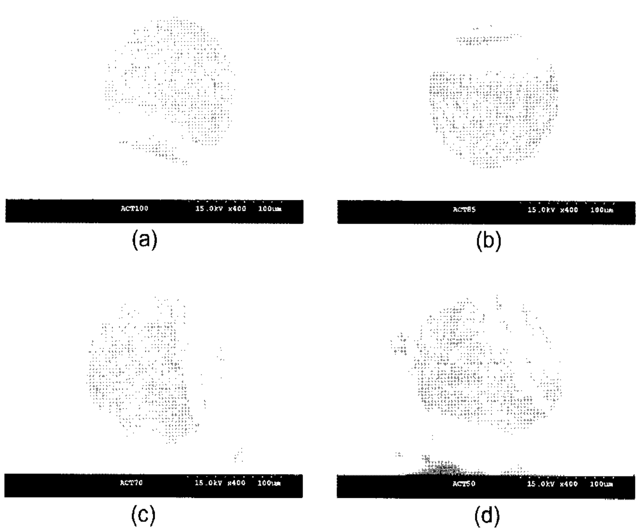


Fig. 3. Cross-section of wet spun regenerated SF/nylon 6 blend filaments with various blend ratios coagulated in acetone; (a) 100/0, (b) 85/75, (c) 70/30, and (d) 50/50.

Figs. 2~6.

Fig. 2 showed the cross-section of wet spun regenerated SF/nylon 6 blend filaments coagulated in methanol with various blend ratios. In the blend ratio of 85/15, SF/nylon filament showed a circular shape and did not exhibit any symptom of phase-separation. However, in the 70/30 blend, though phase separation did not appear, it seems that the fiber shape started deviating from the circularity. In the 50/50 blend, the fiber shape deviated from the circularity apparently showing the irregular structure. In addition, severe macro-phase separation was observed in this sample indicating there is no miscibility of two poly-

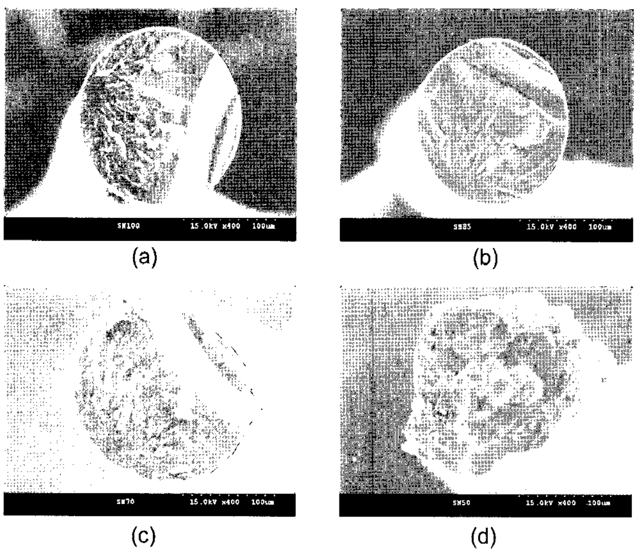


Fig. 2. The cross-section of wet spun regenerated SF/Nylon 6 blend filaments with various blend ratios coagulated in methanol; (a) 100/0, (b) 85/15, (c) 70/30, and (d) 50/50.

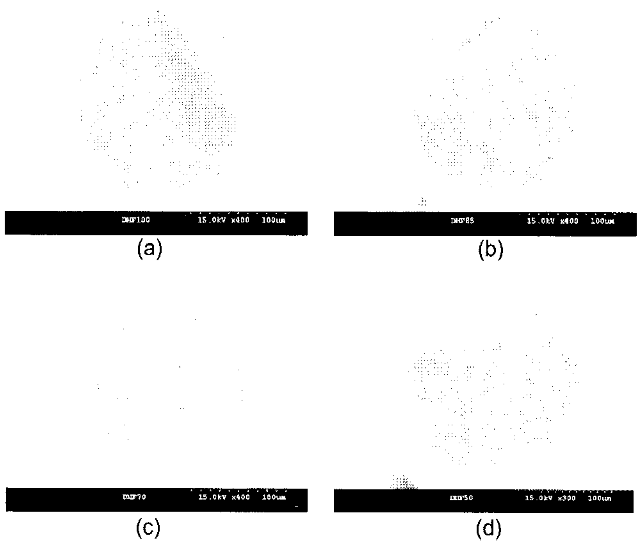


Fig. 4. Cross-section of wet spun regenerated SF/nylon 6 blend filaments with various blend ratios coagulated in DMF; (a) 100/0, (b) 85/75, (c) 70/30, and (d) 50/50.

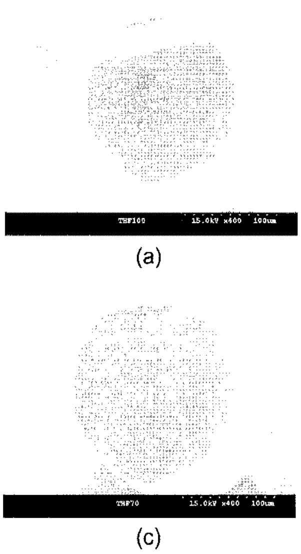


Fig. 5. Cross-section of wet spun regenerated SF/nylon 6 blend filaments with various blend ratios coagulated in THF; (a) 100/0, (b) 85/75, (c) 70/30, and (d) 50/50.

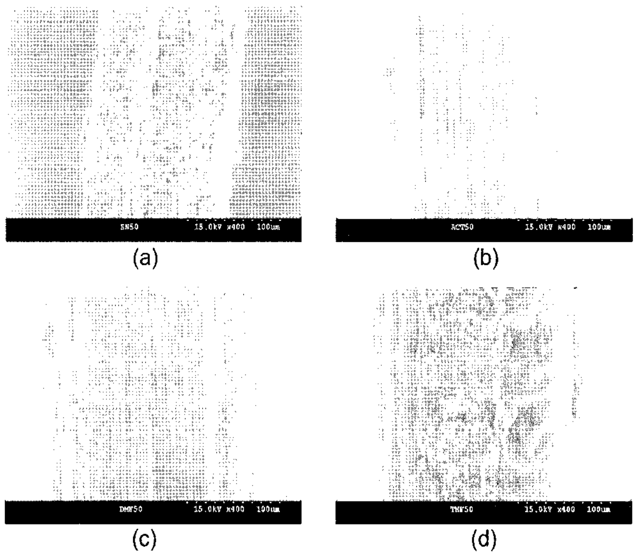


Fig. 6. The surface of wet spun regenerated SF/Nylon 6 blend filaments (50/50) coagulated in different coagulants; (a) methanol, (b) acetone, (c) DMF, and (d) THF.

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In case of acetone (Fig. 3), the filament showed more uniform morphology. In the 70/30 blend ratio, though the cross section deviated from the circularity slightly, the regular structure was obtained. However, in the 50/50 blend ratio, the cross section deviated from the circularity apparently though the severe phase separation did not take place. DMF (Fig. 4) displayed similar morphology with that of acetone. Though the irregular cross section appeared in the 50/50 blend, the phase separation did not occur. In the filament coagulated in THF, the phase separation was occurred (Fig. 5). Above 70% SF content, the uniform cross section was observed. However, in 50/50 blend ratio, the morphology became irregular showing severe phase separation.

The phase behavior of wet spun SF/nylon 6 blend filaments can be summarized as follows. As nylon 6 content increased, the cross section deviated from circularity and the morphological structure became irregular regardless of type of coagulant. In particular, at 50% nylon 6 content, the severe phase separation was occurred in the filaments coagulated in methanol and THF. The phase separation behavior could be confirmed by observing the surface of filaments (Fig. 6). The filament coagulated in methanol and THF displayed the irregular separated structure. The striped pattern and irregular structure were also shown in the surface of filaments coagulated in acetone and DMF implying that the two polymers also has no miscibility at this region.

According to the results of coagulation strength and fiber morphology, it seems that the result of maximum draw ratio of blend filaments is resulted from the mixed effect of coagulation strength of coagulants and fiber morphology. Above 70% SF content, all blend filaments has the uniform and regular morphological structure not showing any evidence of macro-phase separation. Therefore, in these regions, the coagulation strength dominates the maximum draw ratio of blend filament exhibiting that the best coagulant, methanol, has the highest maximum draw ratio. However, below 70% SF content, the morphology and phase behavior of filament dominate the behavior of post-drawing of filament. That is, the morphology of all filaments becomes irregular showing that some coagulants yield severe phase separation. Therefore, at 50% SF content, regardless of type of coagulant, the post drawing becomes impossible.

Conclusions

In this paper, the regenerated SF/nylon 6 blend filaments were fabricated by wet spinning and the effect of coagulant on the post drawing and morphology was investigated to find out the best coagulation system for wet spinning of SF/nylon 6 blends. The results of wet spinnability, maximum draw ratio and electron microscopy provided a better understanding for wet spinning of SF/nylon 6. First of all, methanol was the best coagulation for wet spinning of SF/nylon 6 blends regardless of blend ratio. In addition, the maximum draw ratio, strongly related to mechanical properties, was decreased with reduction of SF content making the post drawing process impossible at 50% SF content regardless of coagulant type.

Considering those results, in the following study, the regenerated SF / nylon 6 blend filaments will be prepared using methanol as a coagulant and their structural characteristics and properties will be investigated.

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