Compatibilization of Acrylic Polymer–Silk Fibroin Blend Fibers: 2. Morphology and Mechanical Properties of the Compatilized Blend Fibers

YUYU SUN, ZHENGZHONG SHAO, JIE ZHOU, TONGYIN YU

Department of Macromolecular Science and the Laboratory of Macromolecular Engineering of Polymers, Fudan University, Shanghai 200433, People's Republic of China

ABSTRACT: Three synthesized acrylonitrile-graft-silk fibroin copolymers (AN-g-SF), denoted as COP-65, COP-87, and COP-106, were used as potential compatilizers for acrylic polymer–silk fibroin blend fibers. Due to their different molecular weights and architecture, the compatibilizing efficiency is in the order of COP-106 > COP-65 > COP-87. To maintain the "sheath-core" structure of the blend fiber, COP-65 was chosen as the compatilizer. It was found that the addition of a small amount of COP-65 (up to 2 wt %) results in finer and more even distribution of the SF fibrils. On the contrary, excess COP-65 will cause flocculation and coalescence of the SF phase. Similarly, mechanical properties are enhanced with an optimum amount of the compatilizers. However, when excess COP-65 is added, the mechanical properties of the blend fibers are even worse than that of the uncompatilized samples. The mechanism of these findings is also discussed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2255–2264, 1999

Key words: silk fibroin; acrylonitrile; fiber; compatilizer

INTRODUCTION

Silk fibroin (SF) and acrylic polymers are important materials in the textile industry. Although both of them possess some outstanding characteristics, they suffer from some inferior properties. Thus, many attempts have been made to improve their properties.[1–8] It has been reported in our laboratory that acrylic polymer–SF could form useful blend fibers, which would combine the merits of the two fibers and enlarge the range of their applications.[9,10] However, due to the incompatibility of these two polymers, the mechanical properties of the fibers would be deteriorated upon blending.

It is believed that the poor mechanical properties of the blend fibers can be improved by adding a properly chosen copolymer, or, a compatilizer. In the first article of this series, the graft copolymerization of acrylonitrile onto SF were investigated in detail.[11] In this article, the relationships between the mechanical behavior of the blend fibers and their composition, as well as the molecular weight and architecture of the compatilizers were studied with respect to morphological changes. The tensile parameters of strength, modulus, and elongation were investigated, which are interpreted in accordance with the morphological observations.

EXPERIMENTAL

Materials

Acrylic polymer (denoted as PAC, MW = 60,000–80,000) used in this study was kindly supplied by

---

Table I   Characterization Data of the Graft Copolymers

Polymer Code	MW of Grafted PAN (Kd)	PAN/SF[a] (mol/mol)	MW_{hop}/MW_{cop}[b]
COP-65	65	2.2	0.9–1.2
COP-87	87	4	0.7–0.9
COP-106	106	1.5	0.6–0.8

SF, silk fibroin; PAN, polyacrylonitrile.

[a] The value of PAN/SF indicates the numbers of PAN branch (average) on the SF backbone, according to the definition in the literature.[11]

[b] MW_{hop} and MW_{cop} denote the molecular weight of PAC used in this study and that of the grafted PAN of the copolymers.

Jinshan Acrylic Fiber Factory, Shanghai, P.R. China. Pyrolytic chromatography results, which were provided by the manufacturer, showed that the acrylic polymer was made of acrylonitrile (91.7%), methyl acrylate (7%), and sodium methyl propenyl sulfonate (1.3%).

In our previous article,[11] the synthetic method of the compatilizer, i.e., the homogeneous graft copolymerization of acrylonitrile onto silk fibroin, initiated by potassium persulfate–sodium bisulfite redox system in 60 wt % $ZnCl_2$ aqueous solution, has been reported in detail. Also, the influence of the reaction conditions on the molecular architecture of the graft copolymers has been discussed. According to this, the graft copolymers used in the present study were synthesized; their molecular parameters are listed in Table I. It seems all the graft copolymers are broadly similar, except they differ from each other in the numbers of branch [the value of polyacrylonitrile (PAN)/SF] and the molecular weights of grafted PAN.

Preparation of the Blend Fibers

Degummed silk fibroin from waste Bombyx mori silk fiber, PAC, and compatilizers were dissolved in 55 wt % aqueous NaSCN solutions, separately. The polymer concentration of these solutions was made up to be 12% by weight. A fixed PAC/SF ratio, i.e., 70/30 (wt/wt), was used throughout this work. Varied amounts of the compatilizer solutions, expressed as compatilizer/(SF + PAN) weight ratios, were added to the PAC–SF blend solutions, and stirred for at least 2 h to obtain homogenous solutions. After degassing, the blend solutions were extruded from a 30-hole (0.08 mm diameter) die into a 10% NaSCN aqueous coagulation bath at $0 \sim 5$°C to form the fibers. The as-spun fibers were washed and drawn in boiling water (the draw ratio is four for all the samples), then dried at 120°C for 30 min.

Measurements

Tensile tests were carried out on an Instron machine model 1121 (Instron, UK). All tests were performed on single filament using a gauge length of 50 mm and crosshead speed of 20 mm/min. The average of 50 readings was presented for each sample.

A HITACHI S-520 scanning electron microscope (Hitachi, Japan) was used to study the morphological structure of the blend fibers. To improve the contrast of the images, the samples were partially immersed in 9.5 mol/L LiBr aqueous solution around 80°C for some time to dissolve out SF. The resultant fibers were then washed and dried. After tensile test, the cross sections of the fibers were examined. All the samples were then coated with gold under vacuum for microscopic inspection.

RESULTS AND DISCUSSION

Effect of Various Compatilizers on Dispersed Phase Size

As it has been pointed out,[12] the addition of effective compatilizers to an incompatible blend system would: 1. reduce the interfacial energy between the phases; 2. permit a finer dispersing during mixing; 3. provide a measure of stability against gross segregation; and 4. result in improved interfacial adhesion. The efficiency of these processes depend on many factors such as mixing conditions, molecular weight, architecture and concentration of the compatilizers, interaction of the compatilizer with the various phases, and the rate of absorption of the compatilizers at the interface.

Figure 1(A) shows the longitudinal section of a 70/30 blend fiber containing no compatilizer after treatment with LiBr aqueous solution. Because SF is the minor component of the blend fiber, it is

Figure 1 SEM photomicrographs of the longitudinal sections of the 70/30 blend fibers treated with LiBr aqueous solution. The fibers contained different compatilizers: (A) control, scale bar: 6.0 μm; (B) 2 wt % COP-65, scale bar: 4.3 μm; (C) 2 wt % COP-87, scale bar: 6.0 μm; and (D) 2 wt % COP-106, scale bar: 4.3 μm.

believed that after treatment with hot 9.5 mol/L LiBr aqueous solution for some time, most of the SF component was dissolved out. It is seen that SF forms long fibrils along the flow direction of the blend fiber, which must be caused by the elongational flow during the fiber formation. The fibrils are bundled together, indicating gross phase separation and poor adhesion between SF

and PAC. However, on adding 2 wt % COP-65, COP-87, and COP-106 into the blend fiber, the diameter of the SF fibrils, which exhibits more homogenous distributions, decreases sharply [Fig. 1(B–D), respectively]. Since the domain size is directly proportional to the interfacial tension, this finding definitely indicates good compatibilizing effect of the graft copolymers.

Also noteworthy about these SEM photomicrographs is that although all the graft copolymers exhibit compatibilizing effect, their efficiencies are different—the SF fibrils diameters in the COP-87 compatilized sample are relatively large, suggesting that COP-87 is not an effective compatilizer. On the contrary, COP-106 shows excellent compatibilizing effect—the SF fibrils are barely detectable, indicating good dispersion of SF and enhanced adhesion between the two phases.

These phenomena can be explained by the molecular weight and architecture of the copolymers. As pointed out by Paul and Newman,[12] among the requirements on an effective compatilizer, two of them stand out: 1. the architecture of the copolymer should be as simple as possible; and 2. the molecular weight of individual segments has to be equal or higher than those of corresponding homopolymers. In the present study, because of the associated entropy loss, the multiple branches of COP-87 (see Table I) would certainly restrict the opportunities for the backbone to penetrate its homopolymer phase. COP-106 is an effective compatilizer because each SF backbone has only one PAN branch (one should keep in mind that this value is a matter of average), and the MW_{hop}/MW_{cop} is less than 1. As to COP-65, its MW_{hop}/MW_{cop} is around 1, and each SF backbone has about two PAN branches. Consequently, the order of the compatibilizing efficiency of the copolymers is COP-106 > COP-65 > COP-87.

It should be pointed out that in some cases the goal of compatibilization is always to disperse the minor phase into the finest drops.[13,14] In the present study, however, if SF and PAC are too compatible, it will prevent the formation of the "sheath-core" structure[10] of the blend fibers, as can be seen in Figure 1(D), which will thus deteriorate some desired properties of the blend fibers, such as handle, luster, etc. As a consequence, although COP-106 is the most effective compatilizer, it is not suitable to be used in this work. We believe that COP-65 is a more suitable compatilizer—it will enhance the adhesion between the two polymers, while the "sheath-core" structure can be maintained.

Morphology of the COP-65 Compatibilized Blend Fibers

Figure 2 shows the longitudinal section of various concentrations of COP-65 compatibilized fibers after treated with LiBr aqueous solution. It can be seen that when a small amount of COP-65 was added to the blend fibers (up to 2 wt %), the SF fibrils are more evenly distributed and finer in size than the uncompatibilized blend [note particularly the difference between Figure 1(A) and Figure 2(A–C]. For blends containing more than 2 wt % of COP-65 [Fig. 2(D–F)], however, SF fibrils are poorly distributed and thicker than when 2 wt % COP-65 was added to the blends. When 8 wt % COP-65 was added, poorly distributed thick fibrils as well as gross stubby particles can be detected.

Figure 3 shows the SEM micrographs of the fractured surfaces after tensile testing. For the uncompatibilized fiber [Fig. 3(A,B)], gross cracks are observed. This kind of failure is supposed to occur by cracking or slipping, along the planes close to the fiber surface.[15] Due to the inhomogeneous fibril structure there would be shear stress in these planes. While the slippage grows slowly, the remaining fiber cross section continues to deform plastically to some extent. At a point determined by the sizes of the crack and of the remaining cross section and by the fiber properties, rapid transverse crack propagation occurs. These findings indicate poor adhesion between SF and PAC. When a small amount of COP-65 was added to the blend fibers, evenly distributed fibrils, instead of large cracks, can be observed in the immediate region of the fracture area [Fig. 3 (C–H)]. The interfacial adhesion looks good (pull-out fibrils are barely detected), suggesting that the compatibilization takes place at the interface. However, similar to the results mentioned above, the dimension of SF domains increase after an optimum value of 2 wt % COP-65 content is reached. When the concentration of COP-65 is 8 wt %, large cracks, instead of fibrils, can be observed [Fig. 3 (M,N)].

These findings suggest that when a small amount of COP-65 (up to 2 wt %) is added to the blend fibers, good compatibilizing effect can be obtained. However, excess compatilizer will lead to "flocculation" of the SF domains. It is generally accepted that flocculation of the dispersed phase occurs because of strong interparticle interactions,[16] as has been observed in other compatibilized systems.[17,18] In the present study, some special interactions, such as hydrogen bonds between the grafted and ungrafted SF, may prevent some of the graft copolymers from locating at the interface. As a result, instead of size reduction, excess COP-65 tends to coalesce the dispersed SF phase before fibrils are formed, and thus result in poor dispersion of SF in PAC matrix, which will deteriorate the mechanical properties of the blend fibers, as discussed below. The same trend is also

Figure 2 SEM photomicrographs of the longitudinal sections of the 70/30 blend fibers treated with LiBr aqueous solution. The fibers contained various amounts of COP-65: (A) 0.5 wt %, scale bar: 6.0 μm; (B) 1 wt %, scale bar: 6.0 μm; (C) 2 wt %, scale bar: 4.3 μm; (D) 4 wt %, scale bar: 4.3 μm; (E) 6 wt %, scale bar: 6.0 μm; and (F) 8 wt %, scale bar: 6.0 μm.

Figure 3 SEM photomicrographs of the fracture surfaces of the 70/30 blend fibers after tensile testing. The fibers contained various amount of COP-65: (A) 0, scale bar: 43 μm; (B) 0, scale bar: 7.5 μm; (C) 0.5 wt %, scale bar: 43 μm; (D) 0.5 wt %, scale bar: 4.3 μm; (E) 1 wt %, scale bar: 20 μm; (F) 1 wt %, scale bar: 4.3 μm; (G) 2 wt %, scale bar: 25 μm; (H) 2 wt %, scale bar: 4.3 μm; (I) 4 wt %, scale bar: 60 μm; (J) 4 wt %, scale bar: 4.3 μm; (K) 6 wt %, scale bar: 30 μm; (L) 6 wt %, scale bar: 6.0 μm; (M) 8 wt %, scale bar: 60 μm; and (N) 8 wt %, scale bar: 6.0 μm.

Figure 3 *(Continued from the previous page)*

observed in COP-87 compatibilized blends as shown in Figure 4. As for the COP-106 compatibilized system, however, no such trend can be detected in the present study, suggesting that there is a high level of compatibility in this ternary blends system, which will be studied further.

M   N

Figure 3 *(Continued from previous page)*

Mechanical Properties of COP-65 Compatilized Blend Fibers

Figure 5(A) shows the tensile strength of the blend fibers vs COP-65 content. It can be seen that the tensile strength is significantly increased with the increase of added COP-65. When 2 wt % COP-65 is added, the tensile strength is about 2.3 cN/dtex, which is about 50% higher than that of the uncompatilized fiber. This increasing trend can be attributed to a more uniform distribution and finer SF fibril formation on the addition of the compatilizer. However, when COP-65 content is higher than 2 wt %, further increasing the concentration will lead to depression of the tensile strength. When the COP-65 content is 8 wt %, a tensile strength of 1.38 cN/dtex is obtained, which is about 10% lower than that of the uncompatilized sample. This decreasing trend must be caused by the flocculation and coalescence of the SF phase. As discussed above, excess compatilizers lead to poor distribution of the SF phase. When 8 wt % of COP-65 is added, the SF phase forms fibrils as well as gross stubby particles. These poorly dispersed SF thick fibrils and/or particles may include part of the compatilizer, which acts as a defect in the fiber. As a result, the tensile strength of the blend fibers containing excess COP-65 (more than 2 wt %) becomes even worse than that of the uncompatibilized sample.

Figure 5(B) shows the relationship between initial modulus and COP-65 content in the blends. A similar trend to that of the tensile strength can be observed; the initial modulus increases with the increase of COP-65 content until an optimum value, say, 2 wt % is reached, and thereafter, it decreases. This finding further strengthens the "flocculation" idea mentioned above, and it is reasonable to conclude that a small amount of COP-65 improves the mechanical properties of the blend fibers, whereas excess compatilizers will deteriorate the performance of the compatilized fibers.

The relationship between elongation at break of the blend fibers and the COP-65 content is shown in Figure 5(C). It is noteworthy that similar to the strength and modulus, a peak of elongation at 2 wt % COP-65 can be observed. These phenomena can be ascribed to the improved adhesion between SF and PAC when a small amount of COP-65 was added. As pointed out by other authors in other systems,[18] improved adhesion increases the friction between the dispersed SF fibrils and PAC matrix. Thus, SF fibrils will connect tightly to the crack gaps between the matrix until additional work is in operation. Consequently, it is not unexpected that the elongation at the break will be increased on adding a small amount of COP-65. However, excess compatilizers lead to flocculation and coalescence of the SF phase, which will decrease the total contacting area. As a result, the decreasing trend of elongation can be observed.

It should be pointed out that there is no reason to believe that the spinning conditions used here are the optimum parameters. Therefore, more suitable spinning conditions may be used when the process is examined on a cost-benefit basis. However, it can be seen that on addition of a small amount of COP-65, the mechanical properties of the blend samples are greatly improved, which have already characterized them as usable fibers.

Figure 4 SEM photomicrographs of the longitudinal sections of the 70/30 blend fibers treated with LiBr aqueous solution. The fibers contained various amount of COP-87: (A) 2 wt %, scale bar: 60 μm; (B) 6 wt %, scale bar: 43 μm; and (C) 10 wt %, scale bar: 60 μm.

CONCLUSIONS

The results of present study can be summarized as follows:

1. Due to the differences in molecular weight and architecture of the selected three AN-g-SF copolymers, their compatibilizing effi-ciency for SF–PAC blend fibers is in the order of COP-106 > COP-65 > COP-87. To obtain improved mechanical properties and maintain the "sheath-core" structure of the blend fibers, COP-65 is chosen as the com-patilizer for this blend system.

2. The addition of a small amount of COP-65 (up to 2 wt %) results in finer distribution of

Figure 5 Relationship between (A) the tensile strength; (B) the initial modulus; and (C) the breaking elongation of the 70/30 blend fibers and the amounts of added COP-65.

the SF fibrils and improved adhesion between the phases. However, excess of COP-65 causes flocculation and coalescence of the SF phase.

3. The strength, initial modulus, and elongation of the compatibilized fibers increase with the increase of the COP-65 content until an optimum value, and thereafter these values decrease.

REFERENCES

1. Tsukada, M. J Appl Polym Sci 1988, 35, 2133.
2. Tsukada, M.; Nagura, M.; Ishikawa, H.; Shiozaki, H. J Appl Polym Sci 1993, 49, 593.
3. Liu, J.; Yu, T. Fudan Xue Bao (Ziran Kexue Ban) (Chinese) 1994, 33, 371.
4. Cates, D. M.; White, H. J., Jr. J Polym Sci 1956, 20, 155.
5. Cates, D. M.; White, H. J., Jr. J Polym Sci 1956, 21, 125.
6. Lennox-Keer, P. Tex Inst Ind 1983, 19, 83.
7. Qin, J. J Appl Polym Sci 1992, 44, 1095.
8. Bajaj, P.; Kumari, S. J Macromol Sci, Rev Macromol Chem Phys 1987, C27,181.
9. P. R. China Pat. CN 1107906A.
10. Sun, Y.; Shao, Z.; Ma, M.; Hu, P.; Liu, Y.; Yu, T. J Appl Polym Sci 1997, 65, 959.
11. Sun, Y.; Shao, Z.; Zhou, J.; Yu, T. J Appl Polym Sci 1998, 69, 1089.
12. Paul, D. R.; Newman, S. Polymer Blends; Academic Press: New York, 1978.
13. Xanthos, M.; Young, M. W.; Bisenberger, J. A. Polym Eng Sci 1990, 30, 355.
14. Ide, F.; Hasegawa, A. J Appl Polym Sci 1974, 18, 963.
15. Kausch, H. H. Polymer Fracture; Springer-Verlag, Berlin, 1978.
16. Piirma, I. Polymeric Surfactants; Marcel Dekker: New York, 1992.
17. Plochocki, A. P.; Dagli, S. S.; Andrews, R. D. Polym Eng Sci 1990, 30, 741.
18. Seo, Y.; Hong, S. M.; Hwang, S. S.; Park, T. S.; Kim, K. U.; Lee, S.; Lee, J. Polymer 1995, 36, 525.