Effects of Superfine Silk Protein Powders on Mechanical Properties of Wet-Spun Polyurethane Fibers

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ABSTRACT: Mechanical measurements were employed to investigate the effects of three types of superfine silk protein powder on tensile strength, elongation, and elasticity of wet-spun Pellethane® 2363-80AE polyurethane (PU) fiber. These superfine silk protein powders included undegummed silk (with both native silk fibroin and sericin, water insoluble), native silk fibroin (with native silk fibroin only, water insoluble), and regenerated silk fibroin (with regenerated silk fibroin only, water soluble) in powder form. Experimental data derived from the mechanical measurements illustrated that the miscibility between the PU and regenerated silk fibroin were superior to that between PU and the other two silk proteins. This may be attributed to the similar chemical structure and microphase separation of PU and regenerated silk fibroin with lower molecular weight than native silk fibroin. This preliminary work may provide some information for biomimetic processing of silk-inspired PU biofibers, which combine elasticity of synthetic PU with biofunction of natural silk fibroin for special biomedical applications. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3428–3433, 2009

Key words: fibers; polyurethane; mechanical properties; silk; powder

INTRODUCTION

Synthetic polyurethane (PU) is a kind of versatile polymeric material, which offers high elasticity, good wear property, tear resistance, flexural capability, oil resistance, and excellent blood compatibility.[1–5] Foam and plastic, elastomer, paint, adhesive, elastomeric fiber, and synthetic leather, which are made from PU resin whose structure and properties can be tailored due to a controlled combination of hard and soft segments, play an important role in modern industry.[6] Correspondingly, silk fibroin extracted from *Bombyx mori* silkworm cocoons has been investigated as a highly promising natural protein material that can be applied to biotechnological and biomedical fields, although mechanical properties, especially the elasticity of regenerated silk fibroin fiber, cannot meet the requirements of specific applications.[7–10] Consequently, biomimetic elastic silk fibroin fibers are desirable for some biomedical applications. Biomimetic silk fibers may be classified into three broad categories: shape-mimetic, structure-mimetic, and even function-mimetic. Alkali peeling processing of polyester fibers has been widely employed to mimic the shape of silk fibers. To mimic the structure and even function of silk fiber, the spinning of silk fibroin regenerated from raw silk fiber has been intensively investigated.[11–15] Properties comparison of regenerated and natural silk fibers is summarized in Table I. Biosynthesis of silk-like polymers and recombinant technology have also been performed.[16,17]

Producing protein/polymer hybrids or protein-inspired polymers as biomaterials chemically and/or physically is a highly promising method,[18,19] combining biofunction of natural macromolecules with controllable structure and properties of synthetic polymers. Particularly, elastic biofibers have attracted considerable attention and have generated intense research into their properties.[20] Noticeably, PU and silk fibroin have similar molecular architecture in their primary structure (imido links) and secondary structure (microphase separation). Moreover, both PU and silk fibroin were employed as scaffold materials for tissue engineering due to their biocompatibility, and putting silk fibroin into PU fibers may improve the compatibility to reduce thrombosis.[3,9,21] In the present work, biomedical PU/silk protein biohybrid fibers were fabricated by a facile wet spinning process. As it is difficult to find a suitable

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TABLE I
Properties Comparison of Regenerated and Natural Silk Fibers

Refs.	Solvent for natural silk	Regenerated silk fibroin concentration (%)	Coagulation bath	Regenerated silk fibroin fiber		
				Diameter (μm)	Tensile strength (MPa)	Breaking elongation (%)
11	$NMMO/H_2O$	13[a]	Ethanol	18.5	120	35
12	$CaCl_2/H_2O/EtOH$	15[b]	Methanol	120	172	8.4
13	$HCOOH/H_3PO_4$	18[c]	Methanol	120	275	18
14	$LiBr/H_2O$	17[a]	Ethanol	28	116	8.6
15	Natural silk fiber (with silk sericin)			11.5	500	19
	Degummed silk fiber (without silk sericin)			9.3	610–690	4–16

[a] Solvents for regenerated silk fibroin denoted in superscript 'a,' 'b,' and 'c' are NMMO, 98% HCOOH, and HCOOH/H_3PO_4, respectively.

solvent, which can dissolve both the synthetic polymer (PU) and the natural macromolecule (silk protein) simultaneously, silk proteins ground in superfine powder form were dispersed into PU/dimethyl formamide (DMF) solution to prepare PU/silk protein biohybrid fibers. The effects of superfine silk protein powders on the mechanical properties of wet-spun PU fibers were investigated to identify the advantages and disadvantages of various superfine silk protein powders. The future further work is to enhance the compatibility and intermolecular interactions between PU and native silk fibroin. Alternatively, it is a valuable approach that remains a challenge to develop regenerated silk fibroin avoiding being degraded.

EXPERIMENTAL

Materials and reagents

Raw *B. mori* silk fiber was provided by Luotian Silk Incorporation of Hubei Province, China. Superfine undegummed silk fiber powder and superfine native silk fibroin powder were physically prepared from the above silk fiber with a custom-built machine,[22] both of which were water insoluble. Water-soluble superfine regenerated silk fibroin powder was derived from salt-dissolved, dialyzed, and freeze-dried silk fibroin.[8] Expositively, the average particle sizes of the three types of superfine silk protein powder are 5.86, 3.58, and 4.80 μm, respectively, and all of them are at the micrometer length and very close to each other, measured by JL-1166 Laser Particle Analyzer (Chengdu Jingxin Powder Measurement Instrument, China). Figure 1 shows the difference of production of these three types of silk protein powder.

Pellethane® 2363-80AE, a commercially available biomedical grade segmented PU, was obtained as pellets from Shanghai Dow Center, China. Extraction of PU was performed with ethanol in a Soxhlet extractor to remove impurity. The received PU pellets were extracted for 72 h in refluxing ethanol and dried for 72 h at 40°C before dissolving in DMF to form a dope solution. Chemical reagents such as DMF were purchased from Bodi Chemical Reagent (Tianjin, China) and used without further purification.

Preparation of fiber samples

To prepare PU/silk protein powder blend dope solution, each type of superfine silk protein powder and PU (10%, w/w) were thoroughly dispersed in DMF. The PU/silk protein powder dope solution concentration was fixed at 25% (w/v) for wet spinning. After being degassed in a vacuum, the PU/superfine silk protein powder blend dope solution was immediately spun with a Microinfusion Pump (LION WZ-50G, Medical Instrument Factory of Zhejiang University, China) into a distilled warm water coagulation bath (30°C) at a controlled flow rate of 40 mL/h. The as-spun PU/superfine silk protein powder hybrid fiber was left in the coagulation bath overnight for complete solidification, drawn at a compatible ratio in length and then dried under tension. By using the same machine in similar conditions, PU/superfine undegummed silk powder hybrid fiber, PU/superfine native silk fibroin powder hybrid fiber, PU/superfine regenerated silk fibroin powder hybrid fiber, and the pure PU fiber were prepared and they were formulated as fiber samples A, B, C, and D, respectively, with similar linear densities of around 90 denier.

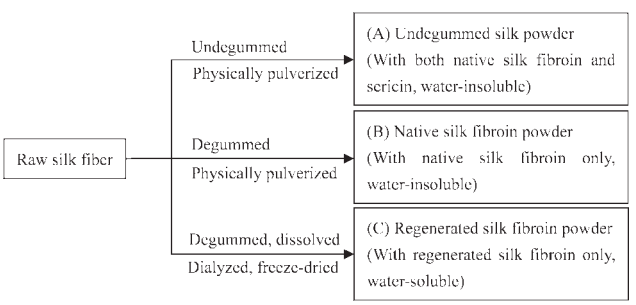


Figure 1 Schematic flow chart for production of three types of superfine silk protein powder.

Observation of fiber surface

Scanning electron microscopy (SEM) measurements for the fiber samples were carried out on a JSM-5610LV scanning electron microscope (JEOL, Japan) at an accelerating voltage of 20 kV, after the samples were sputter-coated with a 10- to 15-nm layer of gold. Prior to observation, all fiber samples were washed with distilled water, dried at room temperature, and then preconditioned at 20°C and 65% relative humidity for 24 h.

Measurement of mechanical properties

Tensile tests were carried out on an Instron universal material testing system (Model 5566, Instron Corporation, MA), at a gauge length of 50 mm and strain rate of 500 mm/min. All fiber samples were preconditioned at 20°C and 65% relative humidity for 24 h before testing. All tensile data were measured with 10 specimens for each fiber sample and represented as mean ± SD. Breaking tenacity, breaking elongation, and elasticity were determined in accordance with the Chinese Textile Industrial Standards FZ/T 50006-94 and FZ/T 50007-94 (idt. BISFA Test methods for bare elastane yarns). Distinguishingly, each fiber sample was drawn to 300% elongation (i.e., stretching fiber from 50 to 200 mm in length) and relaxed to the original length (50 mm) cyclically for seven times during elasticity testing, while the effective data were derived from the sixth cycle. Care was taken to avoid stretching the fibers plastically during the whole experiment.

RESULTS AND DISCUSSION

Fiber formation

Generally, there are a variety of methods for producing PU fibers: dry, wet, melt, reaction spinning, and electro-spinning. There are advantages and disadvantages for each method. Although dry spinning is the dominant method and melt spinning method provides an advantage of improving chemical and environmental resistance compared with wet spinning method, wet spinning method should not be negligible when producing differential and functional fiber at a low temperature. The biggest challenge for PU/silk protein wet-spinning is to find a suitable solvent, which can dissolve both the synthetic polymer and the natural macromolecule simultaneously. As known, DMF was successfully used as a solvent for dry and wet spinning of synthetic PU. Correspondingly, raw silk fiber is obtained by reeling from silk cocoons as a natural protein fiber, and silk fibroin is purified from sericin by boiling silk cocoons in an alkaline solution. About 25–30% of the silk cocoon mass is sericin, which is removed during the degumming process,[23] and the residual is native silk fibroin. Native silk fibroin cannot be dissolved by water, while sericin can be dissolved by boiling water to an extent. The water-insoluble superfine native silk fibroin powder employed in the current experiment is physically pulverized from this native silk fibroin. Native silk fibroin can be dissolved in aqueous lithium bromide (LiBr-H_2O),[23] $CaCl_2/H_2O$/EtOH (molar ratio: 1/8/2) ternary solvent,[8] NMMO monohydrate,[11] or formic acid,[8] etc., and then dialyzed to remove salts to produce aqueous solution of regenerated silk fibroin. However, it is difficult to find a suitable solvent to dissolve both PU and native silk fibroin. In the present report, PU/three types of superfine silk protein powder blends formed hybrid biofibers by using a wet spinning method. During fiber formation, DMF in dope solution and H_2O in coagulation bath diffused and penetrated each other, while superfine silk protein powders were enwrapped in coagulated PU.

Fiber surface morphology

Figure 2 shows the selected SEM micrographs of as-spun PU/three types of silk protein powder hybrid fibers and pure PU fiber with similar diameters of ~ 110 μm. Although there was no significant difference between SEM micrographs, as-spun fiber surface was generally substantial, with some clotted superfine silk protein powders and a few fine granules whose morphology changed depending on various types of superfine silk protein powder. From fiber sample A to C, shown in Figure 2, superfine silk protein powders enwrapped in PU and clotted on fiber surface stepwisely became thinner, and their distribution became more regular. The well-known tendency of silk fibroin chains to self-assemble into globular clusters by establishing a strong network of intermolecular interactions between the hydrophobic polypeptide blocks forming its primary structure could be responsible for these morphological features.[24] Aforementioned regular changes of axial alignment of silk protein powders in the corresponding hybrid fibers preliminarily demonstrated that the miscibility and compatibility between PU and water-soluble regenerated silk fibroin were superior to those between PU and the other two silk proteins.

Mechanical properties

Mechanical properties, particularly breaking tenacity and breaking elongation, are important for evaluating the fiber performance for proper application. Figure 3 illustrates the tensile properties of PU/different types of superfine silk protein powder hybrid fibers and two associated fibers. As shown in Figure 3, PU/three types of superfine silk protein powder

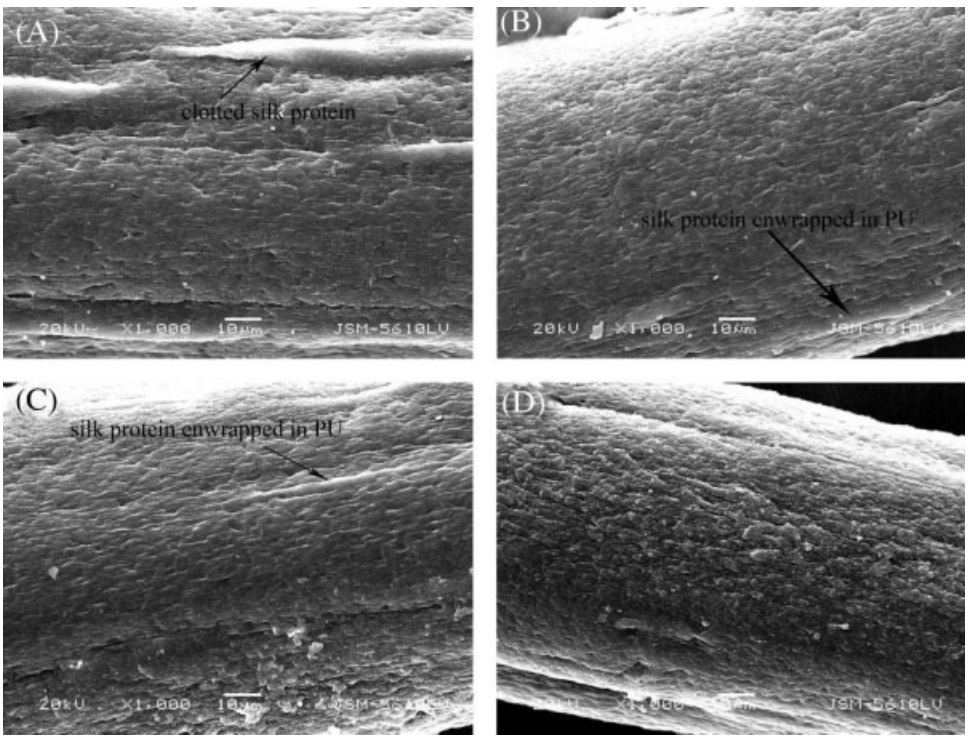


Figure 2 SEM micrographs of the as-spun PU/three types of superfine silk protein powder hybrid fibers and pure PU fiber: (A) PU/superfine undegummed silk powder hybrid fiber; (B) PU/superfine native silk fibroin powder hybrid fiber; (C) PU/superfine regenerated silk fibroin powder hybrid fiber; (D) pure PU fiber.

hybrid fibers (Sample A, B, and C) showed relative lower values of breaking tenacity compared with the pure PU fiber (Sample D). Of these, PU/water-soluble superfine regenerated silk fibroin powder hybrid fiber (Sample C) showed a relative high breaking tenacity and breaking elongation. Generally, phase separation occurs in immiscible blends, which can largely affect the synthetic polymer (PU)/natural macromolecule (silk fibroin) hybrids properties, when the PU is solidifying rapidly in the coagulation bath. We reasonably supposed that the aforementioned tensile features may be attributed to the similar chemical structure and molecular architecture of PU and silk fibroin (shown in Table II, summarized from the literature[1,7,23]), and there may be weak intermolecular interactions between molecular chains of PU and silk protein. The presence of regenerated silk fibroin destroyed PU fiber property most slightly due to its partial degradation during regeneration, while molecular chains of raw silk and native silk fibroin were longer and destroyed PU fiber property more severely. Therefore, it can be concluded that the intermolecular interactions between PU and water-soluble superfine regenerated silk fibroin powder is relatively approving.

Figure 4 illustrates the typical force–displacement curves for PU/three types of superfine silk protein powder hybrid fibers and the pure PU fiber. As shown in Figure 4, the as-spun PU/three types of superfine silk protein powder hybrid fibers exhibited analogical elastic modulus, while all the values of elastic modulus were much higher than that of the pure PU fiber. Figure 5 shows the tensile force–time curves for four related fiber samples while being drawn and relaxed cyclically 7 times. The effective

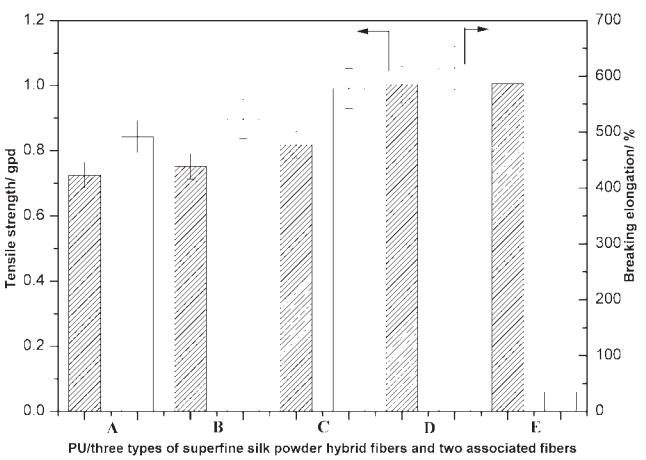
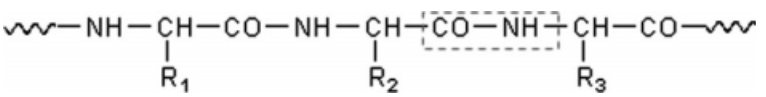
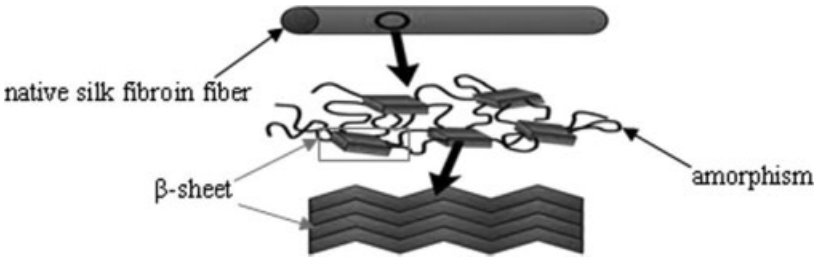
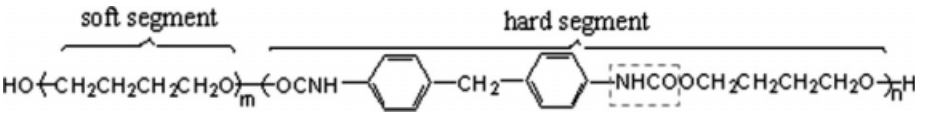
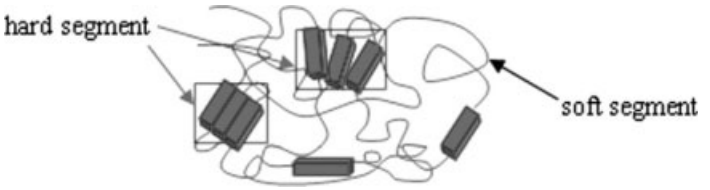


Figure 3 Tensile properties comparison of PU/three types of superfine silk protein powder hybrid fibers and two associated fibers: (A) PU/superfine undegummed silk powder hybrid fiber; (B) PU/superfine native silk fibroin powder hybrid fiber; (C) PU/superfine regenerated silk fibroin powder hybrid fiber; (D) pure PU fiber; (E) regenerated silk fibroin fiber (data cited and modified from Ref. 11).

TABLE II
Chemical Structure and Molecular Architecture of Silk Fibroin and Segmented PU

	Schematic chemical structure of silk fibroin (most of R_i are H, CH_3, or CH_2OH, $i = 1, 2, 3, ...$).
	Schematic molecular architecture of native silk fibroin fiber consisting of alanine-rich β-sheet crystalline domains and a glycine-rich unorder matrix.
	Schematic chemical structure of synthetic block copolyurethane (Pellethane® series, produced by Dow Chemical).
	Schematic molecular architecture of segmented polyurethane.

data should be derived from the sixth cycle, according to the stated standard mentioned in Materials and Methods. The PU/superfine undegummed silk powder hybrid fiber (Sample A) exhibited a peak tensile force of 31.2 cN, which was the maximal; the PU/superfine native silk fibroin powder hybrid fiber (Sample B) exhibited a peak tensile force of 29.8 cN. The PU/superfine regenerated silk fibroin powder hybrid fiber (Sample C) exhibited a peak tensile force of 23.2 cN, while the pure PU fiber exhibited a peak tensile force of 15.5 cN, which was the minimal. As known, the elasticity of PU fiber is mainly attributed to soft segment in its molecular chain. Regenerated silk fibroin with a lower molecular weight[25] can be enwrapped in PU chain easily and may move following the soft segment of PU closely during stretching, so the elasticity of PU/superfine regenerated silk fibroin powder hybrid fiber (Sample C) had an analogy to that of the pure PU fiber.

CONCLUSIONS

Pellethane® 2363-80AE PU/three types of superfine silk protein powder hybrid biofibers were prepared by using a facile wet spinning method. SEM micrographs indicated that silk proteins were enwrapped in PU and self-assembled into clusters. Experimental data derived from mechanical measurements

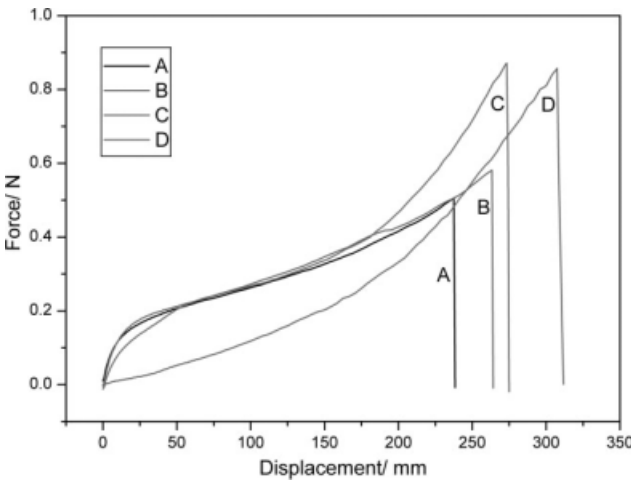


Figure 4 Force–displacement curves for PU/three types of superfine silk protein powder hybrid fibers and the pure PU fiber: (A) PU/superfine undegummed silk powder hybrid fiber; (B) PU/superfine native silk fibroin powder hybrid fiber; (C) PU/superfine regenerated silk fibroin powder hybrid fiber; (D) pure PU fiber.

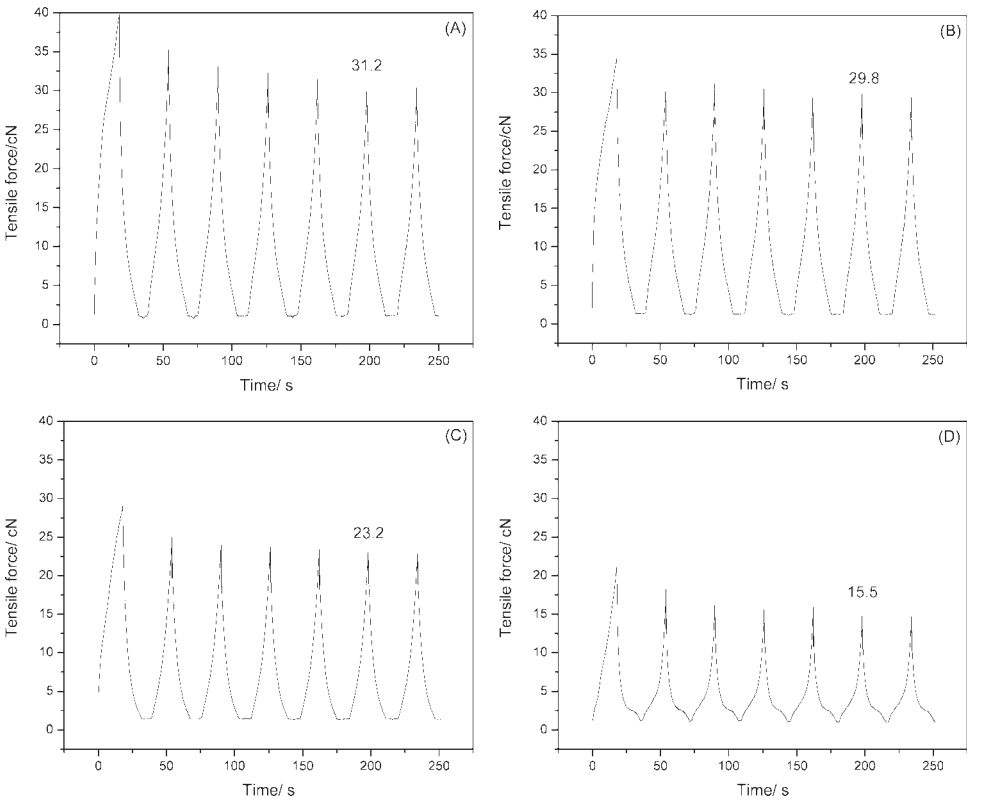


Figure 5 Elasticity comparison of PU/three types of superfine silk protein powder hybrid fibers and the pure PU fiber: (A) PU/superfine undegummed silk powder hybrid fiber; (B) PU/superfine native silk fibroin powder hybrid fiber; (C) PU/superfine regenerated silk fibroin powder hybrid fiber; (D) pure PU fiber.

illustrated that PU/three types of superfine silk protein powder hybrid fibers showed higher values of elastic modulus and relative lower values of breaking tenacity and elasicity, compared with the pure PU fiber. Of these, the miscibility between PU and water-soluble regenerated silk fibroin were superior to that between PU and the other two silk proteins.

References

1. Krol, P. Prog Mater Sci 2007, 52, 915.
2. Stankus, J. J.; Soletti, L.; Fujimoto, K.; Hong, Y.; Vorp, D. A.; Wagner, W. R. Biomaterials 2007, 28, 2738.
3. Stankus, J. J.; Guan, J.; Fujimoto, K.; Wagner, W. R. Biomaterials 2006, 27, 735.
4. Sanders, J. E.; Lamont, S. E.; Karchin, A.; Golledge, S. L.; Ratner, B. D. Biomaterials 2005, 26, 813.
5. Tang, Z. G.; Teoh, S. H. Colloid Surf B 2000, 19, 19.
6. Chattopadhyay, D. K.; Raju, K. V. S. N. Prog Polym Sci 2007, 32, 352.
7. Vepari, C.; Kaplan, D. L. Prog Polym Sci 2007, 32, 991.
8. Lee, K. H.; Baek, D. H.; Ki, C. S.; Park, Y. H. Int J Biol Macromol 2007, 41, 168.
9. Petrini, P.; Parolari, C.; Tanzi, M. C. J Mater Sci Mater M 2001, 12, 849.
10. Tsujino, M.; Isobe, T.; Senna, M. J. Sol–Gel Sci Technol 2000, 19, 785.
11. Marsano, E.; Corsini, P.; Arosio, C.; Boschi, A.; Morminoc, M.; Freddi, G. Int J Biol Macromol 2005, 37, 179.
12. Ki, C. S.; Kim, J. W.; Oh, H. J.; Lee, K. H.; Park, Y. H. Int J Biol Macromol 2007, 41, 346.
13. Ki, C. S.; Lee, K. H.; Baek, D. H.; Hattori, M.; Um, I. C.; Ihm, D. W.; Park, Y. H. J Appl Polym Sci 2007, 105, 1605.
14. Corsini, P.; Perez-Rigueiro, J.; Guinea, G. V.; Plaza, G. R.; Elices, M.; Marsano, E.; Carnasciali, M. M.; Freddi, G. J Polym Sci B 2007, 45, 2568.
15. Pérez-Rigueiro, J.; Viney, C.; Llorca, J.; Elices, M. J Appl Polym Sci 2000, 75, 1270.
16. Yang, M. Y.; Yamauchi, K.; Kurokawa, M.; Asakura, T. Tissue Eng 2007, 13, 2941.
17. Taddei, P.; Asakura, T.; Yao, J. M.; Monti, P. Biopolymers 2004, 75, 314.
18. Smeenk, J. M.; Ayres, L.; Stunnenberg, H. G.; Van Hest, J. C. M. Macromol Symp 2005, 225, 1.
19. Yao, J.; Xiao, D.; Chen, X.; Zhou, P.; Yu, T.; Shao, Z. Macromolecules 2003, 36, 7508.
20. Kielty, C. M.; Stephan, S.; Sherratt, M. J.; Williamson, M.; Shuttleworth, C. A. Philos Trans Roy Soc B 2007, 362, 1293.
21. Kavlock, K. D.; Pechar, T. W.; Hollinger, J. O.; Guelcher, S. A.; Goldstein, A. S. Acta Biomaterialia 2007, 3, 475.
22. Li, Y.; Xu, W. L. U.S. Pat. 7,000,858B2 (2006).
23. Zhao, C.; Asakura, T. Prog Nucl Mag Res SP 2004, 39, 301.
24. Jin, H.; Kaplan, D. L. Nature 2003, 424, 1057.
25. Zuo, B.; Dai, L.; Wu, Z. J Mater Sci 2006, 41, 3357.