



Flexible nanofibers-reinforced silk fibroin films plasticized by glycerol

Xiufang Li^a, Huijie Zhang^b, Lei He^a, Zhen Chen^c, Ziqi Tan^a, Renchuan You^{a,b,*}, Dong Wang^{a,**}

^a Hubei Key Laboratory of Advanced Textile Materials & Application, School of Materials Science and Engineering, Wuhan Textile University, Wuhan 430200, China

^b State Key Laboratory of New Textile Materials and Advanced Processing Technology, School of Textile Science and Engineering, Wuhan Textile University, Wuhan 430200, China

^c College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, China

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ABSTRACT

The difficulty of dispersing nanofillers and the insufficient of flexibility remains major obstacle to the expansion of nanocomposite applications. In this study, silk fibroin (SF) based nanocomposite materials were obtained using glycerol plasticized SF as the matrix and short polymer nanofibers as the reinforcing phase. Highly flexible SF films with silk I structure were fabricated by using glycerol as a plasticizer. More importantly, plasticizer glycerol significantly improved the homogeneous dispersion of short PVA-co-PE nanofibers in SF films through interfacial interactions, forming flexible and robust nanofiber-reinforced composite films. FTIR and XRD results showed that no significant change was found on secondary structure and crystal structure of SF protein after adding PVA-co-PE nanofibers. It was found that nanofiber content showed significant influence on the mechanical behavior of nanocomposite films, where the addition of 5–10% short PVA-co-PE nanofibers is preferred for achieving enhanced flexibility and strength. This study provides new options for the fabrication of robust and flexible SF nanocomposites for functional applications.

1. Introduction

Polymer nanocomposites have drawn a great deal of interest in recent years because these materials possess high potential to achieve great property improvement by adding a small amount of nanoscale reinforcements in the polymer matrices [1,2]. Silk is a natural biopolymer extracted from *Bombyx mori* silkworm. As a functional material, the applications of silk-based materials have been extended from traditional textile materials to different fields in high-technology directions, such as biomedicine, photonics, and electronics, because of its excellent biocompatibility, tunable degradability, and all aqueous processing [3–6]. To meet these requirements, the use of nanoscale reinforcements is often required for to improving the mechanical properties and other functionality [7–9].

Silk fibers can be processed into aqueous silk fibroin (SF) solution for subsequent formation of various material formats, such as films, sponges and gels [10]. SF protein can form densely packed β -sheets when treated with organic solvents like methanol, which makes the material water-insoluble, but very brittle and rigid when dry [11–13]. The use of nanofillers often showed a higher tensile strength and modulus but nearly no increase in the elongation at break in the

resulting nanocomposites. To meet the requirements of flexible devices, the polymer nanocomposites with excellent flexibility are desired [14,15]. To overcome these inherent drawbacks, the use of plasticizers such as glycerol showed a significant improvement for the ductility of SF film [12,13]. Glycerol can induce structural changes, resulting in increased crystallinity, yet the resulting materials are generally softer and highly flexible. The ability of glycerol plasticization to induce crystallinity and insolubility provides options for the fabrication of soft, flexible, biodegradable and biocompatible SF materials. However, the effect of plasticizer on SF nanocomposites has not been investigated in detail.

On the other hand, the properties of polymer nanocomposites not only depend on the intrinsic properties of the reinforcements, but also on the distribution of the reinforcements [16,17]. The mechanical property and functionalized efficiency of same composites can be variable depending upon the dispersion and interaction of nanofillers with the polymer matrix. Therefore, the poor dispersion of nanoscale additives in polymer matrix is often a significant barrier. The glycerol has been shown to reduce phase separation between SF protein and synthetic polymers such as PVA in the SF matrix [18]. However, it is unclear whether glycerol plasticization influences the dispersion of

* Corresponding author. State Key Laboratory of New Textile Materials and Advanced Processing Technology, School of Textile Science and Engineering, Wuhan Textile University, Wuhan 430200, China.

** Corresponding author.

E-mail addresses: youchuan1182@126.com (R. You), wangdon08@126.com (D. Wang).

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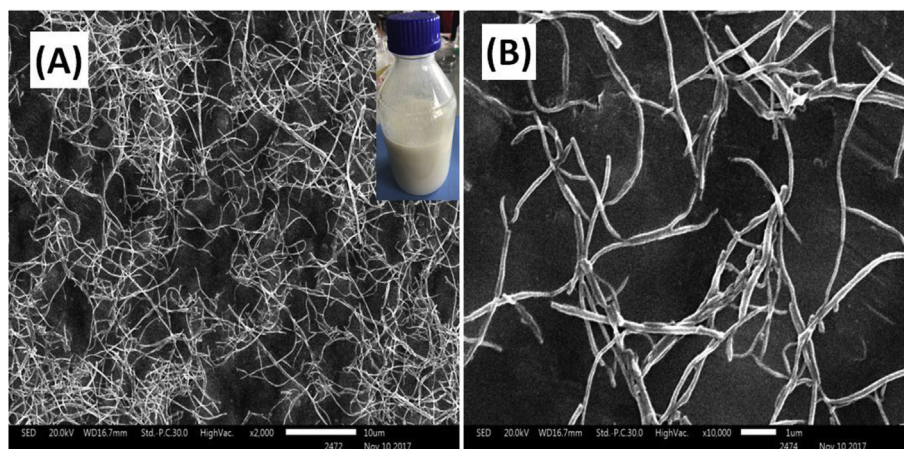


Fig. 1. (A, B) SEM images of short PVA-co-PE nanofibers. Inset is the photograph of dispersions of short nanofibers in water. Scale bars: (A) 10 μm , (B) 1 μm .

nanoscale polymer reinforcements in SF films.

Recently, polymer nanofibers produced by electrospinning or sea-island spinning have been attracting more and more attention for the preparation of nanofibers-reinforced composites [19–22]. In the present study, the flexible poly (vinyl alcohol-co-ethylene) (PVA-co-PE) nanofibers-reinforced SF films plasticized by glycerol were prepared. In the search for an elegant strategy that would eliminate dispersion and flexibility barriers but would still enable the use of polymer nanofibers as reinforcement, we investigated the effect of glycerol on short PVA-co-PE nanofibers reinforced SF films.

2. Experimental procedures

2.1. SF purification

Bombyx mori raw silk fibers (Huzhou, China) were boiled three times in a 0.05% Na_2CO_3 solution for 30 min to remove sericin and dried at 60 $^\circ\text{C}$ after thorough rinsing. The degummed fibroin was dissolved in 9.3 M LiBr solution at 60 ± 2 $^\circ\text{C}$ for 1 h. Regenerated SF solution was obtained after dialysis (MWCO 9–14 kDa) in deionized water for 3 days.

2.2. Preparation of short PVA-co-PE nanofibers

PVA-co-PE nanofibers with diameter of 100–300 nm were prepared via direct melt extrusion of immiscible blends of the corresponding thermoplastic polymer with cellulose acetate butyrate (CAB) respectively and subsequent extraction removal of CAB according to our previous studies [23]. The PVA-co-PE nanofibers were fragmented using a high speed shear mixer. In brief, the nanofibers were dispersed in aqueous alcohol solution, and then fragmented (shear speed, 10,000 rpm) to form short nanofibers suspension. The suspension was centrifuged at 10,000 rpm and washed three times with deionized water. 100 μL of suspension was dropped on conductive adhesive tape and observed using a scanning electron microscope (SEM, JSM-6510L) after air-drying and gold sputtering. The size analysis of the short nanofibers was calculated by measuring the diameters and lengths of 100 different nanofibers in SEM images. The fragmented nanofibers were lyophilized and re-dispersed in deionized water before using.

2.3. Preparation of nanofibers-reinforced SF nanocomposites

5 g short PVA-co-PE nanofibers powder was resuspended in 50 ml deionized water using an ultrasonic cell disruptor with an energy output of 200 W for 3 min (working for 3 s with intervals of 3 s). 15 ml of glycerol solution (10 wt%, Sigma-Aldrich) was added into 100 ml of SF solution (4.5 wt%) to obtain SF solution with 30 wt% glycerol after

slow stirring. The nanofibers suspension was added into the SF/glycerol solution dropwise, and then stirred slowly for 30 min to form homogeneous blend solution. Next, a 15 ml blend solution was cast into poly (methyl methacrylate) plate to form nanocomposite films after drying at 25 $^\circ\text{C}$. The final nanofiber contents in the composite films were 0, 5, 10 and 20 wt% relative to the weight of SF, respectively. To investigate the influence of glycerol on nanofiber dispersion, the nanofiber-reinforced composite films without glycerol were used as a control.

2.4. Morphological observation and structural analysis

The surface and fracture-surface of the composite films was observed using a SEM after sputtering with gold. The secondary structure of the films was analyzed by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) on a VERTEX 70 spectrometer (Bruker, Germany). All spectra were taken in the spectral range of $4000 - 400 \text{ cm}^{-1}$ using an accumulation of 64 scans with a resolution of 4 cm^{-1} . Furthermore, x-ray diffraction (XRD) was used to determine the crystal structures of the films using an x-ray diffractometer (D/max 2500, Rigaku, Japan) with $\text{Cu K}\alpha$ radiation at 40 kV and 200 mA.

2.5. Mechanical properties of the composites

The mechanical properties of composite films were measured on a universal tensile testing machine (Instron 5967) at 25 $^\circ\text{C}$ and $50 \pm 5\%$ RH for dried films and for wet films after water soaking. The films were cut as uniform strips with a size of 50 mm \times 10 mm ($n = 5$ for each sample). The gauge length and the drawing speed were preset at 10 mm and 10 mm/min, respectively.

3. Results and discussion

Nanofiber is preferred filler component with high specific surface area. Sea-island spinning is a rapid, high-throughput and controllable technique that can produce nanofibers. In this work, PVA-co-PE nanofibers produced by sea-island spinning were prepared using our previous method [23]. From Fig. 1(a), it can be found that the original PVA-co-PE nanofibers have a diameter of 100–300 nm (average diameter $147.2 \pm 40.5 \text{ nm}$). Fragmentation was performed to obtain shortened nanofibers with a length. With the method of nanofiber cutting reported here, homogeneous dispersion of short PVA-co-PE fibers with fiber length of 5–50 μm (average length $10.5 \pm 4.9 \mu\text{m}$) were obtained (Fig. 1).

The intrinsic van der Waals interactions between additives easily results in agglomeration, and these challenges become even more prominent with high aspect ratio additives like nanofibers (they tend to

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