Modified Silk Sericin Nanoparticles and Nanofibers by Electrospinning

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Introduction

Until now, there is no report on electrospraying and electrospinning of sericin, a good moisturizer and antioxidant [1], because it is easy to form gel in water. On the other hand, there are many reports on electrospinning of silk fibroin. Modification of silk sericin with synthetic polymer can help to generate sericin nanoparticles and nanofibers. In this research work, water soluble biocompatible polymer like polyacrylamide (PAM) is chosen to mix with silk sericin. These mixtures are made into nanoparticles and nanofibers by electrospinning technique.

Experimental

The 10 wt% sericin (SS) and 50 wt% polyacrylamide (PAM) in water were mixed at different ratios, i.e. 10/90, 20/80 and 30/70 SS/PAM, w/w, overnight before electrospinning. Besides, the SS/PAM blend solution was poured into a 9-cm diameter of polyethylene plate at room temperature for 24 h and then placed in a vacuum oven for 24 h. The obtained films were used for characterization by ^{1}H-NMR (BRUKER BIOSPIN AG Switzerland (DPX-300), 300.13 MHz with 99.9% of D_2O solvent) and thermogravimetry analysis (Pyris Diamond TG/DTA) at heating rate of 10 °C/min from ambient to 700 °C with nitrogen purge 200 ml/min.

Electrospinning of Modified Sericin (SS/PAM)

The SS/PAM blend solutions with different mixing ratios were contained in syringe with ID 0.9 mm of a syringe needle. The electrospun SS/PAM was collected on a target which was placed at a distance of 15 cm from the syringe needle. A voltage at 15, 20 and 25 kV was applied to the syringe needle by a high voltage power supply. The morphology of the nanoparticles and nanofibers were observed by JEOL Scanning Electron Microscope (JSM-6400).

Results and Discussion

The aqueous solutions of sericin and PAM were cast into thin sheets for the study of thermal degradation and the results are listed in Table 1. The amino groups of PAM decompose at 294 °C while those of sericin decompose at higher temperature 306 °C. But the mixtures of them show lower degradation temperatures and degraded content together with a new generated high temperature resistance species (521-564 °C) and very low char residue. This suggests that SS and PAM readily interact to form gel, crosslinking structure or higher molecular weight species. When studied by ^{1}H NMR, the chemical shifts of H^{α} and H^{β} PAM and sericin are changed to higher value suggesting that their interactions such as hydrogen bonding were occurred because sericin is full of hydroxyl and amide groups while PAM is polyamino groups [2]. This bonding can be condensed at high temperature.

Effect of electrical power on morphology of the blends

The solution mixtures of SS/PAM were electrospun and the morphology was observed by SEM. Figure 1 is for 10/90 SS/PAM aqueous solution; when the electrical power increases, number of fiber strands increase or denser weaving. These electrospun fibers are nanofibers of 150-300 nm diameters. Not only nanofibers were revealed, but also very tiny white dots (smaller than the nanofibers) of conical shape. These nanoparticles were possibly come from the new generated species of high molecular weight. The interaction could be quite strong to make it rather rigid so when it spun from the tip of the needle, it was stretched tightly and broken into small conical beads. At higher voltage, there is less number of small conical beads.

Effect of concentration on the morphology of the blends

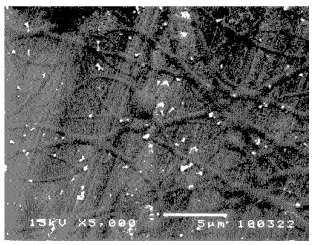
Figure 2 shows that at 25 KV supplied power, pure PAM 50 wt% aqueous solution could be electrospun as non-woven nanofiber mat. When PAM content decreases to 80 wt% or SS content increases to 20 wt%, there is no more fiber found only the nanobeads are generated and the beads become bigger and aggregated as SS concentration increases due to the strong interaction. At the tip of the needle, heat loss could be occurred during electrons flow and the heat was high enough to trigger condensation and make strong covalent bonds or crosslinking. Therefore as SS content increases, spinnability is lost.

Table 1. Temperature degradation and % weight loss of modified sericin by solution blending (SS/PAM)

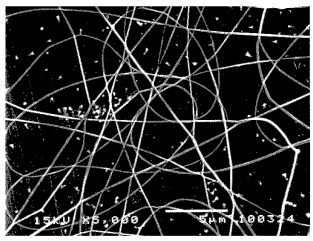
SS/PAM (w/w)	Weight loss transition								% Char
	Water		NH_2 groups		Imide groups		High MW species		
	Td_1 °C	%wt loss	Td_2 °C	%wt loss	Td_3 °C	%wt loss	Td_4 °C	%wt loss	
0/100	70	12.2	294	17.5	343	39.5	-	-	30.8
10/90	<200	9.3	289	17.7	345	30.6	564	39.5	2.9
20/80	<200	11.0	283	15.4	352	27.4	528	40.0	6.2
30/70	<200	15.8	278	14.3	346	27.1	521	34.3	8.5
100/0	70	8.0	Degradation temp. of Sericin 306 °C						27.0

Table 2 ^{1}H-NMR chemical shifts of modified sericin by solution blending (SS/PAM)

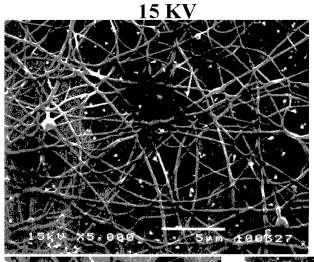
SS/PAM (w/w)	Chemical shift (ppm)			
	Proton of sericin	Proton of PAM		
	Ser β	H^{β}	H^{α}	H^{γ}
0/100	-	1.425	1.978	6.781
10/90	3.633	1.505	2.042	6.761
20/80	3.602	1.504	2.041	6.771
30/70	3.656	1.505	2.059	6.795
100/0	3.633	-	-	-



15 KV

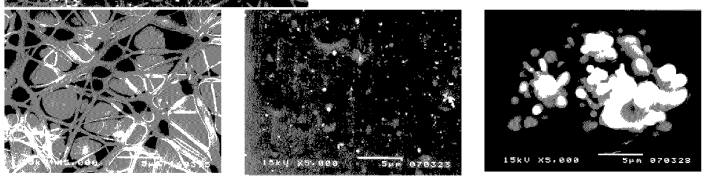


20 KV



25 KV

Figure 1 SEM images (at magnification of 5000 and scale bar = 5 μm) of electrospun 10/90 w/w SS/PAM from solution mixing in water at different power supply 15-25 kV



100% PAM **20/80 w/w SS/PAM** **30/70 w/w SS/PAM**

Figure 2 SEM images at 5,000x of SS/PAM aqueous solution at various concentrations electrospun at 25 KV

Conclusions

Sericin silk protein is mixed well with polyacrylamide in aqueous solution. NMR and thermogravimetry analysis reveal that both components has strong interaction by their functional groups from hydrogen bonding to crosslinking structure. The interaction results in the production of both nanofibers and nanoparticles at low sericin content. At higher Sericin content, the interaction is more intense yielding only nanoparticles and their aggregates without nanofiber.

References

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[2] Wang, Q.; He, L. *Polymer* **1997**, 38, 3931.