Amirkabir Journal of Mechanical Engineering

Amirkabir Journal of Mechanical Engineering, 49(2) (2017) 115-116
DOI:10.22060/ceej.2015.371

Investigation of Coagulant Type Effect on Wet–Spinning Process of Regenerated Silk Fibroin

S. A. Siadat and J. Mokhtari*

Department of Textile Engineering, Faculty of Engineering, University of Guilan, Rasht, Iran

ABSTRACT: Re-generated silk fibroin (RSF) with various concentrations including 8, 10, 12.5 and 13% (w/w), was dissolved in N-methyl morpholine N-oxide (NMMO) to prepare spinning solutions. The effect of several coagulants such as methanol, ethanol and 1-propanol, and temperatures of spinning including 95, 110 and 120 °C, on the wet spinnability of the silk fibroin solutions were investigated. Tenacity at break of undrawn fibers, which were produced by various concentrations and coagulants, were measured. Bead free fibers with high tenacity and elongation at break (1.6 cN/dtex and 34.25% respectively) were produced at concentration of 8% (w/w), temperature of 95 °C and by presenting of methanol coagulant. Also by increasing of concentrations from 8% to 10, 12.5 and 13%, the tenacity was decreased to 0.81, 0.70 and 0.20 cN/dtex, respectively. Tenacity of fibers were obtained in 1-propanol (0.6 cN/dtex) was lower than those in ethanol and methanol coagulation bath, 0.8 and 1.6 cN/dtex, respectively. These results were shown that chemical structure type of coagulant strongly influenced the wet spinnability of undrawn regenerated silk fibers.

Review History:
Received: 16 May 2014
Revised: 22 November 2014
Accepted: 15 April 2015
Available Online: 6 May 2015

Keywords:
Regenerated Silk Fibroin
N - Methyl Morpholine N - Oxide
Coagulants
Wet Spinnability
Tenacity

1- Introduction

Today some silk wastage of Bombyx mori cocoon can be recycled into desirable forms to meet specific biomedical applications. One of the desirable forms is regenerated silk fiber (RSF). For this purpose, aqueous silk fibroin solution can be obtained by using N-methylmorpholin-N-oxide (NMMO) as a solvent. This solvent due to being environmentally friendly and easily recyclable as well as having relatively low melting point allows conducting dissolution of silk fibroin in a reasonably safe temperature range (90-110 °C) [1]. In spite of that, many researchers have used various solvent/coagulant systems to prepare the RSF with similar mechanical properties to natural silk fiber [1-3]. Yoo et al, in 2010 used formic acid solvent for producing RSF and they show that the coagulant type has a decisive role in determining morphology of fibers, also they were expected that the coagulant can be influenced the wet spinnability [3]. However the production of RSF from NMMO solvent alongside different coagulants such as methanol, ethanol and 1-propanol weren't compared with each other until now. In this research, N-methyl morpholin N-oxide (NMMO) was used as a solvent for spinning dope. SF/NMMO dope was spun by using a lab-scale wet spinning line. The mean goal of this study was to investigate the effect of spinning temperature, concentration of spinning dope and coagulation bath on the morphology and tenacity of undrawn RSF.

2- Methodology

For estimating the mechanical properties of RSF; dried wastage cocoon was boiled in aqueous solution of sodium carbonate and then the resulting fibroin was dispersed in a commercial aqueous solution of NMMO/H_2O (50/50, w/w) to form a slurry. In order to obtain the optimum dissolving conditions, dissolution of fibroin in a NMMO monohydrate was performed at 95, 110 and 120°C for 60, 30 and 15 min, respectively. The solutions were stirred at 560 rpm at a constant temperature under a nitrogen atmosphere. Spinning dope with various concentrations including 8, 10, 12.5 and 13% (w/w), was spun by using a syringe and syringe pump and with extruding the dope solution through 18-gauge needle into various coagulation baths including methanol, ethanol and 1-propanol. An extrusion rate was 5.14 ml/min. The wet spun silk filaments were left into the coagulant for 24 h to allow the solvent (NMMO) to diffuse out completely from the filament, and then stored in water for 48 h.

3- Results

The most obvious finding to emerge from this study was that: As the result revealed, re-generated silk fibroin treated with $CaCl_2/H_2O$/EtOH had a molecular weight from about 127 to nearly 261 kDa. This observation is in good accordance with findings by previous studies from Zhang and et al [4]. Fourier-transform infrared (FTIR) spectroscopy was performed for re-generated fibroin and degummed silk. In re-generated fibroin vibration bands around 1650 cm^{-1}, 1544 and 1228 cm^{-1} correspond to amide I, II and III bands, respectively. All these characteristic absorbance peaks indicated the existence of a hydrogen-bonded NH group and α-helix conformations of re-generated silk fibroin. The absorption bands at 1637, 1520 and 1135 cm^{-1} in degummed silk which correspond to amide

*Corresponding author, Email: j.mokhtari@guilan.ac.ir

I, II and III bands, respectively, confirms that the degummed silk was mainly in β-sheet conformation. This observation is corresponding with finding of other workers [4, 5].

Thermal decomposition peak of re-generated silk fibroin and fibers were shifted to a lower temperature than the native silk fiber, to about 314.5 and 277.7 °C, respectively. This was indicated the lower thermal stability of re-generated samples. Also low thermal stability can be caused to decrease molecular weight and crystallinity of fibers during the degumming and re-generating process. Viscosity of spinning dope was decreased as temperature increased; spinning dope of 8% (w/w) had viscosity near to 0.55 Pa s.

Optimum temperature for fibroin dissolution was set at 95 °C. At this temperature, silk fibroin was slowly dissolved and prevented from the destruction of its structure and also the color of the spinning dope was changed to yellowish.

By increasing in percentage of dope concentrations, specific stress of samples is decreases. According to this tip and from the results shown in Figures 1 and 2, it is obvious that dope concentration of 8% (w/w) and methanol coagulant provided stronger undrawn fibers with high specific stress and elongation at break, 1.60 ±0.35 cN/dtex and 34.25% ±0.50 , repeatedly. The resulted fibers in the methanol bath were so strong due to less bead formation [3]. Also, with an increase of R group size of alcohol (R-OH) the coagulation rate of silk dope solution is reduced [3].

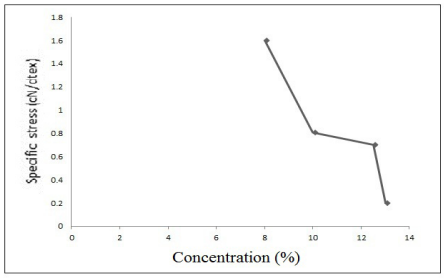

Figure 1: Comparison of tenacity versus spinning dope concentrations (in methanol coagulation bath).

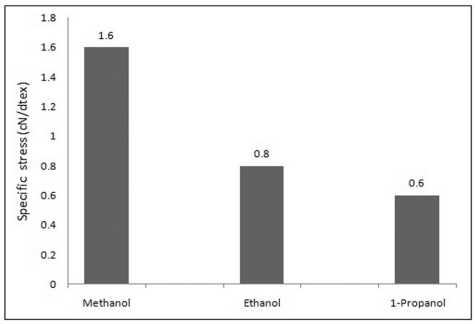

Figure 2: Comparison of tenacity versus several coagulation baths (in spinning dope concentration of 8% (w/w)).

According to Figure 3, silk fibers were prepared in methanol coagulant clearly showed a uniform and homogeneously structure, this means when spinning dope extruded into the coagulation bath, a solid skin formed rapidly, which prevented the penetration of coagulant into fibers.

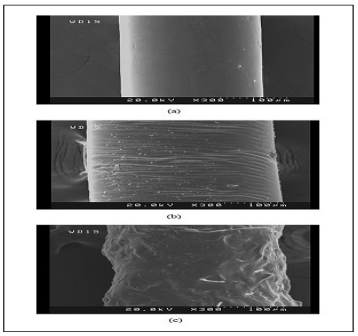

Figure 3: FE-SEM images of RSF subjected to dope concentration of 8% (W/W) and in several coagulation baths: (a) Methanol, (b) Ethanol and (c) 1-Propanol.

4- Conclusion

Undrawn silk fibers showed the mechanical behavior typical of a brittle material. However with changing the spinning condition, the mechanical properties can be improved. Dope concentration of 8% (w/w) with methanol coagulation bath have been introduced as the most appropriate condition for producing strongest undrawn fibers in compered with other conditions process.

References

[1] E. Marsano, P. Corsini, C. Arosio, A. Boschi, M. Mormino, G. Freddi, Wet spinning of Bombyx mori silk fibroin dissolved in N-methyl morpholine N-oxide and properties of regenerated fibres, International Journal of Biological Macromolecules, 37(4) (2005) 179-188.

[2] Y. Xu, Y. Zhang, H. Shao, X. Hu, Solubility and rheological behavior of silk fibroin (Bombyx mori) in N-methyl morpholine N-oxide, International Journal of Biological Macromolecules, 35(3) (2005) 155-161.

[3] Y.-J.K. Yoo, Ung-Jin; Um, In-Chul, The Effect of Coagulant and Molecular Weight on the Wet Spinnability of Regenerated Silk Fibroin solution, International Journal of Industrial Entomology, 21(1) (2010) 145-150.

[4] H. Zhang, L.-l. Li, F.-y. Dai, H.-h. Zhang, B. Ni, W. Zhou, X. Yang, Y.-z. Wu, Preparation and characterization of silk fibroin as a biomaterial with potential for drug delivery, Journal of Translational Medicine, 10(1) (2012) 117.

[5] A. Gholami, H. Tavanai, A.R. Moradi, Production of fibroin nanopowder through electrospraying, Journal of Nanoparticle Research, 13(5) (2011) 2089-2098.

Please cite this article using:

S. A. Siadat, J. Mokhtari, " Investigation of Coagulant Type Effect on Wet–Spinning Process of Regenerated Silk Fibroin". *Amirkabir J.Civil Eng.,* 49 (2) (2017) 115-116.

DOI:10.22060/ceej.2015.371