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Study on the Properties and Structure of Nano-TiO_2 Modified Silk Fibroin Films

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Abstract

A kind of regenerated Silk Fibroin (SF), nano-blended membrane, was made using an ionic liquid as a solvent. The membranes were characterized by SEM, XRD, FTIR, TG. The SEM showed that more agglomerations were observed with the increase of blended nano-TiO_2 (TD). XRD and FTIR verified that nano-TD made conformational changes in SF membrane and the conformation changes from random coil or Silk I into Silk II with the increase of nano TD. The TG analysis showed that pure silk fibroin membrane and nano TD membranes had only one apparent thermal transition region, at about 300℃. Based on the mechanical performance test of SF membranes, tensile strength obviously increased when the amount of nano TD increased, which indicated that the mechanical strength improved with the addition of certain amount of nano TD.

Keywords: Silk Fibroin; Titanium Dioxide; Membrane

1 Introduction

Silkworm silk, namely silk produced by *Bombyx mori*, has been studied extensively because of its long (at least 5000-year) history and use as a source of textile-grade fibers [1]. To date, with the development of science and technology, silk has received increased interest in non-apparel area due to the good biocompatibility and oxygen permeability of its main component—silk fibroin (SF). After dissolution in proper solvents, fibroin can be processed to obtain powder, fibers, films and other types of materials.

The SF, a kind of natural polymer fibrin, accounts for about 70%-80% of the silk. It contains 18 kinds of amino acids, among which glycin, alanine, and serine constitute above 80%. Fibroin contains outstanding mechanical, physical and chemical properties, such as good flexibility, high strength, good breathable moisture permeability, slow release ability [2-4]. In addition, various forms including fiber, solution, power, membrane, gel could obtain through different treatments [5-7].

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In this study, silk spun by Bombyx mori was dissolved in 1-methylallyl-3-methylimidazolium chloride ([(MA)MIM]Cl) and then regenerated by distilled water. Pure SF membrane is easily soluble in water. This limits the applications of SF membranes. However, the current general method has been made to modify the solubility by treating the regenerated membrane with ethanol or methanol [8, 9], the SF membrane treated by alcohol is brittle. Based on this point, we added polyvinyl alcohol (PVA) into the SF solution [10], and prepared a novel nanometer titanium dioxide (nano TD)/SF blend membrane by gel, in this paper we report on the properties and structure of this novel SF membrane.

2 Experimental Section

2.1 Materials

The materials used in experiment are listed in Table 1.

Table 1: The materials are used in experiment

Instruments and Reagents	Manufacturer
KQ-100DB NC Ultrasonic Cleaner	Kunshan Ultrasonic Instrument Co., Ltd.
DF-101S Constant temperature magnetic stirrer	Zhengzhou Great Wall Industry and Trade Co., Ltd.
FA(N)/JA(N) Electronic Analytical Balance	Shanghai Minqiao precise science Instrument co., Ltd
DZF-6050 Vacuum oven	Shanghai yiheng Scientific Instrument Co., Ltd.
RE-52A Rotary evaporator	Shanghai Yarong Biochemical Instrument Factory
SHZ-D(III) Water circulation pump	Henan Yuhua Instrument Co., Ltd.
JSM-6360LV Scanning electron microscopy	Japan Electronics Co., Ltd.
Nicolet FT-IR 200 Infrared spectrometer	Thermo Scientific Instruments Company
X'Pert MDP X-ray powder diffraction	Rigaku Electric Co., Ltd.
PRT-1A Thermogravimetric analyzer	Beijing Boyuan Precision Technology Development Co., Ltd.
Universal testing machineInstron	Instron Test Equipment Co., Ltd.
Dialysis bag (27MD: 8000-14400)	Beijing solarbio Technology Co., Ltd.
nano TD (TiO_2)	Beijing Entrepreneur Science & Trading Co., Ltd.
Ethanol(CP)	Beijing Hengtong Chemical Company

2.2 Preparation of SF Membrane

2.2.1 The Dissolution and Dialysis of Silk and the Recovery of Ionic Liquid

Silk (3g) was added into 150ml [(MA) MIM] Cl, and incubated in an oil bath at 90℃ for 4.5 hrs. And then the liquid was cooled to room temperature, the SF was regenerated by adding ethanol into the solution. After that, the SF flocs were collected by a vacuum filtration, followed by a thorough drying/washing with distilled water. After dialyzing for 24 hrs, pure SF solution was obtained. In addition, evaporating the filtrate through a rotary evaporator, the recovery [(MA)MIM]Cl was left. And the recovery rate was approximately 68.7%.