Applied Surface Science 268 (2013) 92–97

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Structure and properties of silk grafted with acrylate fluoride monomers by ATRP

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ARTICLE INFO

Article history:
Received 26 October 2012
Received in revised form
29 November 2012
Accepted 30 November 2012
Available online 20 December 2012

Keywords:
Silk fiber
ATRP
Grafting
Acrylate fluoride
Water repellence
Structure
Properties

ABSTRACT

In order to develop water repellence silk materials, silk was grafted using acrylate fluoride monomers via atom transfer radical polymerization (ATRP) method. Scanning electron microscopy (SEM) photos of the grafted silks showed significant difference from the untreated silk. FT-IR characterization of the modified silk substrate indicated that acrylate fluoride monomers were successfully grafted onto silk surface. Differential scanning calorimetry (DSC) curves indicated that the thermal stability of the grafted silk was improved. The whiteness, breaking strength, elongation at break and air permeability of the grafted silk fabrics decreased slightly compared with the control sample. Surface contact angle test and water repellency rating test showed that the water repellence of the modified silk fabrics were better than the untreated silk. Functional silk fabric with good water repellence property could be obtained by properly controlling the grafting yield, which had little effect on the intrinsic properties of silk fabric.
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1. Introduction

Silk is a kind of natural protein fiber. It is widely used in textile field because of its outstanding mechanical strength, luster and wearability, and is praised as the queen of fibers [1]. However, silk also has many shortcomings, such as wrinkle resistance, easy to yellow, poor color fastness, which seriously affect the use of silk and make its application scope limited. With the rapid development of new synthetic fibers and a variety of man-made fibers appear ceaselessly, silk application prospect is facing enormous challenges. With the progress of the times, people for the requirement of silk dress is higher, even hope that also do not affect its dressing in the fog weather [2,3]. Accordingly, it is important for silk to gain the water repellence property, which can improve the added value of silk fibers [4,5].

Water repellence finishing of silk fabric commonly has four methods. The first kind of method is padding or impregnation process, which is the most common method of water repellence finishing. The second kind of method is coating finishing. It coats or bonds a layer of polymer material on the surface of silk fabric. The third kind of method is chemical grafting, which make hydrophobic group and reactive group of modified fiber form covalent bonds. The four kind of method is nanotechnology and it bases on lotus effect principle [6,7]. Although the processing cost is low, water repellence of padding or impregnation finishing is poor. Chemical reactions of silk fiber and other chemical substances occur on the active groups of the silk proteins amorphous regions. Adopt chemical grafting method to improve water repellence of silk fabric is relatively rational method [8,9].

Living/controlled free radical polymerization is an alternative technique to prepare polymers with predictable molecular weight, narrow polydispersity and well-defined architecture [10]. Atom transfer radical polymerization (ATRP) is the most powerful, versatile, simple and inexpensive method in living/controlled free radical polymerization [11–13].

In order to obtain silk with water repellence property, in this work, silk was grafted with three fluorinated monomers through ATRP in water aqueous. During the copolymerization, CuBr was used as catalyst, N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA) was used as ligand. The structure and properties of the grafted silk was also investigated.

2. Experimental

2.1. Materials and reagents

Degummed silk fabrics i.e. Silk fabrics (plain woven, 43 g/m^2) were supplied by Suzhou Huasi Silk Printing & Dyeing Co., Ltd. (Suzhou, Jiangsu Province, China). Trifluoroethyl methacrylate

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http://dx.doi.org/10.1016/j.apsusc.2012.11.173

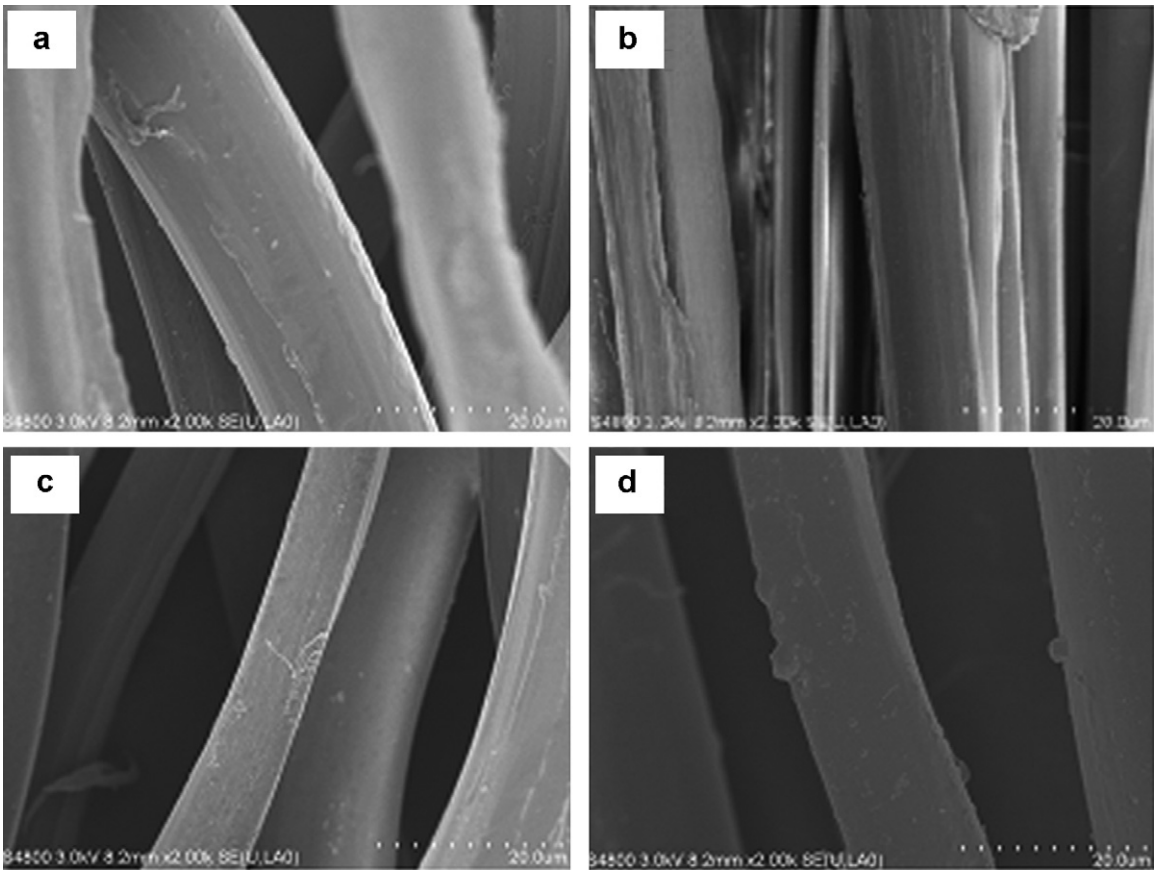

Fig. 1. SEM images of silk with different grafting yields.

(TFEMA), Hexafluorobutyl methacrylate (HFMA), dodecafluoroheptyl methacrylate (DFHMA) were purchased from Harbin Xeogia Fluorine-Silicon Chemical Company. Triethylamine (TEA) and tetrahydrofuran (THF) were dried by CaH_2 overnight, and then distilled under reduced pressure before use. CuBr, N,N,N′,N″,N″-pentamethyldiethylene triamine (PMDETA) and 4-(dimethylamino) pyridine (DMAP) were used as received. 2-Bromoisobutyryl bromide (BriB-Br) (98%, Alfa Aesar) and all other reagents were used without further purification.

2.2. Grafting procedure

1 g silk fabric with a certain amount of tetrahydrofuran (THF) after cleaning in vacuum drying oven drying 60 °C 2 h, placed in the dryer cooling 30 min. Silk macroinitiator (Silk-Br) was prepared by reacting BriB-Br with the amino groups and hydroxyl groups present on silk in the presence of TEA and DMAP catalysis at 50 °C. Typically: 50 mL dry THF, 1.23 mL of TEA and 0.5 g of DMAP was mixed in a 100 mL round bottom flasks under oscillating. The flask was cooled down to 10 °C and 2.22 mL of BriB-Br was added into the flask. And then 1 g of dried silk fabric was added into the mixed solution. The reaction mixture was stirred at 10 °C for 1 h, then left to warm up to 50 °C and reacted for 24 h. The silk sample was thereafter thoroughly washed with THF, then water and finally dried at 60 °C in vacuum oven. Thus the Silk-Br macroinitiator was prepared. The emulsifier FSO and tween60 (FSO 20%, tween60 30%) were dissolved in a certain amount of water and stirred with the emulsified machine a minute, then adding the required fluorinated monomers by dropping. The grafting was accomplished by immersing the silk macroinitiator into the reaction mixture containing certain amount of emulsified fluorinated monomer, CuBr/PMDETA and deionized water in a 100 mL round-bottom flask. After sealing it with a three-way stopcock, the flask was evacuated and back-filled with nitrogen, which was repeated three times. The mixture was placed in water bath and polymerized under oscillating at certain temperature for some time. After the polymerization was completed, the sample was subjected to intense washing in hydrochloric acid, acetone and water to reach constant weight, and then dried under a vacuum oven. Thus silk grafted fluorinated monomers sample was obtained. The grafting condition was as follows: HFMA: pH = 9, n(PMDETA):n(CuBr) = 2:1, reaction time 150 min, reaction temperature 80 °C, monomer concentration 125% (o.w.f), the concentration of catalyst CuBr 0.37 mmol/L; TFEMA: pH = 8, n(PMDETA):n(CuBr) = 1.5:1, reaction time 120 min, reaction temperature 90 °C, monomer concentration 150% (o.w.f), the concentration of catalyst CuBr 0.32 mmol/L; DFHMA: pH = 9, n(PMDETA):n(CuBr) = 1.5:1, reaction time 120 min, reaction temperature 90 °C, monomer concentration 150% (o.w.f), the concentration of catalyst CuBr 0.42 mmol/L; liquor ratio 1:50.

The graft yield was calculated as:

Graft yield (%) = $(w_2 - w_1)/w_1$ where w_1 and w_2 denote the weight of S-Br (silk macroinitiator) and S-g-fluorinated monomers, respectively.

2.3. Characterization and measurements

The surface of the grafted and control sample was examined, after gold coating, with a Hitachi S-4700 scanning electron microscope (SEM) at acceleration voltage of 15 kV.

The infrared spectra of silk fabric were recorded on a Nicolet5700 FTIR equipped with a single reflection ATR system.

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