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Environmentally friendly surface modification of silk fiber: Chitosan grafting and dyeing

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ABSTRACT

In this paper, the surface modification of silk fiber using anhydrides to graft the polysaccharide chitosan and dyeing ability of the grafted silk were studied. Silk fiber was degummed and acylated with two anhydrides, succinic anhydride (SA) and phthalic anhydride (PA), in different solvents (dimethyl sulfoxide (DMSO) and *N*,*N*-dimethyl formamide (DMF)). The effects of anhydrides, solvents, anhydride concentration, liquor ratio (L:R) and reaction time on acylation of silk were studied. The polysaccharide chitosan was grafted to the acylated silk fiber and dyed by acid dye (Acid Black NB.B). The effects of pH, chitosan concentration, and reaction time on chitosan grafting of acylated silk were investigated. The physical properties show sensible changes regardless of weight gain. Scanning electron microscopy (SEM) analysis showed the presence of foreign materials firmly attached to the surface of silk. FTIR spectroscopy provided evidence that chitosan was grafted onto the acylated silk through the formation of new covalent bonds. The dyeing of the chitosan grafted-acylated silk fiber indicated the higher dye ability in comparison to the acylated and degummed silk samples. The mechanism of chitosan grafting over degummed silk through anhydride linkage was proposed. The findings of this research support the potential production of new environmentally friendly textile fibers. It is worthwhile to mention that the grafted samples have antibacterial potential due to the antibacterial property of chitosan molecules.

1. Introduction

The dyeing capability of natural polymers is an important concern. The discharge of colored textile wastewater into natural streams has caused many significant problems, such as increasing the toxicity and COD (chemical oxygen demand) of the effluent, and reducing the light penetration, which has a derogatory effect on photosynthetic phenomenon. Several methods are used to treat the textile wastewater such as nanophotocatalysis, adsorption, etc. [1–13]. The remediation of textile effluents is still far away to satisfactory. Consequently, the increased public concern and the tighter international regulation have challenged the scientists to explore new lines to reduce environmental problems associated with textile industry [14].

Biotechnological tools appear an emerging technology to create a new range of high performing, environmental friendly processes, and materials for traditional and innovative applications by surface modification of natural polymers [15–17]. Silk is a natural polymer, which possesses especial properties such as luminosity, thermo-insulating, and adaptation to skin. In order to achieve these desirable properties, it is necessary to separate, the sericine of silk from the fibroin [18]. Recently, natural polymers are attracted the attention of the researchers because of their availability of resources, cost, easy handling and minimum damage to the environment. In addition, they have unique properties such as being non-toxic, having biological degradability and adaptation to nature [19]. In recent years, attempts have been made to make use of natural polymers such as chitin, alginate and silk by surface modification to improve their properties [17,20–25]. Chitosan grafting on silk has been successfully carried out by enzymatic reactions in solution [17,21].

To our knowledge, there is not a reported research paper dealing with the grafting of chitosan on silk fiber using anhydrides. Silk was acylated and then grafting of chitosan was done. This study aims to investigate the feasibility of silk fiber weighting by grafting the chitosan (natural polymer) using anhydrides as a linkage. The dyeing capability of all samples (degummed, acylated,

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acylated-grafted silk samples) with acidic dye was studied. In addition, attempts were done to propose a grafting mechanism for this process based on the finding of this study.

2. Materials and methods

Ten-folded raw Persian silk yarn (63 6 6.7 Tex and 240 twists per meter) was obtained from Guilan Silk Co. (Rasht, Iran). Chitosan was provided by Kitotak Co. (degree of deacytilation (DD): 85%, MW: 1000 kDa, Iran). Acid Black NB.B was achieved from Alvan Sabet Co. (Iran). All other chemicals were laboratory-grade (analytical reagents, Merck).

An Ahiba 1000 dyeing instrument (Denver, CO) was used for silk degumming.

Mechanical properties of the yarn were measured by an Instron 5566 (Applied Science Co., Ithaca, NY) at 25 °C and 50% relative humidity at a gauge length of 100 mm and strain rate of 40 mm/min.

Scanning electron microscopy (SEM) micrographs of the samples were prepared with a Leo 1455VP scanning electron microscope (Cambridge, England).

FTIR spectra were recorded on a Nicolet Nexus670 instrument. The colorimetric data of the dyeing were obtained using a Gretag MacBeth 7000A spectrophotometer (D65 illumination, 10° observers).

Moisture regain was determined using Sartorius Moisture Analyser A50–IR model. Moisture regain was determined on dried samples at 20 °C and 65% relative humidity for 7 days and expressed as grams of moisture/100 g silk fiber [26].

The fiber weight gain was calculated from the difference in weight of the silk fiber before and after chemical reaction [26].

Silk degumming was performed using raw silk yarn. Silk yarns were treated with 1.5 g/L Marseille soap, 0.5 g/L sodium carbonate, and silvatol (anionic surfactant) at 70–75 °C for 15 min and dried.

Degummed silk fibers were acylated with 100 mg/L succinic anhydride (SA) and phthalic anhydride (PA) in *N*,*N*-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO), at 75 °C for 5 h. The reaction system was connected to a reflux condenser and held at constant temperature in a thermostatic bath. The liquor ratio (L:R) 20:1 was maintained. At the end of the reaction, the fiber samples were washed with DMF or DMSO and then with acetone at 55 °C for 1 h to remove unreacted anhydride. Finally, it was rinsed with water [27]. The effects of anhydrides (SA and PA), solvents (DMF and DMSO), anhydride concentration (20, 40, 60, 100, 200 and 300 g/L), liquor ratio (20:1, 30:1 and 40:1) and reaction time (0.5, 1, 3, 5 and 7 h) on acylation of silk were studied.

The grafting of chitosan (DD: 85%) to the acylated silk samples were carried out in acetic acid media. Fiber weight gain was calculated from the difference in weight of the acylated silk fabric before and after the grafting reaction. The effects of pH (2, 4 and 7), acylated succinic anhydride concentration (0, 40, 60, 100, 200 and 300 mg/L), chitosan concentration (1, 2 and 4 g in 100 mL acetic acid 4%), and reaction time (8, 24, 48 and 72 h) on chitosan grafting of acylated silk were investigated. The physical properties of the chitosan grafted-acylated silk were investigated. In addition, dyeing of substrate was carried out using a liquor ratio of 20:1, pH 4.5 (acetic acid), 2% o.w.f. at 80–90 °C for 45 min in dyeing bath. Then Globar salt (2% o.w.f.) was added and dyeing was continued for 15 min. At the end of dyeing, the substrate was rinsed and dried.

The measurements of mechanical properties, moisture regain and fiber weight gain, etc. were carried out five times. The reproducibility of these tests, calculated as relative standard deviation, was acceptable $\leq$4%.

3. Results and discussion

3.1. Acylation of the degummed silk

The effects of solvents, anhydrides, liquor ratio, anhydride concentration and reaction time on acylation of silk were studied.

3.1.1. Solvents and anhydrides

The chemical modification of silk fibers with succinic and phthalic anhydrides in two dipolar aprotic solvents (DMF and DMSO) was evaluated based on weight gain of silk fibers. Table 1 shows the weight gain of silk by acylation using SA and PA (100 g/L), at 75 °C, L:R 20:1, for 5 h, as determined from the weight increase of the fibers.

Silk fibers attained weight gain values regardless of the solvent (DMF or DMSO) and anhydride (SA or PA) used. Fibers consist of a highly oriented fibrous texture, with fibroin chains held together by a dense network of inter-chain hydrogen bonds, not only in the crystalline regions but also in the amorphous regions. This limits the extent of longitudinal and transversal swelling when they are heated in a solvent [28,29]. The effect of the solvent on the reaction yield was in the following order: DMSO > DMF. The behavior of the two dipolar aprotic solvents is in good agreement with previously reported results [27,29,30]. The reaction yield increase by DMSO might be due to its ability on swelling property in comparison to the DMF. Thus reagent diffusion occurred more efficiently and the reaction kinetics were faster [29,31]. Accordingly, the reaction yield attained higher values. The reactivity of different anhydrides depends on both morphological and steric factors of the fibrous substrate, as well as on chemical factors related to the characteristics of the anhydride substitute [32]. In fact, it has been demonstrated that the bulkier side chain caused the lower reactivity, while the presence of electronegative groups usually enhances the rate of reaction. The higher reactivity of PA anhydride in DMSO toward silk (Table 1) can be attributed to the easier diffusion of chemical and solvent toward the available reactive sites. The color of acylated silk fiber with SA and PA in DMSO changed to yellowish. In addition, the silk fiber was damaged. So, the acylation of silk with SA in DMF were used for further investigation.

3.1.2. Liquor ratio

Water is a valuable material in the textile industry, and a large volume of effluent is produced and it causes serious environmental problems. In this respect, optimizing the liquor ratio is an important factor for the silk acylation process, and by optimizing this factor, considerable amounts of energy and chemicals are saved. To study the effect of L:R ratio, samples were treated at different L:R ratios (20:1, 30:1 and 40:1) at 75 °C, SA: 100 g/L, and 5 h. The silk weight gain percent for different L:R ratios, 20:1, 30:1 and 40:1, were 8.8, 7.9 and 8.7%, respectively. The results showed that the weight gain did not change significantly with an increase in L:R ratios. Thus the best L:R was 20:1. The negligible difference in weight gain yield at different L:R ratios might be the result of saturation of the silk with succinic anhydride by acylation of silk filaments.

Table 1
The effect of anhydrides and solvents on silk weight gain (SA or PA: 100 g/L, at 75 °C, L:R 20:1, 5 h).

Anhydrides and solvents	Weight gain values (%)
SA in DMF	8.7
SA in DMSO	11.9
PA in DMF	7.7
PA in DMSO	15