Journal of Applied Polymer Science

Eco-Friendly Grafting of Natural Biopolymer Chitosan onto Acylated Wool Fabrics Using Ultrasonic and Study Its Properties

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ABSTRACT: The use of ultrasonic for accelerating the chemical and physical processes of wool has gained high importance. This study aims to develop a method for reducing the energy and material consumption and decreasing fiber damage. Ultrasonic equipment (20 kHz) was used for grafting chitosan to wool fabric. Experiments were carried out under different times and chitosan concentration. The results showed using this technique decreases the time required for grafting chitosan onto wool which is less than the other procedures. Differential scanning calorimetry, Fourier transform infra-red, and weight gain analyses provided evidence that chitosan was grafted onto the acylated wool through the formation of new covalent bonds in a short time. Scanning electron microscope was used to study the morphology of wool samples before and after modification. The dyeing of the chitosan grafted-acylated wool fabrics indicates higher dye ability and lower shrinkage compared to the acylated and raw wool samples. The findings of this study support the potential of using ultrasonic as a friendly environment method for grafting chitosan onto wool with enhanced dye ability and reduced shrinkage properties. The grafted samples showed good antibacterial properties against *Staphylococcus aureus* as gram-positive and *Pseudomonas aeruginosa* as gram negative bacteria. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 707–713, 2013

KEYWORDS: biopolymers and renewable polymers; textiles; grafting; polysaccharides

Received 8 September 2012; accepted 3 November 2012; published online 23 November 2012
DOI: 10.1002/app.38796

INTRODUCTION

Nowadays, using energy in the form of radio waves, microwaves, infrared radiation, and ultrasound is one solution to speed mass transfers as well as reducing processing time, decreasing water consumption, energy savings, and process enhancement in textile wet treatments as an alternative to the conventional methods.[1–3] These advanced techniques have proved to be very effective. For example, in desizing of cotton fabric,[4] bleaching of linen fabrics,[5] dyeing,[6,7] and washing of textiles.[8] The effects of ultrasound on several wool dyeing and finishing processes have been studied extensively.[6,9]

Ultrasonic energy is sound wave with frequencies above the human hearing.[2] In liquid, these high-frequency waves produce microscopic bubbles or cavitations that result in heating of the liquid. With collapsing cavitational bubbles produced by ultrasound in the liquid, tiny but powerful shock waves are generated. In the case of fibers, this heat can result in increasing the rate of dye diffusion into the fiber, remove air trapped between fibers, interrupt the fiber–liquid boundary layer, and finally increases the area of the fiber–liquid interface which improves dyeing ability.[2,10]

Wool is a high-quality protein fiber and is widely used in textile industry because of its lightness, warmth, softness, and smoothness. In textile finishing treatments, the structure of wool fiber is so important and the covalently bound fatty acids and the high amount of disulphide bridges make the outer wool surface hydrophobic. Therefore, the diffusion of the hydrophilic dyes into the fibers becomes difficult. To improve dye absorbing of wool fibers, hydrophilicity properties of the wool fiber should be increased.[10,11]

The structure and configuration of the cuticle scales on the surface of wool fiber and the mechanical action of aqueous washing causes the advanced entanglement of wool fibers, leading to irreversible shrinkage of wool fabric. By increasing environmental legislation, one should ignore the processes which use a chlorination pretreatment or chlorine-containing polymers because of serious ecological problems and contamination of wastewater effluent.[12] Chitin is a natural aminopolysaccharides which is extracted from crustaceans' shells (crabs, etc.) which are waste products (now byproducts) of food industry. Chitosan is prepared by alkaline or enzymatic deacetylation of chitin. It has unique structures, multidimensional properties, highly sophisticated functions, and wide ranging applications in biomedical and other industrial areas.[13–15] The effect of ultrasonic conditions on the degradation of chitosan has been reported.[16] Liu et al.[17] reported the effect of ultrasonic treatment on the

degradation behavior of chitosan. They reported that ultrasonic treatment decreased the molecular weight and enhanced antibacterial activity of chitosan. Useful properties of this polysaccharide such as nontoxicity, biodegradability, biocompatibility, chemical reactivity, antimicrobial activity, film-forming ability, and producing polycation in acidic water solution for binding with other polymers make it an acceptable substitute for synthetic polymers in textile finishing.[18–20] In wool finishing, chitosan has been used as an agent for improving shrinkage resistance[21] and dye ability of wool.[19] Giri Dev et al.[22] applied a natural dye Henna which proved bactericidal properties along with chitosan to wool fabric. It proved that the chitosan-treated wool fabrics have higher dye uptake. Also, fabrics were found to have antimicrobial characteristics because of the Hanna dye and antibacterial property of chitosan. It is important that binding chitosan with wool needs irreversible covalent bonds to get a steady network of chitosan with wool protein and this can be achieved by adding crosslinkers, molecules with at least two reactive functional groups, allowing the formation of bridges between the polymeric chains such as chitosan and wool. These crosslinking agents are poly(carboxylic acid)s, such as citric acid, which have at least two carboxyl groups that can react with active groups of chitosan.[23] Gawish et al.[24] modified woolen fabrics by the grafting of chitosan in the presence of citric acid as a crosslinking agent using the pad–dry cure method. They reported that the modified samples had antibacterial properties. Vílchez et al.[25] applied chitosan on wool before treatment with proteolytic enzymes. The results showed that the chitosan pretreatment reduced the damage caused by the subsequent enzymatic treatment.

In our previous study, chitosan was grafted onto wool fabric using succinic anhydride (SA) as crosslinker for the formation of irreversible covalent bonds. However, this process requires a long time and more material.[26] In this study, the focus is on the use of ultrasonic power for grafting chitosan on acylated wool by acceleration process and studying shrinkage resistance, dyeing properties, and antibacterial characteristics of the samples.

EXPERIMENTAL

Materials

The experimental woolen fabric with a yarn number of 48 scoured in 2 g/L nonionic detergent ultravon GP and pH 8.5 at 70°C for 45 min. Chitosan was provided by Chitotech (Tehran). Iran (degree of deacetylated [DD]: 85%, MW: 1000 kDa). All other chemicals were of laboratory grade (analytical reagents, Merck, Delhi, India).

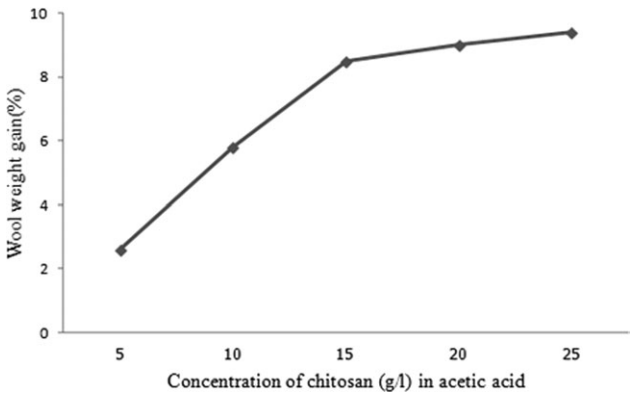

Figure 1. Effect of chitosan concentration on weight gain of acylated wool.

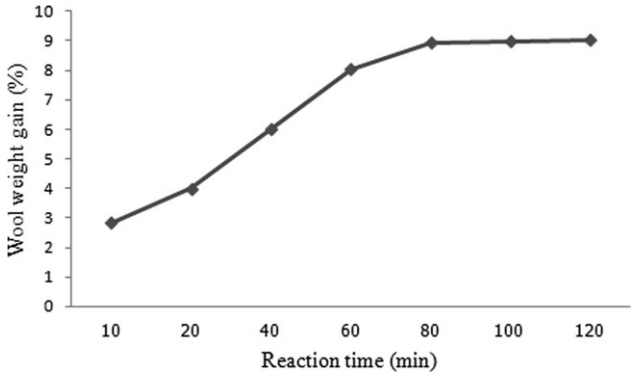

Figure 2. Effect of reaction time on weight gain of wool fabric.

Methods

Acylation of Wool. Wool fabrics were acylated with 40 g/L SA in dimethyl sulfoxide (DMSO), at 65°C for 2 h. The reaction system was connected to a reflux condenser and held at a constant temperature in a thermostatic bath. The liquor ratio ($L : R$) was 20 : 1. At the end of the reaction, the fabric samples were washed with DMSO and then with acetone at 55°C for 1 h to remove unreacted anhydride. Finally, it was rinsed with water and dyed.

Chitosan Grafting onto Acylated Wool Fabrics. The grafting of chitosan (DD: 85%) to the acylated wool samples was carried out with ultrasonic, (Elmasonic P120H Ultrasonic Bath) with frequency of 20 kHz. Then, the fabrics were squeezed and washed with warm water at 50°C for 30 min and afterward the weight gain of samples was calculated. The effects of chitosan concentration (0.5–3 g in 100 mL acetic acid 4%), and reaction time (10–120 min) with ultrasonic on chitosan grafting of acylated wool were investigated (Figures 1 and 2).

Dyeing Procedure

Dyeing of treated samples was carried out with 2.0% o.w.f. Polar Brilliant Red 3BN and 1.0% Albegal B as leveling agent using a liquor ratio of 40 : 1, pH 4.5 (acetic acid) at 80–90°C for 30 min in dyeing bath. At the end of dyeing, the substrate was rinsed and dried.

Antibacterial Testing

Antibacterial activity of the different samples was done by paper disk diffusion method.[27] *Staphylococcus aureus* ATCC 25923 and *Pseudomonas aeruginosa* ATCC 27853 were used as examples of gram-positive and gram-negative bacteria. In this test, grafted accylated samples and control wool fabric were cut in the size of 1 cm^2, and then they were sterilized by the exposure to γ rays. Stock culture of test bacteria was grown in TBS medium at 37°C for 24 h. Final cell concentrations were adjusted to 108 cfu/mL with reference to the McFarland turbid meter.[28] In brief, 1 mL of these inoculums was added on the surface of each plate containing Mueller–Hinton agar by sterile cotton swab and allowed to remain in contact for 1 min. The plate allowed to remain 1 h at room temperature to diffuse the sample across

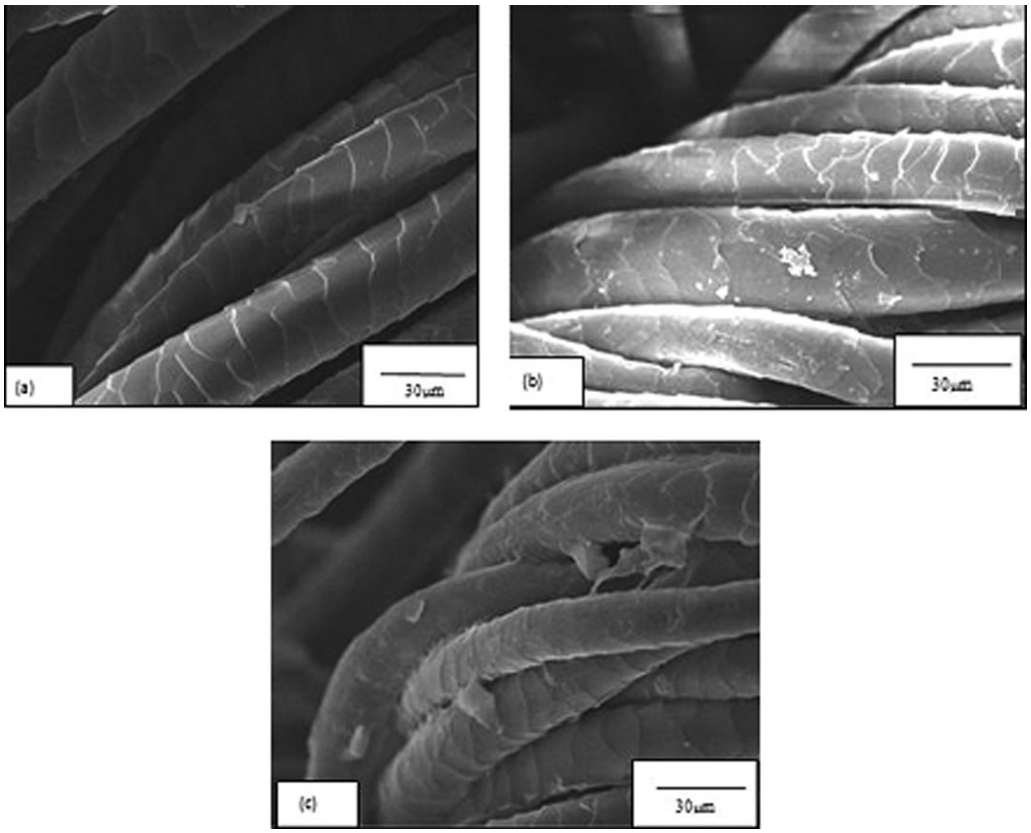

Figure 3. SEM images of samples: (a) wool, (b) acylated wool with SA, and (c) chitosan grafted-acylated wool.

the surface and then was kept in the incubator at 37 ± 0.5°C for 24 h. The inhibition zone around each disk was measured in millimeter and the assay was carried out three times for each sample. Depending on the charges of the bacteria, the inhibition zone in different states of resistance, semi-resistance, and sensitive is different. The antibacterial experiment was performed in the medical center of Yazd in the branch of medical university of Shahid Sadughi. The measurements of moisture, regain, fiber weight gain, and so on, were carried out five times. The reproducibility of these tests, calculated as relative standard deviation, was acceptable ≤4%.

Analysis

Heat-flow analysis differential scanning calorimetry (DSC) measurements were performed using a TA instrument 2010 at a heating rate of 10°C/min. The open aluminum cell was swept with N_2 during the analysis. Scanning electron micrographs of the samples were carried out using AIS-2100 scanning electron microscope (SEM) (Seron Technology-Korea). Fourier transform infra red (FTIR) spectra were recorded on a Nicolet Nexus670 instrument. The colorimetric data of the dyeing were obtained using a Gretag MacBeth 7000 A spectrophotometer (D65 illumination, 10° observers). The fabric weight gain was calculated from the difference in weight of the wool fabric before and after chemical reaction. The wash fastness test was carried out according to WASH TEST NO.2, ISO/R 150/N, Part g. Moisture regain was determined using Sartorius Moisture Analyzer A50-IR model. It was also determined on dried samples at 20°C and 65% relative humidity for 7 days and expressed as grams of moisture/100 g wool fibers.

RESULTS AND DISCUSSION

Effect of Chitosan Concentration and Reaction Time on Grafting Yield

Ultrasonic can be used for grafting chitosan onto acylated wool fabric. Figure 1 shows that for 15 g/L, the weight gain increases linearly with increasing concentration and beyond this concentration the weight gain is slowed down and it is owing to increase of chitosan viscosity which decreases the ability of chitosan to penetrate wool fabric. Therefore, the fabric with 15 g/L chitosan was chosen as the optimum concentration.

The results of chitosan grafting for the acylated wool at different time intervals are shown in Figure 2 in which the weight gain of grafted-acylated wool increased more rapidly during the first 60 min and then preceded at a lower rate, and hence increasing the processing time did not cause an important increase in the results. This technique needs a short time compared with the previous articles.[26] This is achieved by employing ultrasonic energy to dissipate solution and creating cavitations. Cavitation with producing vibrational wave energy, shear stresses at the cavitation interphase, and local high pressure and temperature can make diffusing of chitosan in to wool more easier.[29,30]

Scanning Electron Microscope

Hydrophobic properties of wool fibers are owing to the presence of a thin fatty layer which is covalently bound to the epicuticle and surround each cuticle cell.[31] SEM determines the extent of fiber damage and any changes of the external surface of the fiber. The SEM of untreated wool in Figure 3(a) shows the scales and the

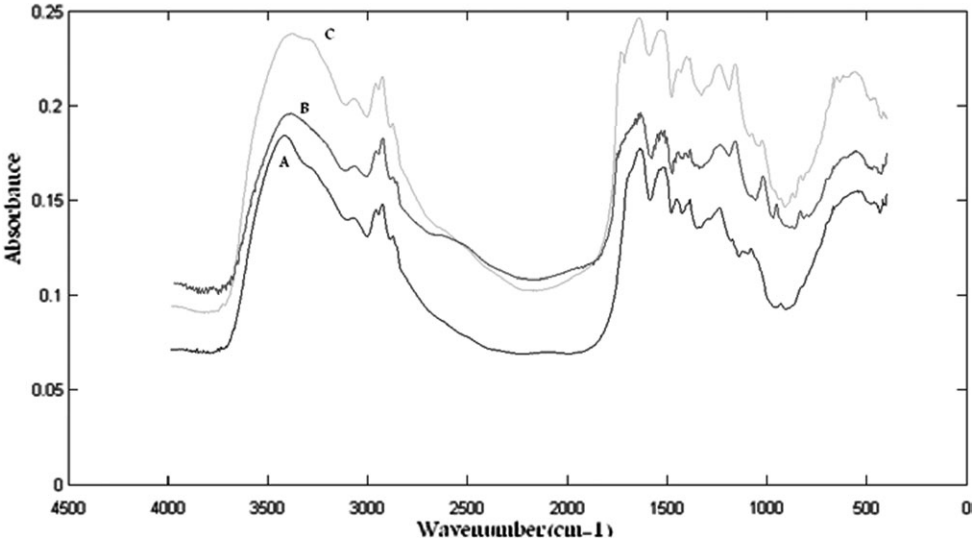

Figure 4. FTIR spectra of wool samples (a) wool, (b) acylated wool with SA, and (c) wool with chitosan, and (d) grafting anhydride-treated wool samples with chitosan.

overlapping between them on the wool surface. Fabrics treated with SA [Figure 3(b)] exhibited the existence of different amounts of foreign material deposited onto their surface. Acylated-grafted fibers [Figure 3(c)] showed that the rougher deposition on the wool surface and ultrasonic process did not create any sensible changes on the morphology of wool fibers.

FTIR Analysis

Wool is composed of more than 20 α-amino acids, which can be cationic, anionic, nonpolar, and polar. The most important functional groups in wool structure are carboxyl, amino, and hydroxyl groups. Hence, the chemical groups are extremely active for reaction. Figure 4 shows the FTIR spectra of raw wool, acylated wool, and acylated-grafted wool. Wool fabrics showed absorption bands at 3300 (N—H and O—H), 2850 (—CH2), 1627 (Amide I), 1520 (Amide II), and 1233 cm^{-1} (Amide III) [Figure 4(a)].[32] FTIR spectrum of acylated wool fabrics [Figure 4(b)] showed partial disappearance of the peaks at 3000–3400 cm^{-1} that might be related in reaction of amino groups of wool with anhydride. Figure 4(c) shows the formation of new band (∼ 1733) in grafted sample that clearly displayed chitosan, which has been grafted on the acylated wool and the omitted peak at 3400–3000 cm^{-1} reappeared.

DSC Analysis

The heat treatment DSC curve of the acylated woolen fabric and acylated-grafted wool [Figure 5(c)] is shown in Figure 5. There was a prominent peak owing to the water removal from the samples with peak temperature around 80°C. Another peak was related in α-keratin crystallization melting peak. This endothermic reaction starts from 222°C for wool untreated sample [Figure 5(a)]. However, for acylated sample [Figure 5(b)] the onset of this endothermic reaction shifts to much lower temperature at 183°C. The presence of chitosan in the molecular structure of wool as a grafting agent seems to improve the thermal behavior of the acylated wool sample and the onset of this endothermic reaction starts at 188°C. This indicates that the presence of chitosan affected the thermal properties of the treated samples. Another important observation is the type and the mechanism of the thermal degradation of the treated samples. Peaks at

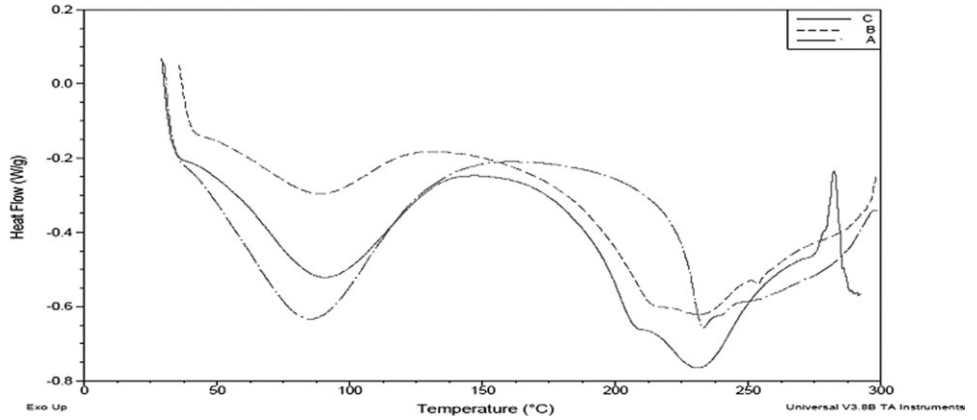

Figure 5. DSC curves of wool fabrics, (a) raw wool, (b) acylated wool, and (c) acylated-grafted wool.

Table I. The Dye Absorption Properties of Raw Wool, Acylated, and Grafted-Acylated Wool Samples

	Reflectance		
Sample	R	R_0	K/S
Raw wool	1.83	23.85	25.11
Acylated wool	1.94	36.93	24.22
Grafted-acylated wool	1.53	33.30	31.02

233°C seem to be somehow sharp for wool fabric. However, for acylated and grafted wool samples, these peaks are broad and doublet in nature. The main peak appears almost at the same temperature but another peak appearing at lower temperature for acylated and acylated-grafted samples (212°C, 206°C for acylated and acylated-grafted samples, respectively), indicating different degradation reactions. This difference in temperatures is because of the formation of bonds such as amide in chitosan-grafted samples.

Moisture Regain

Moisture content is an important physical parameter, which can influence the functional properties of wool such as comfort and crease recovery. The results showed that the moisture contents of wool, acylated, and chitosan grafted-acylated wool samples were 12, 10.9, and 13.9%, respectively. This decrease in the moisture regain of acylated wool might be owing to the diminution of hydrophilic groups of wool samples by introducing anhydride groups. After grafting of fabrics with chitosan, increasing the number of amino groups increases the formation of hydrogen bond by water molecules.

Washing Fastness

The results of wash fastness experiments showed little reduction in the weight loss (0.35%) which can be related to the loss of unreacted chitosan molecules with acylated wool samples. The most important histological components in wool fibers are cortical and cuticular cells where the surface of cuticular cells is hydrophobic owing to the presence of a fatty acid monolayer (F-layer) covalently bounded to the epicuticle protein layer. The influence of F-layer is considerable on the shrinkage properties of wool fabrics during an aqueous washing process because it is a barrier for different hydrophilic chemical products such as dyes.[33]

Dyeing

One of the most sensitive steps in wool processing is dyeing. Slightest changes in wool fibers containing different previous processing steps and treatments affect their dyeing properties.[10] In this study, the dyeing capability of all samples (raw wool, acylated, and acylated-grafted wool samples) with acidic dye was studied. To compare the dye adsorption, K/S for different samples was determined using the following equation.

$$K/S = \frac{(1-R)^2}{2R} - \frac{(1-R_0)^2}{2R_0}$$

where R is the minimum reflectance of dyed sample, R_0 is the minimum reflectance of undyed sample, K is the absorbance coefficient, and S is the scatter coefficient. Mostly, acidic dyes were used to dye wool and natural fibers. Table I summarizes that K/S is decreased with acylated samples. This might be owing to the engagement of reactive cites such as amine and carboxylic groups of wool with anhydride molecules which prevents the ionic bond formation of dye molecules by acylated samples. But for chitosan-grafted samples, the K/S values and dye absorption increase owing to the increase of amine and hydroxyl groups, which are provided by chitosan molecules.[34]

Antibacterial Analysis

Antibacterial activity of acylated-grafted fabrics was tested by an agar plate method as described by Baron and Finegold.[35] Two different initial microbial charges were used to determine the influence of cell density on the effectiveness of samples. *S. aureus* ATCC 25923 and *P. aeruginosa* ATCC 27853 were used for gram-positive and gram-negative bacteria, respectively. The data of Table II summarize that the controlled wool fabric did not show any antibacterial properties. However, for the treated samples it observed sensible changes in the antibacterial properties and increased the inhibition zone.

Table II. Antibacterial Activity

	P. aeruginosa (ATCC 27853) gram negative			*S. aureus* (ATCC 25923) gram positive		
Chitosan concentration (g/L)	Result	Zone (mm)	MBC (μg/mL)	Result	Zone (mm)	MBC (μg/mL)
	R[a]	-	31.2	R	-	31.2
10	SS[b]	15.5	31.2	S	36	31.2
15	S[c]	27	62.5	S	34	62.5
30	S	25	62.5	S	31	62.5
Final result in the base of measuring the inhibition zones	Gram-negative bacteria result: Sensitive (S) ≥ 20 mm			Gram-positive bacteria result: Sensitive (S) ≥ 21 mm		
	Semi Sensitive(SS) = 15–19			Semi Sensitive(SS) = 18–22		
	Resistant (R) ≤ 14 mm			Resistant (R) ≤ 17 mm		

[a]Resistant (R): It shows that the bacteria can grow on the sample and there is no resistance of untreated fabric toward bacteria, [b]Semi-sensitive(SS): It shows that the sample treated with 10 g/L chitosan can prevent the bacteria's growth to some extent. It should be mentioned that this result does not have any application in medicine, [c]Sensitive (S): It shows that the sample has the desirable anti-bacterial properties.

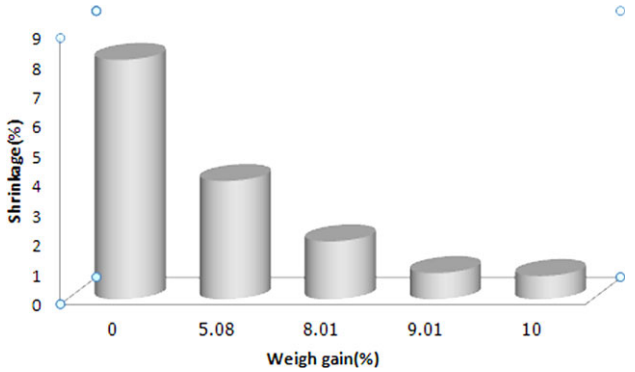

Figure 6. Effect of the grafting on the wool shrinkage. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Shrinkage Resistance Testing

The mechanical action of aqueous washing causes the progressive entanglement and irreversible shrinkage of wool fibers because of cuticle scales on its surface. Hence, for achieving a washable wool product, this typical property of wool must be controlled. There is a close inter-relationship between shrinkage resistance and hydrophilicity of wool fabrics and as hydrophilicity property increases, this defect can decrease. A way to justify the relationship between the hydrophilicity of the treated wool and the decrease in the shrinkage would be that the absorbed water could play a role as a plasticizer among the surface scales of the wool; therefore, shrinkage could be decreased.[36] In the case of chitosan-grafted samples, owing to the availability of extra number of hydrophilic groups such as amine and hydroxyl because of chitosan molecules, shrinkage resistance has been increased.

For testing shrinkage resistance, raw wool and treated samples were immersed in a solution containing 1% nonionic detergent at 50°C in $L : R$ 40 : 1 and were agitated for 45 min, according to ISIRI 1454 standard. Before and after this process, the surface dimensions of the fabrics were measured, and the results were reported as percentages based on the fallowing equation.

$$\frac{(A_1 - A_2)}{A_1} \times 100$$

where A_1 is the primary surface area of the fabric and A_2 is the surface area of the samples after shrinkage. Figure 6 shows that the shrinkage rate is reduced from 9.1% in raw wool to 0.7% in an acylated-grafted wool samples.

CONCLUSIONS

Current wet textile processes suffer from important challenges: large process time and low energy efficiency. Ultrasonic is an important technique which can be used for increasing the mass transfer toward the wool fabrics. This method reduces long processing times, large amounts of water, chemical and energy consumption. The efficiency of wet finishing processes is increased by increasing the mass transfer toward the inner parts of the textile material. This technique offers fabrics with antibacterial properties. The fabrics have weight gain about 10% and the suitable time for treating acylated fabrics with chitosan by ultrasonic was 60 min. The grafting biopolymer (chitosan) was successfully performed on the acylated wool by ultrasonic. The optimum conditions were achieved by grafting of wool with 15 g/L chitosan for 1 h. The results of DSC for wool, acylated, and chitosan grafted-acylated samples supported the FTIR findings.

ACKNOWLEDGMENTS

Authors thank the Center for Excellence Modern Textile Characterization, Tehran Iran for their support in providing the means for conducting experiments.

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