

Chemical and Mechanical Properties of Butyl Methacrylate Grafted Wool Fiber

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Received 9 January 2003; accepted 30 July 2003

ABSTRACT: Because polymer-grafted wool fibers had been reported to have better functional performance, a $K_2S_2O_8$ - $NaHSO_3$ redox system was used as the initiator for the grafting copolymerization of butyl methacrylate (BMA) onto wool fibers. Grafted samples of wool-g-BMA with different grafting percentages (5.2–25.86) were obtained through variations in the monomer concentration in the reaction system. The evidence for grafting was provided by scanning electron microscopy and infrared spectroscopy. After the grafting, the moisture retention of the wool-g-BMA fibers decreased slightly. Optical measurements showed that

the birefringence decreased, indicating a lower degree of molecular orientation of the wool-g-BMA fibers. The tensile strength increased as the grafting percentage increased. Beyond an 18–25% grafting percentage, the elongation at break decreased, and this indicated a reduction of the elastic deformation, which meant that the flexibility of the modified fibers may have deteriorated. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3813–3817, 2004

Key words: fibers; graft copolymers; strength

INTRODUCTION

Wool, a natural biopolymer fiber, is one of the most important textile materials, having some outstanding characteristics and an aesthetic style for the textile industry. Because of the presence of overlapping scales on the wool fiber surface, an interlocking effect of scales on adjacent fibers can occur during washing and friction, causing the fibers to migrate until they are completely entangled and thus producing permanent shrinkage, which is the most important disadvantage of woolen fabrics.^{1,2} The elimination of felting shrinkage by chemical modification with a polymer has been investigated extensively.^{3–11}

Traditionally, the shrink proofing of wool has been approached with polymer deposition or interfacial condensation techniques. The methods of polymer deposition are more common in industry because they do not require special equipment, which is needed for the interfacial condensation technique. The drawback of polymer deposition methods is that, for even film formation to be ensured, the fibers generally require pretreatments, such as chlorination, to produce a homogeneous surface and, therefore, an even film deposition.⁸ Such pretreatments mean higher costs, a less efficient use of equipment, and an increasingly unacceptable environmental impact because of the elimination of absorbable organic halogens during the chlo-

ration. Nowadays, alternative processes, such as low-temperature plasma treatment¹² and enzymatic treatments,^{13–16} have been put into industrial use. Unfortunately, both of these processes produce unavoidable tensile strength damage to modified wool. Another process, the grafting copolymerization of vinyl monomers to wool, which has been reported extensively^{3–11,17–20} during the last 3 decades, has not been popular because grafting copolymerization, especially at high grafting percentages, can have some side effects on wool (e.g., stiffness and slightly poor handle). However, some reports^{9,17,18} have shown that with suitable polymerization systems (highly reactive monomers and redox couple initiators) and polymerization conditions (lower grafting percentages and relatively low reaction temperatures), grafting copolymerization can be accomplished without deleterious effects on wool handle and end-use performance.

A given large number of single wool fibers forms a fiber bundle, and with twisting, the bundle becomes yarn. How the fiber properties translate into yarn properties thus depends on, among other factors, the surface morphology of the single fiber and the interaction of the fibers, and so it is important to investigate the properties of the fiber, and to predict the properties of the yarn and fabrics.

It has been reported in the literature that polymer-grafted wool fibers and fabrics have better shrinkage resistance.^{7,18} Hence, this study was aimed at demonstrating that the chemical and mechanical properties of modified wool fibers could be significantly improved by relatively low levels of grafting while the intrinsic fiber properties were maintained. Further-

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more, the wool fabric properties remained unchanged. Butyl methacrylate (BMA) was chosen because the corresponding homopolymer poly(butyl methacrylate) (PBMA) had a low glass-transition temperature and, therefore, was not expected to deteriorate the flexibility of the wool fibers. Moreover, work was carried out with a view toward exploiting commercial available treatments and bridging the gap between scientific and industrial applications.

EXPERIMENTAL

Materials

The wool yarn, kindly provided by Ruyi Textile Co. (Shandong, China) and having a single-fiber fineness of 0.26–0.3 tex, was purified and characterized by a method described in the literature.¹⁰ The monomer BMA was washed with a 10% NaOH solution and distilled water for the removal of the inhibitor and alkali, respectively. Then, it was distilled under reduced pressure, and the middle fraction was collected. Other chemicals were analytical-reagent-grade.

Grafting procedure

The graft copolymerization of BMA onto wool was conducted with a $K_2S_2O_8/NaHSO_3$ redox couple as a catalyst. The preweighed wool was added to an aqueous solution containing the monomer and catalyst in a three-necked, round-bottom flask equipped with a stirrer. The flask was then purged with nitrogen for 15 min to remove oxygen before it was heated to 50°C and held at this temperature for 3 h. The concentration of the monomer, the duration, and the temperature of the reaction were varied, as earlier reported,¹⁷ in order to obtain a different percentage range (5.2–25.86%) of grafted samples of wool-g-BMA.



Figure 1 Scanning electron micrograph of a control wool fiber.

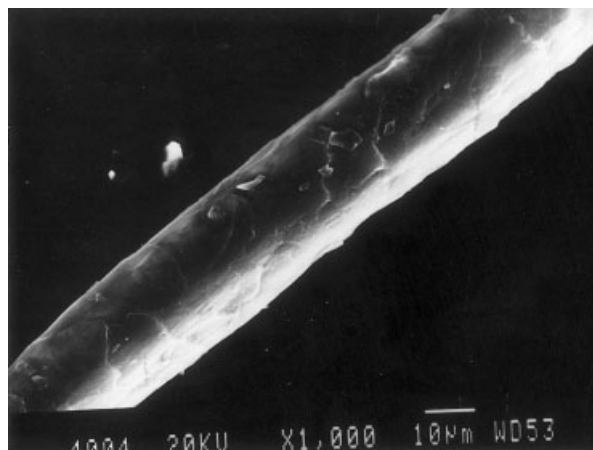


Figure 2 Scanning electron micrograph of a grafted wool fiber (grafting percentage = 25%).

After the copolymerization, the grafted samples were extracted with benzene, a solvent for the poly(methacrylate esters) used in this study, in a Soxhlet apparatus for 48 h for the complete removal of the homopolymer. Finally, the grafting copolymerization samples of wool-g-BMA were dried at 50°C in a vacuum oven to a constant weight.

The percentage of grafting was determined with the following relationship:

$$\text{Grafting percentage} = [(W_2 - W_1) / W_1] \times 100$$

where W_1 and W_2 are the weight of the wool and the weight of wool-g-BMA (after the solvent extraction of the homopolymer), respectively.

Evidence of grafting

Wool-g-BMA samples were hydrolyzed with 6N HCl at 115°C for 24 h. All the wool went into solution, leaving behind resinous masses, which were purified and identified by infrared spectroscopy. The carbonyl stretching band lay between 1700 and 1725 cm^{-1} , and the carbon-hydrogen stretching band lay between 2915 and 2960 cm^{-1} ; these are the characteristic bands of PBMA.

Scanning electron micrographs of control wool and grafted wool samples were obtained with a JEOL JSM scanning electron microscope (the samples were mounted on Al stubs with double-sided tape and were sputter-coated with Au/Pd (30 nm).

Furthermore, a comparative study of scanning electron micrographs of control wool and grafted wool fibers indicated that a fiber was obtained with significant amounts of polymer forming a continuous film over the fiber surface and the surface structure and morphology of the wool fiber and that grafting had taken place (Figs. 1 and 2).

TABLE I
Moisture Retention (*M*) of Wool-g-BMA

G (%)	0	5.20	8.70	12.10	15.82	18.30	20.23	23.10	25.00
M (%)	14.0	12.8	11.1	9.8	8.3	7.7	6.2	5.7	4.3

G = grafting percentage.

Mechanical measurements

The moisture regain was determined under standard conditions of 20°C and 65% relative humidity (RH) by the weighing of original samples and oven-dried samples (120°C and 50 min). The moisture regain was calculated with the following formula:

$$\text{Moisture regain (\%)} = [(W_c - W_d) / W_d] \times 100\%$$

where W_c and W_d are the weights of the control samples and oven-dried samples, respectively.

The refractive indices were measured with the Beche line method with a polarized microscope under monochromatic light (Na light) and under standard conditions.

The tensile properties and elongation at break of single fibers were measured under standard conditions on an Instron (United Kingdom) model 1121 machine with a gauge length of 50 mm and a cross-head speed of 20 mm/min. An average of 50 readings was presented for each sample.

RESULTS AND DISCUSSION

Moisture absorption of wool-g-BMA fibers

Wool fibers are highly hygroscopic. The mechanical properties of wool change with RH because of moisture retention. The higher RH is, the lower the initial modulus and tensile strength are of wool fibers. The moisture absorption of fibers in air depends not only on RH and temperature but also on the basic chemical components, macromolecular structure, and morphological structure of the fibers. Table I lists the moisture regain of wool-g-BMA fibers with different grafting percentages. Grafting between BMA and wool resulted in a decrease in the moisture regain of modified wool fibers. Moreover, the higher the grafting percentage was, the more the moisture regain decreased. This finding can be explained by the hydrophobicity of the modified-fiber side-chain group PBMA, which masked the hydrophilic hydroxyl groups of the wool fibers. Also, some amount of homopolymer PBMA, produced from *in situ* polymerization, could not be extracted thoroughly, filling in the voids of the wool fibrils and impeding the diffusion of water molecules within the wool fibers. Moreover, the higher the grafting percentage was, the greater the impeding effect was. Liouni et al.⁷ reported a spray test for poly-

(methyl methacrylate)- and PBMA-grafted woolen fabrics, indicating that saturation of untreated woolen fabrics was common, whereas the grafted samples became almost water-repellent. Although the characteristics of fibers and fabrics were slightly different, the grafted products showed a similar hygroscopic trend.

Although the moisture regain to some extent decreased with a higher grafting percentage (the moisture retention decreased to 4.3% when the grafting percentage was greater than 25.86%), it still remained high in comparison with the moisture regain of common synthetic fibers (Table II). This ensured that it would feel comfortable for wearing.

The moisture regain of wool fibers also affects the mechanical properties. Because of the water absorption of the hydrophilic hydroxyl groups in wool fibers, which weakens molecular interactions in the amorphous regions, the chain segment mobility increases, leading to an increase in the number of new water absorption centers. This feature of water affinity results in hydrolytic fission at the wool polypeptide, and so the tensile strength decreases. This may be the main reason that the wool fiber wet strength is lower than its dry strength. The process of grafting copolymerization reduced the reduction of the modified-fiber moisture regain to some extent. Therefore, this process can enhance some mechanical properties of wool fibers and improve their shrinkage resistance.

Molecular orientation of wool-g-BMA

For natural and drawn synthetic fibers, the arrangement of macromolecular chains is uniaxial orientation, and fiber optical anisotropy shows birefringence (Δn) phenomena. Therefore, the measurement of Δn is a useful source of information about the overall oriented fiber structure and is important for investigating

TABLE II
Moisture Retention (*M*) of Common Fibers

Fiber	<i>M</i>	Fiber	<i>M</i>
Cotton	7–8	Silk	10
Silk cotton	>12	Nylon 66	4.2
Viscose rayon	12–13	Nylon 6	4
Cellulose acetate	6	PET	0.4
PVC	5	PAN	0.9–2.0

TABLE III
 Δn of Wool-g-BMA

Grafting percentage	0	5.20	8.70	12.10	15.82	18.30	20.23	23.10	25.00
Δn	0.010	0.006	0.005	0.004	0.003	0.003	0.002	0.001	0.0011

the relationship between the extent of orientation and the mechanical properties. Table III shows the Δn values of control and modified wool fibers.

Untreated fibers showed a Δn value of 0.01; this placed wool within the group of poorly oriented textile fibers. According to the results listed in Table III, grafting induced a notable decrease in the value of Δn . Hence, Δn may be regarded as an estimate of the average molecular orientation of a fibrous polymer because it reflects the orientation of the polymer chains in both the amorphous and crystalline regions. The appreciable reduction of molecular orientation should be primarily attributed to the presence of the grafted polymer, which disturbs the arrangement of the keratin chains in the amorphous regions and the arrangement of the fibrils in the crystalline regions.

The decrease in the orientation resulting from grafting copolymerization is substantially different from that of synthetic fibers in the disorientation process. The latter derives from the disruption of crystalline regions and the rearrangement of the segments, whereas grafting copolymerization induces side-chain groups and, therefore, reduces the arrangement of uniaxially oriented fibers. Consequently, the decrease in the orientation of the modified fibers should not cause strength failure; however, inducing some polar ester groups as side chains enhances the interaction or interaction of amorphous and crystalline fiber regions, and so grafting results in an increase in the strength of the modified fibers.

Tensile behavior of wool-g-BMA

The tensile behavior is an important parameter in the assessment of the properties and functional perfor-

mance of textile fibers (e.g., handle, comfort, and maintenance). Figures 3–6 show stress–strain curves of untreated wool fibers and wool fibers with various grafting percentages. These curves express the relationship between the tensile stress and the corresponding elongation during the drawing process, in which the fiber is drawn along the fiber axis direction until it breaks.

In a comparison of wool-g-BMA fibers with various grafting percentages and untreated wool fibers, we found that the corresponding stress–strain curves showed different characteristics. At first, the tensile strength of the fiber with a lower grafting percentage was lower than that of an untreated wool fiber, and then the tensile strength increased as the grafting percentage increased. This tensile behavior may be attributed to two kinds of opposing interactions. On the one hand, wool fibers are known to be quite sensitive to wet treatment. Grafting copolymerization conditions may cause the hydrolysis of some sensitive peptide bonds, resulting in a failure, more or less, of the wool fiber backbone chain. On the other hand, grafting copolymerization induces PBMA groups to the fiber backbone as side chains and leads to a strengthening effect brought about by interactions among polar ester groups. This is similar to the textile process, in which the fiber is laterally made tight by twisting so that parallel fibers cannot slide easily because of the frictional force among them. With a lower grafting percentage, the main effect is the hydrolysis of wool fiber peptide bonds, and only a small number of side chains is not enough to balance the damage of hydrolysis, whereas with greater and greater grafting percentages, the tensile behavior might have been governed

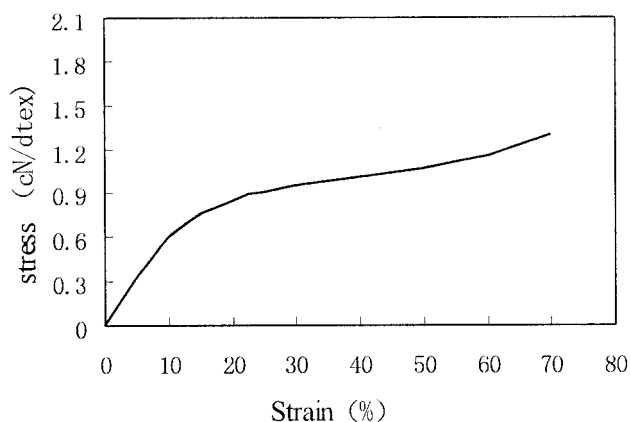


Figure 3 Stress–strain curve of control wool (grafting percentage = 0%).

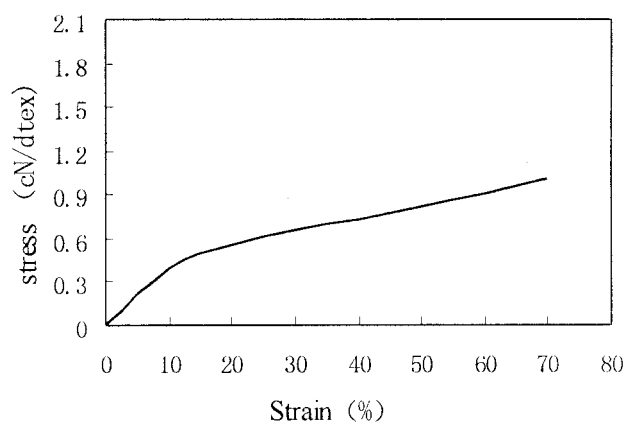


Figure 4 Stress–strain curve of grafted wool (grafting percentage = 5.2%).

by the balance of two opposite effects, the strengthening effect prevailing at a higher grafting percentage. As Figures 3 and 4 show, when the grafting percentage increased to 25%, the tensile strength increased by 16%. This result was consistent with the results of Tsukada et al.⁵ Additionally, at higher grafting percentages, the initial modulus increased as the grafting percentage increased, but the elongation at break was lower than that of the untreated fiber. This may be attributed to the increased density of polar ester groups, which hindered segmental motion and inhibited forced elastic deformation. Consequently, although the tensile strength was improved, the stress-strain curves of the modified fibers showed obvious strain-hardening phenomena. It is reasonable to assume that at higher grafting percentages (e.g., >25%), both the elastic deformation and plastic deformation may be reduced, and negative consequences (stiffness and poor handle) will occur.

CONCLUSIONS

The results reported in this study show that the active monomer BMA can be successfully grafted to wool fibers. The hygroscopicity of wool-g-BMA fibers decreases as the grafting percentage increases. When the grafting percentage is kept below 25%, the moisture retention of wool-g-BMA fibers will still be higher than that of common synthetic fibers. It is reasonable to assume that grafting copolymerization can improve the wet strength and maintain a comfortable feel for wearing. Although optical measurements show an orientation reduction of modified fibers, grafting does

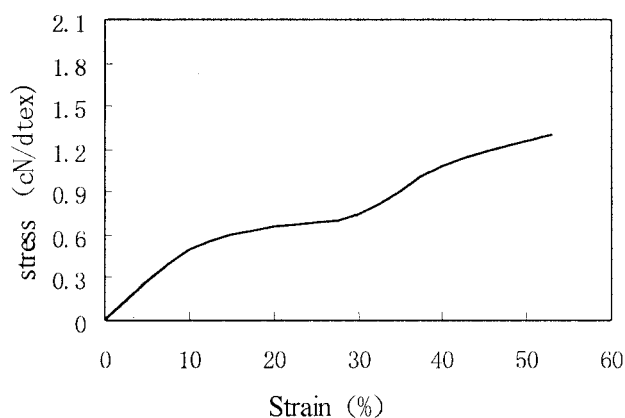


Figure 5 Stress-strain curve of grafted wool (grafting percentage = 15.82%).

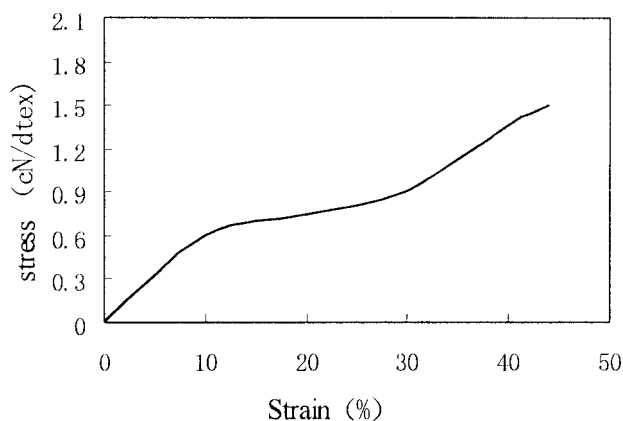


Figure 6 Stress-strain curve of grafted wool (grafting percentage = 25%).

not result in fibrous strength failure. On the contrary, inducing a large number of polar ester groups increases the interactions of fiber chains, and so the strength of the wool-g-BMA fibers increases. The tensile strength decreases at first and then increases with an increase in the grafting percentage. The value of the tensile strength increases by 16% when the grafting percentage is greater than 25%, but the elongation at break decreases slightly.

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