

Localization of Methyl Acrylate Graft Copolymerization in Exposed Cortex of Abraided Wool Fibers

INTRODUCTION

Wool fibers are chemically and physically complex like most proteinaceous materials. Their diverse chemical composition invites a large number of chemical reactions to modify various fiber properties. One can easily visualize reaction of wool with many different reagents under many different conditions. Examples of reactions abound, including an entire issue of *Textile Progress* citing 569 references devoted to the chemical reactivity and modification of keratin fibers,¹ a paper containing 600 references surveying the literature on crosslinking agents as they relate to wool keratin,² and a review citing 114 references about reactions involved in grafting vinyl monomers onto wool keratin.³ This brief list leaves little doubt that keratin may be reacted successfully with an enormous and diverse group of chemicals under a variety of conditions.

The intricate physical organization of the proteins in wool leads to the expectation of morphological specificity in the physical location of at least some chemical reactions. Wrinkle-resistant and shrink-resistant finishes are common examples of modifications based on internal and surface deposition, respectively. The amounts of deposition required to achieve the desired modification from these finishes creates undesirable side effects, however. Ideally, deposition should be restricted to those morphological areas having the greatest impact on desirable changes in fiber properties, while minimizing deposition in areas having the greatest impact on undesirable properties.

The cuticle of wool fibers contains a high proportion of sulfur-rich proteins, which are crosslinked. The cuticle acts as a tough armorlike covering which protects the low-sulfur proteins of the cortex from abrasion damage. Areas of cuticle may become worn away during abrasion so that they are unable to protect the cortex from further damage. However, the abrasion resistance of such fibers conceivably could be restored, if a polymer were deposited so that it filled the areas where cuticle was absent. In addition, if polymer deposition could be restricted only to these areas, a minimum increase in stiffness or other undesirable properties of the whole fiber would result.

The goal of this research was to develop a finishing process that would allow polymerization of a monomer in areas where cuticle has been damaged but would not allow polymerization of monomer elsewhere on the fibers, so that abrasion resistance would be increased with a minimum change in other textile properties. The general class of monomers suitable for this process should be capable of participating in two different reactions. One reaction involves placing monomer in desired areas (exposed cortex) of the fibers. The second reaction involves reaction of these monomer molecules with one another.

These reactions are illustrated in Figure 1. The first step of the procedure involves dipping the fibers in a liquid containing the monomer under conditions that encourage reaction between the monomer and exposed cortical protein but not between the monomer and the cuticle. This is illustrated in Figure 1 by the formation of covalent bonds between exposed cortex and the functional group of the monomer labeled A. The second step is rinsing unreacted monomer from the fiber. This involves removing most of the monomer from cuticle material where bonds between A and wool protein have not formed but leaving monomer in the areas of exposed cortex where bonding has occurred. In the third step, the monomer bonded to the cortex is cured by heating at a temperature above the polymerization initiation temperature of the remaining monomer to cause bond formation between monomers. This is illustrated in Figure 1 by bonding between B groups. Figure 2 shows how this might be used in a commercial application, where it would involve a pad, rinse, cure/dry sequence.

A specific class of commercially important reagents suitable for this process are acrylic derivatives. Many of these reagents are capable of acylating wool, where the carbonyl moiety

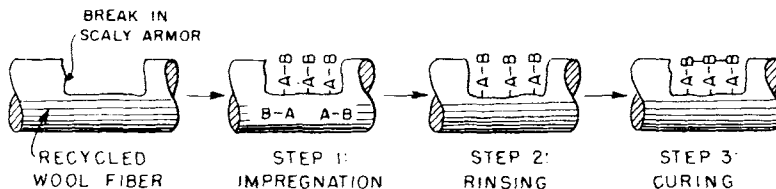


Fig. 1. Illustration of reaction of monomer with abraided wool.

would serve as the A functional group in the general example provided. A number of acrylic and related compounds have been condensed with wool, including ethyl acrylate, acryl chloride, *N*-carbonyl maleimide, and maleic anhydride.⁴ Many other reagents differing considerably in structure and reactivity are known to acylate wool, including activated esters,⁵ and aliphatic carboxylic acid chlorides.⁶

Once a compound is condensed on wool by reaction with one functional group, the double bond is available for addition polymerization with other condensed monomers. Methyl acrylate was used in this study since other studies indicated this monomer should be capable of both acylation and vinyl polymerization. Tetravalent cerium was chosen for initiation and it is presumed that both graft copolymerization as well as homopolymerization occur, although copolymerization would be expected to be favored with this process where most unbonded monomer is removed by thorough rinsing.

EXPERIMENTAL

Finish Application. A woven 100% reused wool fabric having a nominal area density of 16 oz/yd² was padded through a constantly stirred finishing formulation at 50°C using two dips and two nips on a three-roll laboratory padder with a squeeze pressure of 40 psi to a wet pickup of 80–100%. The pad bath contained the following components: 600 mL methyl acrylate; 5.0 g ceric ammonium sulfate; 40 mL Triton X-100 (nonionic surfactant); 50 mL concentrated sulfuric acid; and 5000 mL distilled water. This formulation was intended to encourage acid-catalyzed acylation of wool by methyl acrylate followed by cerium-initiated vinyl polymerization. Surfactant was added to aid in mixing the methyl acrylate and water. After pad-applying the above solution onto the fabric, the fabric immediately was rinsed for 30–60 s in water, depending on the amount of polymer desired on the fabric. The fabric then was cured for 5 min in a microwave oven and subsequently allowed to dry at room temperature.

Physical Testing of Fabric. Fabric area density was determined using procedures designated in ASTM D3776-79,⁷ fabric thickness by ASTM D-1777-64,⁸ abrasion resistance by ASTM D4158-82,⁹ fabric tensile strength by ASTM D1682-64,¹⁰ and stiffness using an air-operated King Fabric Stiffness Tester.

Scanning Electron Microscopy (SEM). Six single wool fibers were removed from the untreated fabric and cut into two pieces. Each piece was labeled by sandwiching one end between a thin tantalum metal foil and then notching the foil in an identifiable way. The

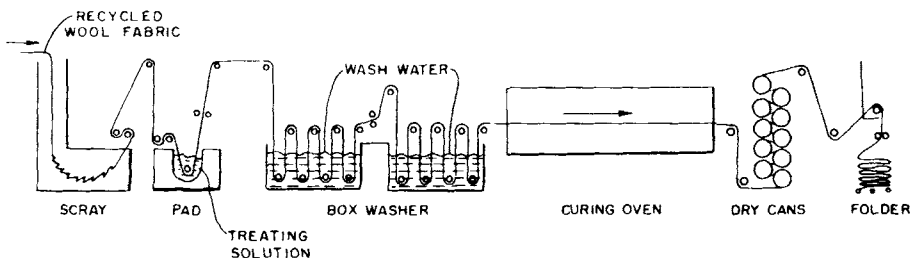


Fig. 2. Possible commercial application of polymerization process.

foils then were dipped into a solution of poly(methyl methacrylate) and chloroform, removed, and the solvent was allowed to evaporate. This was repeated until a thin film of poly(methyl methacrylate) covered each foil to mask the tantalum in order to prevent interference from it during staining. One half of each of the six single fibers was combined and treated with monomer while the other halves were treated identically except without monomer. These treatments were done similar to that described previously, except that a small beaker instead of the laboratory padder and a temperature of 25°C were used. A fabric sample measuring approximately 7.6 cm² (4 × 4 in.) also was placed into the beakers so that a measurement of weight gain could be obtained and was found to be 3.1%. After treatments, the fiber halves were stained with a Biuret reagent consisting of an aqueous solution of copper sulfate and sodium potassium tartrate.¹¹ Finally, the fiber halves were mounted on SEM stubs, evaporatively coated with carbon, and subjected to elemental analysis with an energy dispersive X-ray detector.

RESULTS AND DISCUSSION

Physical properties of the reused wool fabric as received, after being subjected to the finish application process described above except with monomer excluded, and after being subjected to the finish application described above with methyl acrylate monomer included are presented in Table I. This table includes data for two replications of the untreated fabric, three of the monomer-excluded treatment, and three of the monomer-included treatment. In Table II, changes in the average values of measurements from the monomer-excluded and monomer-included treatments are compared to the average values of these measurements from the untreated fabric.

The monomer-excluded treatment showed an average weight loss of 0.7% resulting from fiber loss during fabric treatment. On the other hand, the monomer-included treatment showed an average weight gain of 0.8%, reflecting the additional weight resulting from polymer formation in these samples. The average polymer add-on level, thus, was about 1.5%. The variation in weight gain among the treated samples was controlled by variation in the fabric rinse time. Weight gain was reduced by prolonging the fabric rinse time. This indicates that at least some of the monomer on the fabric prior to vinyl polymerization existed loosely bound rather than covalently bonded to wool protein. This monomer, however, would be expected to polymerize during the second reaction of the process along with covalently bound monomer. Fabric area density and thickness measurements indicated that fabric shrinkage occurred during treatment. The monomer-included treated fabric showed a slightly greater thickness and density which apparently reflects the presence of polymer finish.

TABLE I
Fabric Properties

Fabric treatment	Replication	Weight change (%)	Area density (oz/yd ²)	Thickness (cm)	Abrasion damage (% weight loss)	Tensile strength (lb)	Stiffness (kg)
Untreated	1	—	16.0	0.190	9.2	38.1	5.1
	2	—	16.4	0.188	9.0	38.0	5.7
	Average	—	16.2	0.189	9.1	38.1	5.4
Monomer excluded	1	-0.4	17.0	0.201	7.0	37.4	3.7
	2	-0.4	17.3	0.206	7.1	37.2	3.4
	3	-1.2	17.1	0.223	6.9	—	2.8
	Average	-0.7	17.1	0.210	7.0	37.3	3.3
Monomer included	1	0.5	17.3	0.206	6.0	35.1	3.6
	2	0.5	17.3	0.206	—	36.8	3.6
	3	1.4	17.3	0.231	5.8	—	2.8
	Average	0.8	17.3	0.214	5.9	35.9	3.3

TABLE II
Percent Change in Fabric Properties Resulting From Treatment

Fabrics compared	Area density	Thickness	Abrasion damage	Tensile strength	Stiffness
Untreated vs. monomer excluded ^a	5.5	10.7	-23.1	-2.1	-38.9
Untreated vs. monomer included ^b	6.8	12.0	-35.2	-5.8	-38.9

^a% change = [(monomer excluded - untreated)/untreated] × 100.

^b% change = [(monomer included - untreated)/untreated] × 100.

Fiber loss from the monomer excluded fabric during abrasion was 23.1% less than that from the untreated fabric (7.0 vs. 9.1%). This improvement more than likely resulted from lubrication of fibers in the fabric by the surfactant included in the pad formulation that remained on the fabric after rinsing. When the fabric was subjected to treatment that included monomer, average fiber loss was 35.2% less than that of the untreated fabric (9.1 vs. 5.9%). Thus, a substantial improvement in abrasion resistance results from the presence of a relatively small amount (1.5%) of poly(methyl acrylate) finish on the fabric.

Tensile strength of both treated fabrics decreased compared to the untreated fabric. The decrease for the monomer excluded fabric treatment probably resulted from lubrication of fibers by the surfactant included in the pad bath, since lubrication would cause increased fiber slippage during mechanical stress. Fabric tensile strength of the fabric treatment that included monomer was reduced even more than the treatment excluding monomer. One possible explanation for this is that the polymer finish had the effect of reducing interfiber friction so that fiber slippage occurred at a lower stress. The effect of polymer finish can be envisioned as smoothing the fiber surface, since abraided areas of the cuticle are partially filled with poly(methyl acrylate).

Stiffness of the untreated fabric was measured to be 5.4 kg and decreased for both treated fabrics to 3.3 kg. These decreases more than likely result from fiber lubrication. Most importantly, however, is the fact that the stiffness of fabrics treated with and without monomer are equal. Thus, presence of the polymer did not increase fabric stiffness measurably, even though abrasion resistance was improved substantially. This suggests that poly(methyl acrylate) was not formed in such a way that large areas of fiber surface were covered or fibers were attached together with polymer.

In an effort to obtain more direct evidence that poly(methyl acrylate) was localized to areas of exposed cortex, a staining technique was used with SEM X-ray analysis to locate poly(methyl acrylate) in the fibers. The stain selected exhibited great affinity for interior cortex, moderate affinity for cuticle, and no affinity for poly(methyl acrylate). An SEM X-ray analysis for copper in exposed cortex and cuticle adjacent to the exposed cortex was conducted on the fiber specimens after staining. If the treatment mechanism resulted in preferential location of poly(methyl acrylate) in areas of exposed cortex as desired, we expected less copper to be found in cortical areas of monomer-treated fibers compared to areas of untreated fibers, and we also expected to find little difference in amounts of copper in cuticle areas of both monomer-treated and untreated fibers.

Results of copper counts recorded for six fibers analyzing three pair of cortex/cuticle areas per fiber half are summarized in Table III. Data are shown as average integrated peak counts

TABLE III
X-ray Analysis of Copper Stained Fibers

Fiber location	Copper counts		Effect of monomer
	Monomer excluded treatment	Monomer included treatment	
Exposed cortex	1462	1069	393
Surface cuticle	412	376	36

of each area of the fibers. Statistical analysis of the data with a confidence level of 0.025 revealed no significant difference between the amounts of copper on the surface cuticles of the fibers treated with and without monomer (412 vs. 376) whereas there was a statistically significant decrease in copper in the exposed interior cortex of fibers treated with monomer compared to those treated without monomer (1462 vs. 1069). This indicates that treatment with monomer did not change the cuticle surface of the wool fibers, but it did change the areas of the exposed cortex in a significant way.

CONCLUSIONS

Measurements of fabric properties (weight, area density, thickness, abrasion damage, tensile strength, and stiffness) and SEM X-ray analysis of single fibers stained with copper indicate that polymerization of methyl acrylate was preferentially localized in areas of exposed cortex resulting from abrasion in recycled wool fibers. The process utilized was a pad, rinse, cure/dry treatment. Reactions presumed to be involved in the treatment are as follows: Treatment conditions were adjusted so that acylation of exposed cortex material occurred during padding but acylation of the relatively inert cuticle did not occur. Most of the unreacted monomer was rinsed from the fibers and then the fabric was heated to induce vinyl polymerization of the monomer double bonds.

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