

# Mechanical Reinforcement of Cotton Fabrics by Grafting Polymerization of Acrylics

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**ABSTRACT:** Grafting polymerization of acrylic monomers onto cellulose chains possesses a great potential for tailoring the properties of cellulose-based materials. In this article, some results concerning the grafting polymerization of ethyl acrylate/methyl methacrylate (EA/MMA) 75/25 wt % on cotton fabrics are reported. The effectiveness of the grafting process as a method for the mechanical reinforcement of cotton without any

modification of its handle is discussed. In addition, SEM observations were carried out to check the morphological modification occurring on cotton after the grafting reaction. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 372–377, 2010

**Key words:** graft copolymers; cellulose; mechanical properties; SEM

## INTRODUCTION

Cotton is one of the most common and versatile natural fibers, possessing several useful textile properties. It can undergo a variety of chemical modifications, with the aim of developing new cellulose-based products characterized by different chemical, physical, and mechanical properties in respect to those of the raw material. The introduction of polymeric chains onto the cellulose backbone leads to new structural characteristics; for example, new cellulose-based materials with improved mechanical properties to those of conventional ones can be developed.

Among the possible reactions, grafting polymerization possesses great potential for tailoring the material properties to specific end uses, because it allows to modify the fiber characteristics. Indeed, the properties of the grafted systems can be tailored by the chemical structure of the monomers, the length of the grafted segment and the grafting level.<sup>1</sup>

The grafting process photo-induced by UV radiations represents a very promising method to obtain grafted systems, as extensively reported in literature.<sup>2–4</sup> The use of low energy UV radiations during the grafting offers some advantages in respect to the application of  $\gamma$  rays, such as a reduced degradation of the backbone polymer and the control over the whole polymerization process, although high graft levels can be difficult to achieve.<sup>5–7</sup>

Graft copolymerization of vinyl monomers onto cellulose has been widely studied from several research groups.<sup>8,9</sup> Our previous investigations performed on linen and cotton fabrics demonstrated that graft polymerization of acrylic monomers, such as methyl methacrylate (MMA) and ethyl acrylate (EA) and their copolymers, confers different structural characteristics to the raw materials.<sup>10–16</sup> It is important to remember that a polymer used as reinforcement for textiles has to be just above its glass transition temperature at its service temperature, and so not in the glassy but in the viscoelastic state. If the grafted acrylic chains are in the viscoelastic state, the typical flexibility of cellulose may be retained and the recovery of the mechanical resistance is achievable.

However, MMA and EA were not suitable for cellulose-based materials. In the former case, due to the high glass transition temperature ( $T_g$ ) of the grafted poly(methyl methacrylate) (PMMA) chains, the treated materials were brittle and stiff,<sup>11</sup> whereas, in the latter, the samples were sticky due to the low  $T_g$  ( $-24^\circ\text{C}$ ) of poly(ethyl acrylate) (PEA).<sup>12</sup> Based on these results, the synthesis of new copolymers with characteristics suitable for cellulose consolidation was deemed necessary, along with further research into the grafting polymerization itself. In previous paper, we reported a detailed investigation regarding the optimum acrylic copolymer for the grafting onto cellulose.<sup>10,14</sup> We selected an EA/MMA copolymer 75/25 wt %, because it has a glass transitions ( $10^\circ\text{C}$ ) appropriate to the service temperature and it is resistant to biological attack.

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In the present research, the grafting polymerization of ethyl acrylate/methyl methacrylate (EA/MMA) 75/25 wt % on cotton fabrics was carried out to impart a mechanical reinforcement to the cellulose fibers when undergo a degradation due to the action of environmental agents, such as light, oxygen, humidity, and temperature. The grafting process was applied on naturally aged cotton samples as well.

To set up the grafting polymerization of acrylics onto the cellulose chains and also to better understand the weathering effect induced by the atmospheric oxygen, an artificially aging treatment was performed on raw cotton before the grafting reaction: the chemical oxidation with sodium metaperiodate ( $\text{NaIO}_4$ ). In this reaction, the oxidative agent attacks merely the C2–C3 bond on the glycosidic ring and converts the 1,2-dihydroxyl groups in two aldehyde groups, without modify the glycosidic bonds and without significant side reactions; the resulting product is the dialdehyde cellulose (DAC).<sup>17</sup> The carbonyl functions formed during the oxidative process on the raw cotton are the photosensitive groups that allow the formation of radical sites where the UV photo-induced grafting process starts. The naturally aged samples did not require any former oxidative treatment before the polymerization, because they already had the photosensitive sites formed during the natural weathering.

The effect of the grafted acrylic chains on the mechanical behavior of the cotton after its aging was studied as well. With this aim, the original, aged, and grafted cotton fabric samples were subjected to bending, shear, and tensile tests to highlight if the grafting process can allow the mechanical reinforcement of cotton fabric without any modification of its peculiar textile characteristics, in particular their "handle."<sup>18</sup>

## EXPERIMENTAL PART

### Materials

The cellulose substrates were cotton fabric manufactured by EMPA (Switzerland); the specimen size was 25 cm × 25 cm.

All the following reagents were commercial products supplied by Aldrich. The monomers, methyl methacrylate, and ethyl acrylate, contained the inhibitor hydroquinone monomethylether, which was removed by passing each monomer through an Aldrich "Inhibitor Removers" column; the purified monomers were subsequently stored at low temperature (4°C) in the dark. Sodium metaperiodate ( $\text{NaIO}_4$ ), acetone, and methanol were laboratory grade products and were used without further purification. Deionised water was used throughout the work.

## Methods

### Oxidation

The cotton samples were mixed in a closed vessel with the metaperiodate solution and the mixture was stirred gently at room temperature in the dark for the chosen time. At the end of the oxidation processes, the samples were filtered, washed with deionised water up to neutral conditions (pH 7), and dried. The ratio sample/solution was kept for all experiments 1 g of sample for 100 mL of water.

The cotton oxidation was carried out in  $\text{NaIO}_4$  solutions with concentration 0.1 M and 0.4 M for different times:

[ $\text{NaIO}_4$ ] 0.1 M for 2, 4, and 24 h

[ $\text{NaIO}_4$ ] 0.4 M for 4 and 24 h

with the aim to obtain "models" useful for investigating the different degradation levels occurring in a real material due to the action of the atmospheric oxygen.

### Natural aging

Cotton samples were also naturally aged. The natural weathering was conducted outdoors in Genova (Italy), in an urban area, where the local traffic is the only source of pollution. Samples were exposed to the south at an angle of 90° from horizontal, for 6 months (from November to May), characterized by sun, rain, and low temperature.

### Grafting reaction

The polymerization reaction was carried out on both naturally aged and chemically oxidized cotton, following the procedure reported elsewhere.<sup>12–14</sup>

The drawback of the graft polymerization is the simultaneous and inevitable formation of the ungrafted polymer constituted by both the EA and MMA homopolymers and EA/MMA copolymers with different compositions, on the basis of the reactivity ratio between EA and MMA and on the amount of monomers in the system throughout the reaction process. The ungrafted polymer is removed from the grafted material by extraction with acetone for 72 h at room temperature.

The quantity of graft monomer is evaluated as the weight increase of the sample after extraction of the homopolymer:

$$\% \text{ Graft Yields (GY)} = [(W_2 - W_1) \times 100] / W_1$$

where  $W_1$  is the initial weight of the sample and  $W_2$  is the grafted weight of extracted sample.

**TABLE I**  
**Low-Stress Mechanical Properties Measured**

Property	Symbol	Parameter	Unit
Bending	B	Bending rigidity	$\mu\text{N m}^2/\text{m}$
	2HB	Bending hysteresis	$\text{mN m}/\text{m}$
Shearing	G	Shear rigidity	$\text{N}/\text{m degree}$
	2HG	Shear hysteresis at shear angle $\phi = 0.5^\circ$	$\text{N}/\text{m}$
	2HG5	Shear hysteresis at shear angle $\phi = 5^\circ$	$\text{N}/\text{m}$

The grafting efficiency is defined as the ratio between the quantity of grafted monomer and the total polymerized monomer:

$$\% \text{ Grafting Efficiency (GE)} = [(W_2 - W_1)/(W_3 - W_1)] \times 100$$

where  $W_3$  is the dry weight of the polymerized sample before homopolymer extraction.

The amount of ungrafted polymer, including both the EA and MMA homopolymers and the EA/MMA copolymers, is quantified according to:

$$\% \text{ Ungrafted Polymer (UP)} = 100 - \% \text{ Grafting Efficiency}$$

#### Scanning electron microscopy (SEM)

All the samples were observed with a Stereoscan 440 Leica-Cambridge Scanning Electron (UK), linked with EDS microprobe Link-Gun Oxford (UK). The image analysis was performed applying the software Image J; the average diameter of fibers was evaluated after calibration of the image, measuring almost 50–60 fibers per image.

#### Mechanical characterization

The fundamental low-stress mechanical properties of the fabrics were measured by means of Kawabata's Evaluation System for Fabrics (KES-F) instruments

that simulate the modes of fabric deformation at the load level used when fabric is evaluated by hand.<sup>18</sup> The properties taken into consideration in this study are summarized in Table I, and grouped according to the Kawabata objective evaluation system for the fabric handle. Among the parameters measured by KES instruments associated with the attribute descriptors commonly used in subjective fabric evaluation, the bending and shear properties were selected because they are related to the fabric stiffness.<sup>19</sup> Indeed, at the beginning of this study, we supposed that grafting polymerization carried out on cotton fabrics could make them slightly stiffer than the original ones.

Before cutting and testing, each sample was conditioned under standard laboratory conditions ( $20^\circ\text{C} \pm 2^\circ\text{C}$  and  $65\% \pm 2\% \text{ RH}$ ) at least for 24 h; specimens of  $20 \text{ cm} \times 20 \text{ cm}$  were used, five for each treatment.

Moreover, the breaking load and elongation at break were evaluated by Instron dynamometer Model 6021 following the standard UNI EN ISO 12945-2.

## RESULTS AND DISCUSSION

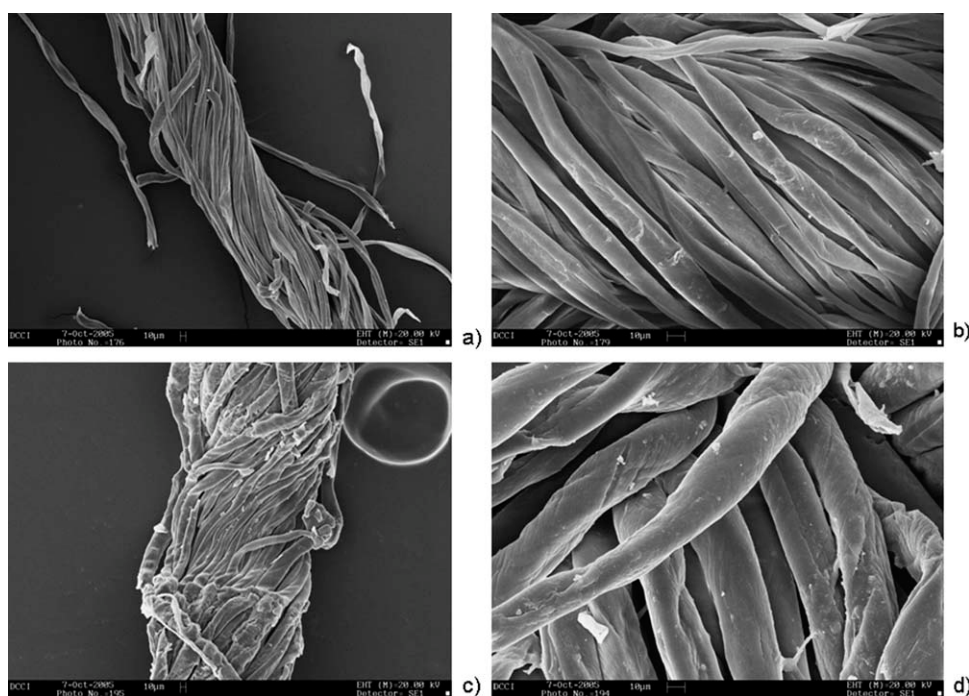
### Grafting polymerization

The first step of our study concerned the set up of the grafting process to establish the best polymerization conditions that allowed maintaining unaltered the typical flexibility of cotton fabrics, the so-called "handle."

Grafting of EA/MMA 75/25 wt % was carried out both on artificially oxidized and naturally aged cotton samples, exploring different polymerization conditions in terms of polymerization time and monomer/cellulose ratio, as shown in Table II. In all these experiments, grafting was favored in respect to the side reactions (homopolymerization and copolymerization) leading to the formation of ungrafted polymers, as detectable from the values of percent grafting efficiency.

**TABLE II**  
**Results of Grafting Process on Artificially and Naturally Aged Cotton Fabrics**

Cotton sample	Monomer/cellulose ratio	Polymerization time (h)	% GY	% GE	% UP
Oxidized with $[\text{NaIO}_4]$ 0.1 M for 2 h	2.5	4	66	81	19
Oxidized with $[\text{NaIO}_4]$ 0.1 M for 2 h	1.5	1	35	84	16
Oxidized with $[\text{NaIO}_4]$ 0.1 M for 4 h	2.5	4	72	78	22
Oxidized with $[\text{NaIO}_4]$ 0.1 M for 4 h	2.5	1	45	84	16
Oxidized with $[\text{NaIO}_4]$ 0.1 M for 24 h	2.5	4	27	80	20
Oxidized with $[\text{NaIO}_4]$ 0.4 M for 4 h	2.5	4	23	67	33
Oxidized with $[\text{NaIO}_4]$ 0.4 M for 24 h	2.5	4	2	47	53
Naturally aged	2.5	4	62	79	21
Naturally aged	1.5	1	30	88	22



**Figure 1** SEM micrographs of: (a) original cotton yarn [500 $\times$ ], (b) cotton fibers [1500 $\times$ ], (c) cotton yarn grafted with EA/MMA 75/25 [500 $\times$ ], and (d) cotton fibers grafted with EA/MMA 75/25 [1500 $\times$ ].

Concerning the artificially aged samples, the grafting yields strongly depended on the oxidation level of cotton; particularly, when high oxidation degrees were reached (by increasing the metaperiodate concentration and the oxidation time), the amount of grafted acrylic copolymer decreased. Looking at the grafting efficiency values, it is evident that, in these cases, the formation of ungrafted polymers is favored in respect to the grafting. This behavior can be ascribed to the oxidation mechanism: the periodate attack onto cellulose chain leads to the formation of clusters in which are present several carbonyl sites. Because these sites are very close to each others, the uptake and the subsequent grafting of acrylic monomers is hampered, leading to a remarkable decreasing of grafting yields.<sup>20</sup>

Preliminary mechanical tests allowed to exclude the oxidation with  $[\text{NaIO}_4]$  0.4 M for whatever time among the treatments suitable to artificially age the cotton fabric, because in these conditions too much high degradation levels were reached in the sample before the grafting and very low amounts of acrylics were grafted onto the cellulose fibers.

Therefore, we focused the set up of grafting process on the fabrics oxidized with periodate 0.1 M, varying the oxidation time between 2 and 4 h. Grafting was carried out for different polymerization time (1 and 4 h), reducing the monomer/cellulose ratio from 2.5 to 1.5, to reach grafting yields that did not alter the visual aspect of cotton fabrics.

Considering the samples oxidized for 4 h, the grafting yields decreased with the polymerization

time from 72% to 45%, but the grafted fabrics lost their typical flexibility. On the contrary, reducing the oxidation level (oxidation time equal to 2 h), the polymerization time (to 1 h), and the monomer/cellulose ratio (to 1.5), it has been possible to obtain the lowest grafting yields (35%), keeping unaltered the typical flexibility of cotton.

The typical “handle” of naturally aged cotton fabrics was kept, decreasing both the polymerization time at 1 h and the monomer/cellulose ratio to 1.5; in this case, grafting yields equal to 30% were reached.

### SEM observations

SEM observations were carried out to check the morphological modifications induced on cotton fabrics by both the metaperiodate oxidation and the grafting process.

In Figure 1(a,b), the SEM micrograph of the original cotton is reported, in which the typical “ribbon like” morphology is immediately detected; the average diameter of fibers is 12  $\mu\text{m}$  (SD = 2.3). Periodate oxidation does not modify the cotton morphology, but induce a slight increase of fiber diameter, especially at high oxidation levels (17  $\mu\text{m}$ , SD = 3.0, for cotton oxidized with  $[\text{NaIO}_4]$  0.4 M for 4 h), coupled with a small reduction of fiber length. This result suggests that the cotton fibers undergo a progressive shrinkage when oxidized with  $\text{NaIO}_4$ .

When EA/MMA 75/25 is grafted [Fig. 1(c,d)], the morphological characteristics of cotton fibers are still



**TABLE III**  
Density Values for Original, Oxidized, and Grafted Cotton Fabrics

Treatment	Area (cm <sup>2</sup> )	Weight (g)	Density (g/m <sup>2</sup> )
[NaIO <sub>4</sub> ] = 0.1 M for 4 h			
Original cotton	97.0	1.067	110
Oxidized	92.2	1.099	120
Grafted	87.4	1.300	150
[NaIO <sub>4</sub> ] = 0.1 M for 24 h			
Original cotton	101.0	1.127	110
Oxidized	91.2	1.174	130
Grafted	89.3	1.478	160
[NaIO <sub>4</sub> ] = 0.4 M for 4 h			
Original cotton	97.0	1.081	110
Oxidized	89.2	1.137	130
Grafted	83.7	1.380	170
[NaIO <sub>4</sub> ] = 0.4 M for 24 h			
Original cotton	103.0	1.145	110
Oxidized	67.2	1.231	180
Grafted	66.4	1.254	190

visible, even if the graft chains swell the diameter of the fiber by about 50%, as it has been measured (average diameter = 32, SD = 5.0). This result supports the bulk grafting of EA/MMA chains onto cellulose.<sup>13</sup>

The fibers shrinkage detected by SEM was quantified by measuring the weight and size variation of fabrics after oxidation and grafting; in this way, a relationship between shrinkage and stiffness could be hypothesized.

Values of area, weight, and density are summarized in Table III; in all cases, the grafting process was carried out for 4 h, keeping the monomer/cellulose ratio equal to 2.5.

Periodate oxidation induces a density increase, especially at higher NaIO<sub>4</sub> concentration and for prolonged treatment times; this numerical data confirms the observed shrinkage and stiffness in the cotton, particularly marked in the sample oxidized with [NaIO<sub>4</sub>] 0.4 M for 24 h that lost its typical flexibility and aspect.

The effect of grafting on the fabric density is strictly related to the amount of grafted polymer

onto cellulose chains; when the grafting yields are about equal to 20–30%, an increase of 3–4% of density in respect to the oxidized sample was observed; whereas in the case of the lowest grafting yield (2%), the density of both the grafted and oxidized cotton are comparable.

### Mechanical characterization

In Table IV, the values of bending and shear properties measured on both the oxidized and naturally aged cotton fabrics are reported. The more is the artificially aging process become stronger, the more is the bending B and shear G rigidities improve. In the case of the cotton fabric oxidized with [NaIO<sub>4</sub>] 0.4 M for 24 h, the KES-F bending meter was not able to measure the bending rigidity B and the bending hysteresis 2HB because, in this condition, the fabric lost completely its textile characteristics.

Results show that the artificial aging by oxidation leads to an increase of the fabric stiffness, valuable whether by touching the textile structure, and by looking at the increase of bending rigidity B. In any case, the oxidation with [NaIO<sub>4</sub>] 0.1 M for 2 h is the artificial aging treatment closer to the natural aging; indeed, except the bending rigidity, all the other measured mechanical parameters are quite similar (Table IV).

The bending, shear, and tensile properties of grafted cotton fabrics are collected in Table V. The grafting polymerization of EA/MMA 75/25 for 4 h (monomer/cellulose ratio 2.5) on the naturally aged cotton leads to the greatest increase of the bending and shear properties in respect to the original and naturally aged fabrics: in terms of bending rigidity, we observe an increase of +133% in respect to the original one and +423% in respect to the naturally aged cotton. In terms of shear rigidity, the observed increases are +98% and +291%, respectively. These data indicate that the grafting process performed with high monomer/cellulose ratio and for long time leads to a stiff fabric that has lost completely its peculiar textile characteristics.

**TABLE IV**  
Bending and Shear Properties for the Original, Oxidized, and Naturally Aged Cotton Fabrics

Cotton sample	B (mN m/m)	2HB (N/m)	G (μN m <sup>2</sup> /m)	2HG (N/m degree)	2HG5 (N/m)
Original	10.954	1.071	2.950	4.602	11.833
Naturally aged	4.878	0.483	1.495	2.582	6.506
Oxidized with [NaIO <sub>4</sub> ] 0.1 M for 2 h	8.588	0.590	1.748	2.319	6.344
Oxidized with [NaIO <sub>4</sub> ] 0.1 M for 4 h	12.815	0.841	2.969	3.735	8.423
Oxidized with [NaIO <sub>4</sub> ] 0.1 M for 24 h	19.268	0.755	3.088	1.654	7.007
Oxidized with [NaIO <sub>4</sub> ] 0.4 M for 4 h	21.878	0.871	3.513	1.904	8.417
Oxidized with [NaIO <sub>4</sub> ] 0.4 M for 24 h	n.d.	n.d.	15.753	22.73	35.57

**TABLE V**  
**Bending, Shear, and Tensile Properties of the Original, Naturally Aged, and Grafted Cotton Fabrics**

Cotton sample	B ( $\mu\text{N m}^2/\text{m}$ )	2HB ( $\text{mN m}/\text{m}$ )	G ( $\text{N}/\text{m degree}$ )	2HG ( $\text{N}/\text{m}$ )	2HG5 ( $\text{N}/\text{m}$ )	Breaking load (N)	Elongation at break $\text{g}/\text{m}^2$ (%)	Weight ( $\text{g}/\text{m}^2$ )
Original	10.954	1.071	2.950	4.602	11.833	447	5.8	107
Naturally aged	4.878	0.483	1.495	2.582	6.506	378	6.6	111
Grafted with EA/MMA 75/25 ( $t = 1$ h, $m/c = 1.5$ )	13.175	1.330	3.239	4.501	9.814	436	9.8	146
Grafted with EA/MMA 75/25 ( $t = 4$ h, $m/c = 2.5$ )	25.491	2.746	5.843	14.791	17.065	420	13.6	205

On the contrary, considering the fabric grafted with EA/MMA 75/25 for 1 h (monomer/cellulose ratio = 1.5), the measured bending and shear values are comparable with those of the original cotton. This means that, after the grafting polymerization, the peculiar textile characteristics was kept essentially unaltered; only a slight increase of stiffness in respect to the original cotton is observed. Moreover, the grafting process imparts mechanical resistance to the cellulose fibers, as showed by the increase of the breaking load for the grafted samples in respect to the value of naturally aged fabric; the breaking load of both the original and grafted samples are quite similar (Table V).

### CONCLUSIONS

Photo-induced grafting copolymerization of acrylic monomers onto cotton fabrics provides an effective tool for modifying the mechanical properties of the cellulose backbone.

Particularly, by choosing polymerization conditions that leads to not too much amount of grafted acrylic chains, it is possible to reinforce the cotton fabrics maintaining its peculiar textile characteristics. The grafting process allows an effective recovery of both the bending rigidity and the breaking load of the aged fabrics that become equal or superior to those of the original cotton.

These evidences indicate the possibility to apply the grafting process onto cotton fabrics for different end uses that involve the necessity to have materials characterized by high mechanical resistance, but without any modification of their typical flexibility

It is worth to note that the artificial aging by metaperiodate oxidation is not able to exactly simulate the weathering effect induced by the atmospheric oxygen. Indeed, the oxidation has a more remark-

able degradative action onto the cellulose fibers than the natural aging.

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