

# New Polymeric Materials for Paper and Textiles Conservation. II. Grafting Polymerization of Ethyl Acrylate/Methyl Methacrylate Copolymers onto Linen and Cotton

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**ABSTRACT:** In the preservation of Cultural Heritage items, the use of polymeric materials for the consolidation and protection of artifacts with historical and artistic value is widely accepted, except for cellulose-based materials, since here there are no suitable products and appropriate application techniques. Grafting polymerization of acrylic monomers onto cellulose chains represents an innovative method of restoration for both artificially and naturally aged textiles. In this article, some results concerning the grafting polymerization of ethyl acrylate/ethyl methacrylate 75/25 and ethyl acrylate/methyl methacrylate/tri-

fluoroethyl methacrylate 73/24.5/2.5 polymers onto linen and cotton are reported. The effectiveness of grafting polymerization as a method for textiles conservation is discussed. The consolidating and protective effects were investigated by evaluating the mechanical properties and the wetting behavior of the grafted samples, and comparing them with the original and aged substrates. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 90–99, 2007

**Key words:** acrylics; grafting polymerization; linen; cotton; ESEM

## INTRODUCTION

The use of polymeric materials for the consolidation and protection of cellulose-based textiles is uncommon and only a small number of studies have been carried out.<sup>1,2</sup> Polymers have been applied in a few cases when traditional restoration methods were not sufficient to improve the mechanical resistance of the degraded artifacts; usually the materials employed are commercial products, with properties not tailored for the conservation of textiles. Starting from these considerations, in our laboratory new acrylic products and an innovative technique for the conservation of cellulose-based textiles have been investigated, to develop a more appropriate method of intervention. Among the various treatments used to improve the properties of natural fibers, the synthesis of graft copolymers<sup>3</sup> seems a suitable method to reduce the ageing phenomena of textiles.<sup>2</sup> The properties of the grafted copolymer can be tailored by the chemical structure of the monomers, the length of the grafted segment, and the grafting level.<sup>4</sup>

Graft polymerization can induce chemical changes in cellulose and the introduction of polymer chains

can confer different structural characteristics to the raw material. In this way new cellulose-based products can be obtained with mechanical properties better than the conventional cellulose. Graft copolymerization of vinyl monomers onto cellulose has been previously investigated,<sup>5,6</sup> acrylic monomers appear particularly suitable because of their characteristics, such as water-repellence, transparency, and good filmability. Grafting directly from the vapor phase onto cellulose results in enhanced mechanical resistance of degraded textiles, without altering the typical flexibility of cellulose and, importantly, no superficial coatings are formed on the grafted samples.<sup>7–9</sup>

Previous studies have shown that monomers such as methyl methacrylate (MMA) and ethyl acrylate (EA) were not suitable for cellulose-based materials. In the former case, because of the high glass transition temperature ( $T_g$ ) of the grafted poly(methyl methacrylate) (PMMA) chains, the treated materials were brittle and stiff,<sup>7</sup> while in the latter the samples were sticky due to the low  $T_g$  ( $-24^\circ\text{C}$ ) of poly(ethyl acrylate) (PEA).<sup>8</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 a previous study,<sup>10</sup> we reported a detailed investigation regarding the optimum acrylic copolymer for the grafting onto cellulose. We selected a

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EA/MMA copolymer 75/25 wt %, because it has a glass transitions (10°C) appropriate to the service temperature and it is resistant to biological attack. By adding a fluorinated termonomer in small amounts, as reported in a earlier study,<sup>11</sup> the water repellence should be improved without modifying the characteristics of the product.<sup>10</sup>

In the present research, grafting polymerization of EA/MMA 75/25 wt % onto linen and cotton fabrics, both artificially and naturally aged, was performed. Since the introduction of fluorine into polymers improves chemical, thermal, and photochemical stability<sup>12</sup> due to the strength of the C—F bond (485 kJ/mol), and also induces hydrophobicity due to the lowered surface energy,<sup>13–15</sup> a commercial fluorinated monomer, 2,2,2-trifluoroethyl methacrylate (TFEMA), was added. Grafting polymerization of the mixture EA/MMA/TFEMA at 73/24.5/2.5 wt % composition was thus carried out to improve the water repellence of the textiles.

To initiate grafting, the creation of free radicals on the cellulose chain is necessary and in this study polymerization is induced by UV light. Because of its low energy, UV radiation offers advantages, such as a reduced degradation of the backbone polymer and a better control over the process compared to other type of radiation, such as  $\gamma$ -rays or X-rays.<sup>2,16–20</sup> The grafting reaction requires photosensitive sites on the cellulose to allow the formation of the radical sites. These were formed by artificial ageing by reaction with a specific oxidizing agent (sodium methaperiodate).<sup>21–24</sup> In this way the glucosidic units are oxidized to dialdehydic groups, which then act as photosensitive agents. UV radiation transforms the carbonyl groups at these sites where radical polymerization subsequently starts.

The assessment of the effectiveness of grafting polymerization as a method for textiles conservation is discussed within the framework of a systematic approach to the problem. The consolidating effect was examined by evaluating the mechanical behavior of the grafted samples, comparing original, aged, and polymerized substrates. The wetting behavior and the protective effect were studied in terms of an increase in the water repellence due to the grafting, as shown by environmental scanning electron microscopy (ESEM) observation.

## EXPERIMENTAL

### Materials

The cellulose substrates were linen *Artemisia* and cotton *Ghinea*, fabrics by Zecchi (Italy). Reagents were commercial products supplied by Aldrich (Milwaukee, WI). Monomers [methyl methacrylate (MMA), ethyl acrylate (EA), and 2,2,2-trifluoroethyl methacrylate (TFEMA)] contained an inhibitor (hydroquinone

monomethylether), which was removed by passing each through an Aldrich "Inhibitor Removers" column; the purified monomers were subsequently stored at low temperature (4°C) in the dark. Sodium methaperiodate (NaIO<sub>4</sub>), acetone and methanol were laboratory grade products and were used without further purification. Deionized water was used throughout the work.

### Artificial ageing of cellulose

With the intent of reproducing the natural oxidative ageing of cellulose<sup>25</sup> an oxidative reaction with sodium methaperiodate was carried out on cotton and linen before the grafting process. Periodate oxidation is a highly specific reaction that cleaves the C2—C3 bond of the glucosidic ring and converts the 2,3-dihydroxyl groups into two aldehyde groups without significant side reactions.<sup>26</sup> The oxidized samples become "models" to investigate the different levels of degradation in real materials. To investigate the behavior at different level of oxidation, the samples were treated with different solutions of sodium methaperiodate and for different times:

Cotton: [NaIO<sub>4</sub>] 0.1M for 4 h

Linen: [NaIO<sub>4</sub>] 0.1M for 2 h and [NaIO<sub>4</sub>] 0.4M for 1 h

The ratio of sample solution was kept at 1 g : 100 mL for all experiments. At the end of the oxidation period the samples were washed with deionized water to neutral conditions and dried.

### Natural ageing of cellulose

Cotton and linen were also naturally ageing. The natural weathering was conducted outdoors in Genova (Italy), in a green area close to the sea, 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 March to September), characterized by sun, no rain, high temperature, and high humidity.

### Viscosity measurements

To obtain the degree of polymerization (DP) of artificially and naturally oxidized textiles, measurements of intrinsic viscosity were performed in cuproethylendiamine (CED). To avoid the fast degrading effect due to oxygen, the solution was prepared by treating the dry samples with CED in a closed vessel under nitrogen and continuous stirring. Viscosity [ $\eta$ ] was measured using a Ubbelöviscometer and the DP obtained from

$$DP = K[\eta]^a \quad (1)$$

where  $K$  and  $a$  are experimental constants.<sup>27</sup>

### Grafting reaction

The photoinitiated grafting reaction was carried out on both naturally and artificially aged textiles. Cellulose samples, after drying in oven, were swollen in deionized water for 24 h to open up the fibrous structure of cellulose and encourage homogeneous uptake of monomers during grafting.<sup>7</sup> This suitable time of swelling was chosen after water absorption tests. The wet samples were placed in the quartz reaction vessel (volume 10 L), which was evacuated for a short time so that the fabrics were still damp, then the liquid monomers mixture was loaded, vaporized, and diffused into the reactor. Two different monomers mixtures were employed: EA/MMA 75/25 wt % and EA/MMA/TFEMA 73/24.5/2.5 wt %.

As found previously,<sup>9</sup> the best monomer to cellulose ratio is 2.5 mmol of acrylic per gram of sample, and this was also used here. Subsequently the whole unit was exposed at room temperature to UV radiation from a mercury vapor lamp (400 W, with complete spectrum emission from 180 nm to visible light), placed at 60 cm from the reactor, so that no cooling system was required. The polymerization was stopped after 4 h by bringing the reactor up to room pressure.<sup>9</sup> Nonreacted monomer was removed by washing the fibers with a mixture methanol–water (30/70 vol), a good solvent for acrylic monomers but not for the polymers. After this the sample containing grafted cellulose and homopolymer was filtered and brought up to constant weight.

The drawback of the graft polymerization is the simultaneous and inevitable formation of homopolymer; this was removed from the grafted material by extraction with acetone for 72 h at room temperature.<sup>4,28</sup> The percentage of synthesized polymer during grafting reaction is calculated as follows:

$$\% \text{ Polymer Loading (PL)} = [(W_2 - W_1) \times 100] / W_1 \quad (2)$$

where  $W_1$  is the initial weight of the sample and  $W_2$  is the dry weight of the polymerized sample before homopolymer extraction. The quantity of grafted monomer is evaluated as the weight increase of the sample after extraction of the homopolymer:

$$\% \text{ Graft Yields (GY)} = [(W_3 - W_1) \times 100] / W_1 \quad (3)$$

where  $W_3$  is the grafted weight of extracted sample. The grafting efficiency is defined as the ratio between the quantity of grafted monomer and the total polymerized monomer:

$$\% \text{ Grafting Efficiency (GE)} = [(W_3 - W_1) / (W_2 - W_1) \times 100] \quad (4)$$

and the amount of homopolymer is quantified according to:

$$\% \text{ Homopolymer (HOMO)} = 100 - \% \text{ Grafting Efficiency} \quad (5)$$

### Differential scanning calorimetry

Differential scanning calorimetry (DSC) was used to detect the glass transition temperature ( $T_g$ ) of the grafted acrylic copolymer. A TA Instruments DSC 2010 differential scanning calorimeter was used at a heating rate of 20°C/min; traces were recorded in the temperature range from –100 to 170°C under a nitrogen atmosphere. To eliminate any effect of thermal history and the typical moisture content of cellulose,<sup>29</sup>  $T_g$  measurements were made from a second heating cycle after heating the sample to 200°C at 20°C/min, followed by quenching to –100°C.

### Mechanical analysis

Dynamic mechanical analysis was carried out using a TA Instruments DMA 2980 dynamic mechanical analyzer. The samples were run in the tension mode, operating at an oscillating frequency of 3 Hz and a heating rate of 2°C/min under nitrogen. Samples were ~ 10 mm wide, 20 mm long, and 0.3 mm thick.  $\tan \delta$  was recorded in the temperature range from –50 to 100°C.

Tensile measurements on yarns gathered from the grafted samples were performed on an Instron tensile tester. Young's modulus ( $E$ ), stress ( $\sigma$ ), and elongation ( $\epsilon$ ) at break were evaluated at room temperature. Yarns were ~ 60–70 mm long and with a diameter of 0.20–0.25 mm. The load cell sensitivity was 0.038 N/mV and samples were tested at 8 mm/min draw rate until breakage. An average of 15 tests for type specimens was used to calculate the tensile properties.

### Environmental scanning electron microscopy

The ESEM, in conjunction with water vapor as the imaging gas, allows an accurate control of a sample's relative humidity through manipulation of temperature and pressure. This feature makes it possible to condense water droplets on the specimen surface and to observe the wetting process on the specimens.<sup>30</sup> Untreated and grafted cotton and linen yarns were observed by means of a Philips XL30 ESEM. Sample was placed on the stage; no treatment before the observation was required. The wet mode was selected from the ESEM controller and the chamber was pumped to 6 Torr. Images were acquired at a temperature of 7°C, since this minimized the risk of accidental freezing.<sup>31</sup> Chamber pressure was then increased

TABLE I  
DP Values for Artificially and Naturally Aged Cotton and Linen

	Ageing treatment	DP
Cotton	Untreated	2130
	Oxidized NaIO <sub>4</sub> 0.1M 4 h	140
	Naturally aged	460
Linen	Untreated	1900
	Oxidized NaIO <sub>4</sub> 0.1M 2 h	190
	Oxidized NaIO <sub>4</sub> 0.4M 1 h	130
	Naturally aged	255

by 0.5 Torr increments. As relative humidity reached 100% ( $\approx 7.5$  Torr), water condensed onto the surface of the sample. Observations of water droplets on fibers were carried out at each point of interest.

### Water repellence

To evaluate any protective effect of the grafting polymerization onto cellulose-based materials, a water absorption test was carried out. The test was performed on three specimens ( $2 \times 1$  cm<sup>2</sup>) of each sample of linen and cotton to ensure reproducibility:

Untreated samples (blank)

Oxidized samples

Grafted samples with EA/MMA and EA/MMA/TFEMA

using a gravimetric sorption technique. Each fabric specimen is soaked in deionized water; the amount of water absorbed is determined by weighing the specimen after 10, 20, 30, 40, and 50 min and 1, 2, 3, 4, 5, 6, 8, 24, and 48 h, to obtain the wet specimen mass ( $\pm 0.0001$  g). The amount of absorbed water  $Q_i$  at the time  $t_i$  is defined as

$$Q_i = (M_i - M_0)/M_0 \quad (6)$$

where  $M_i$  is the specimen mass (g) at the time  $t_i$  and  $M_0$  is the dry specimen mass (g). The  $Q_i$  values are plotted against the time to give the water absorption curve; by comparing untreated and grafted materials, the improvement of water repellence can be evaluated.

## RESULTS AND DISCUSSION

### Grafting reaction

Initially a comparison between natural and artificial ageing on cellulose was performed by measurements of the polymerization degree (DP) before and after each ageing treatment (see Table I). In this way it is possible to evaluate the level of degradation of the samples employed in the grafting process.

Untreated cotton has a DP of 2130; after 4 h of oxidation with NaIO<sub>4</sub> 0.1M, this decreases markedly to 140. Untreated linen shows a DP similar to cotton ( $\sim 1900$ ), and it also decreases to lower values when the material is oxidized with high concentrations of sodium metaperiodate over a long time. Therefore the methaperiodate oxidation brings about a strong depolymerization of cellulose, similar to that in linen and cotton fabrics.<sup>32</sup> During natural ageing the DP also decreased through exposure to the weather, but the effect (on the time-scale used) appears less with respect to the artificial oxidation. After 6 months, cotton shows a DP of 460, whereas linen is lower (255); confirming that linen undergoes a stronger degradation than cotton under the same conditions, as observed previously.<sup>32</sup> The results demonstrate that a natural ageing of 6 months leads to a level of degradation for linen comparable to that obtained with the milder oxidation conditions; for cotton even weaker oxidation would be necessary to achieve the same condition as for natural weathering. Nevertheless, the degradation level of oxidized samples submitted to the grafting process is broadly similar to that of naturally aged fabrics.

Grafting was carried out onto naturally and artificially aged linen and cotton, and Tables II and III report the grafting yields obtained from the two monomer mixtures, EA/MMA 75/25 wt % and EA/MMA/TFEMA 73/24.5/2.5 wt %. It is evident that the reaction of EA/MMA 75/25 leads to higher yields for oxidized cotton with respect to linen, as already observed in previous studies.<sup>9</sup> This effect is possibly due to the presence of lignin in linen (2%),<sup>33</sup> which could act as inhibitor for the grafting process.<sup>34</sup> With the more strongly oxidized linen more glucosidic units are converted to dialdehydic groups that can act as radical sites for the UV polymerization.<sup>33</sup> Notwith-

TABLE II  
Grafting Yields for Naturally and Artificially Aged Cotton and Linen Grafted with EA/MMA 75/25

Sample	Grafting yield (%)	Grafting efficiency (%)	Homopolymer (%)
Cotton oxidized NaIO <sub>4</sub> 0.1M 4 h	66	79	21
Cotton naturally aged	49	81	19
Linen oxidized NaIO <sub>4</sub> 0.1M 2 h	36	82	18
Linen oxidized NaIO <sub>4</sub> 0.4M 1 h	32	78	22
Linen naturally aged	45	71	29



**TABLE III**  
**Grafting Yields for Naturally and Artificially Aged Cotton**  
**and Linen Grafted with EA/MMA/TFEMA 73/24.5/2.5**

Sample	Grafting yield (%)	Grafting efficiency (%)	Homopolymer (%)
Cotton oxidized NaIO <sub>4</sub> 0.1 M 4 h	49	76	24
Cotton naturally aged	37	82	18
Linen oxidized NaIO <sub>4</sub> 0.1M 2 h	26	82	18
Linen oxidized NaIO <sub>4</sub> 0.4M 1 h	28	70	30
Linen naturally aged	35	81	19

standing that more sites for the grafting process are present, the grafting yields do not increase; this effect is not easily explained and could be due to the termination step of the polymerization.

Comparing naturally aged linen and cotton, the trend of grafting yields is similar to that of the artificially aged samples. In all cases the percentage of homopolymer is not high, it is about 20%. Regarding grafting using the monomer mixture EA/MMA/TFEMA 73/24.5/2.5, an equivalent trend in grafting yields and homopolymer formation is observed, as described above (see Table III). Comparing the grafting yields obtained using the two monomers mixtures, EA/MMA and EA/MMA/TFEMA, it is evident that a small decrease occurs in presence of the fluorinated monomer.

It is important point out that the grafting process does not modify the aspect of the fabrics and this is one of the main aspect for a future application of this method for the restoration of objects with historical and artistic interest.

### Differential scanning calorimetry

All grafted fabrics were analyzed by DSC to detect the glass transition temperature of the acrylic copolymer and thus establish if the graft polymerization process has indeed occurred. No  $T_g$  was observed for the cellulose in the scan temperature interval used; unsurprising since it is known that the cellulose  $T_g$  is difficult to detect unless particular scan conditions are employed.<sup>35</sup> Its vinylic copolymers all present a glass transition near room temperature, which is attributed to the acrylic grafted chains. For the EA/MMA 75/25 copolymer  $T_g$  this is about 10°C, the same as obtained for the nongraft copolymer,<sup>10</sup> and such a value gives flexibility to the cellulose-based materials. The corresponding fluorinated terpolymer grafts shows a comparable  $T_g$ ; therefore, the addition of a small percentage of fluorinated monomer to the polymerizing mixture does not modify the glass transition temperature of the polymer to any great extent.

### Dynamic mechanical analysis

DMA measurements on ungrafted and grafted cellulose were performed, and the variation of  $\tan \delta$  and

apparent storage modulus ( $E'$ ) with temperature for original and grafted cotton with EA/MMA are plotted in Figure 1. No distinct transition appear for the untreated cellulose in this scan interval, since its major mechanical relaxations is known to occur at different temperatures.<sup>36</sup> In contrast,  $\tan \delta$  of the grafted samples show pseudosymmetrical curves, as exemplified in the figure, with a peak indicative of a single relaxation, which is assigned to the glass transition of the graft chains at about 22°C. The  $\tan \delta$  maximum is accompanied by a distinct reduction in modulus for the grafted samples. The  $T_g$  values obtained by mechanical analysis are slightly higher than DSC in accord with expectation.<sup>37</sup>

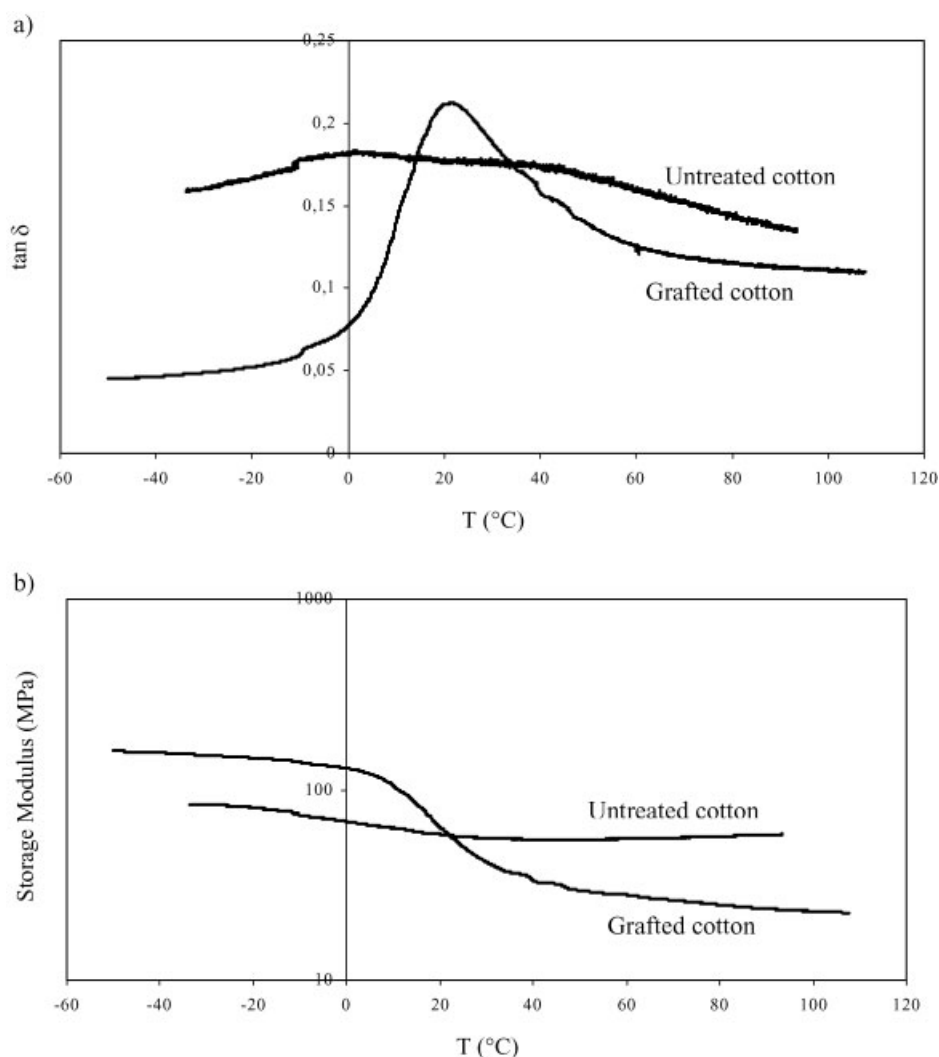
The presence of the fluorinated monomer in the graft system EMA/MA/TFEMA does not modify the dynamic mechanical behavior when compared to that of the corresponding EA/MMA mixture.

### Tensile testing

The stress-strain behavior of original, aged, and grafted textiles was measured by tensile deformation; all samples were tested to breaking. Young's modulus ( $E$ ), stress ( $\sigma_B$ ), and elongation ( $\varepsilon_B$ ) at break for the cotton and linen yarns are collected in Tables IV and V, respectively.

Cotton oxidized with 0.1M sodium methaperiodate exhibits a 50% reduction in the stress at break and a 10% reduction in elongation at break, and Young's modulus decreases markedly. Natural aged cotton shows comparably reduced values of  $\sigma_B$ ,  $\varepsilon_B$ , and  $E$ . By grafting with EA/MMA and EA/MMA/TFEMA, artificially aged cotton becomes more flexible, as evidenced by the elongation at break and Young's modulus values. The naturally aged samples show the same mechanical behavior, albeit with lower  $\varepsilon_B$  values.

The tensile properties of untreated linen yarns exhibit higher values of  $E$  and  $\sigma_B$  with respect to cotton; it is well known that, among cellulosic materials, linen shows good mechanical properties and a high resistance to stress.<sup>38</sup> With the oxidation treatment, stress at break decreases comparably with both NaIO<sub>4</sub> 0.1M and NaIO<sub>4</sub> 0.4M, whereas  $E$  is successively reduced with increasing concentration of the methaperiodate solution. Naturally aged linen loses 50% of the origi-



**Figure 1** (a)  $\tan \delta$  versus temperature for untreated and grafted cotton with EA/MMA 75/25; (b) Storage modulus ( $E'$ ) versus temperature for untreated and grafted cotton with EA/MMA 75/25.

nal stress at break, whereas the elongation at break remains similar to that of raw material; Young's modulus also decreases, but to a value higher in comparison with the artificially aged samples.

By grafting with EA/MMA and EA/MMA/TFEMA, artificially and naturally aged linen becomes more flex-

ible, as seen indicated by the elongation at break and Young's modulus data.

From these results it is evident that the grafting process induces a recovery in the mechanical resistance of the aged textiles, particularly elongation at break, which increases up to values meaningful from

**TABLE IV**  
Tensile Testing for Original, Aged, and Grafted Cotton: Young's Modulus ( $E$ ), Stress ( $\sigma_B$ ), and Elongation at Break ( $\epsilon_B$ ) Values

Sample	$E$ ( $10^7$ ) (N/m)	$\epsilon_B$ (%)	$\sigma_B$ ( $10^6$ ) (N/m $^2$ )
Untreated	$63.3 \pm 21$	$4.16 \pm 0.9$	$15.2 \pm 4.0$
Oxidized $\text{NaIO}_4$ 0.1M 4 h	$6.57 \pm 5.6$	$3.89 \pm 1.0$	$8.19 \pm 2.0$
Naturally aged	$7.63 \pm 10$	$3.88 \pm 0.8$	$9.38 \pm 5.5$
Oxidized 0.1M			
Grafted EA/MMA	$1.36 \pm 4.2$	$10.5 \pm 1.5$	$3.68 \pm 1.1$
Grafted EA/MMA/TFEMA	$1.24 \pm 6.9$	$12.2 \pm 0.6$	$6.43 \pm 1.0$
Naturally aged			
Grafted EA/MMA	$1.02 \pm 4.6$	$7.82 \pm 1.9$	$6.12 \pm 0.9$
Grafted EA/MMA/TFEMA	$3.82 \pm 3.0$	$4.63 \pm 0.9$	$5.65 \pm 1.6$

**TABLE V**  
**Tensile Testing for Original, Aged, and Grafted Linen: Young's Modulus ( $E$ ),**  
**Stress ( $\sigma_B$ ), and Elongation at Break ( $\epsilon_B$ ) Values**

Sample	$E$ ( $10^7$ ) (N/m)	$\epsilon_B$ (%)	$\sigma_B$ ( $10^6$ ) (N/m <sup>2</sup> )
Untreated	155 ± 20	1.96 ± 0.8	40.2 ± 2.3
Oxidized NaIO <sub>4</sub> 0.1M 4 h	5.97 ± 12	3.08 ± 0.9	14.1 ± 4.3
Naturally aged	2.81 ± 11	2.7 ± 0.7	10.3 ± 4.2
Oxidized 0.1M	11 ± 7.2	1.88 ± 0.5	24.2 ± 0.8
Grafted EA/MMA	1.25 ± 6.4	3.4 ± 0.4	18.3 ± 0.6
Grafted EA/MMA/TFEMA	1.4 ± 6.9	3.33 ± 0.9	13.9 ± 0.6
Naturally aged	0.56 ± 3.8	2.78 ± 0.2	6.20 ± 1.6
Grafted EA/MMA	12.9 ± 14	5.63 ± 1.4	11.8 ± 1.4
Grafted EA/MMA/TFEMA	2.30 ± 4.7	3.28 ± 0.8	16.4 ± 0.1

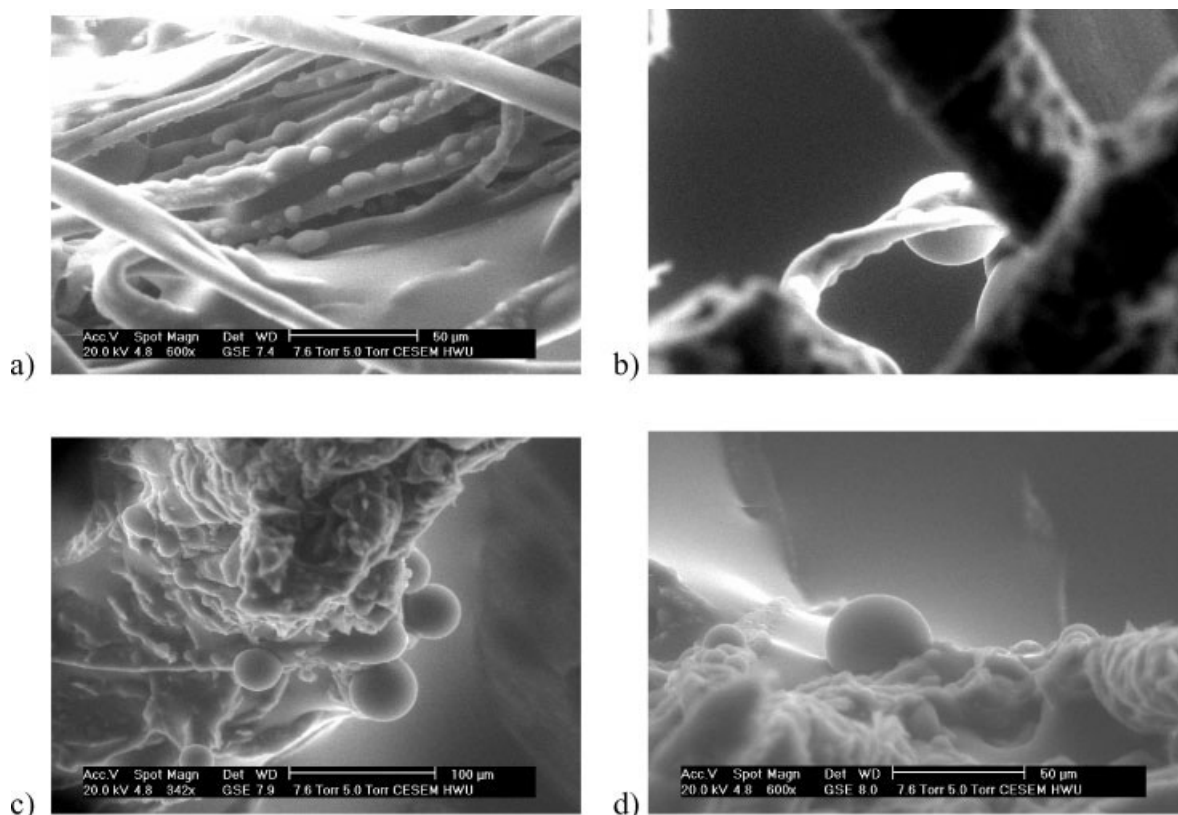
the point of view of the mechanical behavior. EA/MMA 75/25 and EA/MMA/TFEMA 73/24.5/2.5 are rubberlike amorphous copolymers; therefore, their choice for grafting polymerization has been suitable, in that the fabrics retain their typical flexibility after the treatment.

#### Environmental scanning electron microscopy

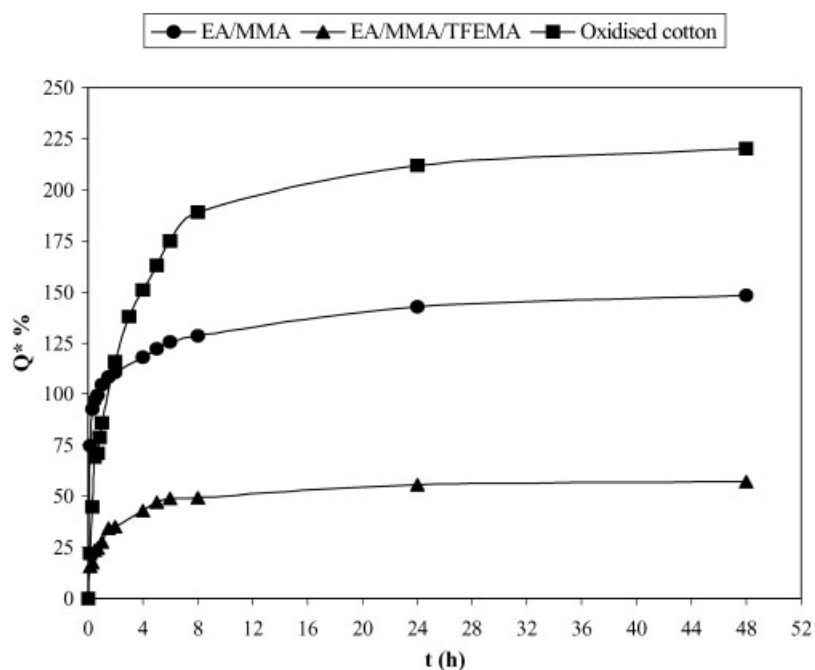
Direct dynamic observation of linen and cotton wetting on a micron level can be achieved with ESEM. This instrument permits high magnification observations of wet specimens with no damage to the material during the hydration process. Wetting phenom-

ena can be examined continuously, and images can be taken during the process in the ESEM.<sup>39</sup> The presence of liquid water in the specimen chamber allows observations of *in situ* hydration without the need for coating or drying the sample.

As relative humidity reaches 100%, the condensation of water is initiated and small water droplets appear on the fiber surfaces; the droplet diameters are only few microns at this stage. As condensation continues, more water droplets form on the fiber surfaces and, as more water condenses, the droplet sizes increase and eventually the closely deposited water droplets coalesce. For untreated material, water forms no spherical droplets on the fiber surfaces and



**Figure 2** Water droplets formed on cotton fiber surfaces in the ESEM: (a) untreated cotton; (b, c) cotton grafted with EA/MMA; (d) cotton grafted with EA/MMA/TFEMA.

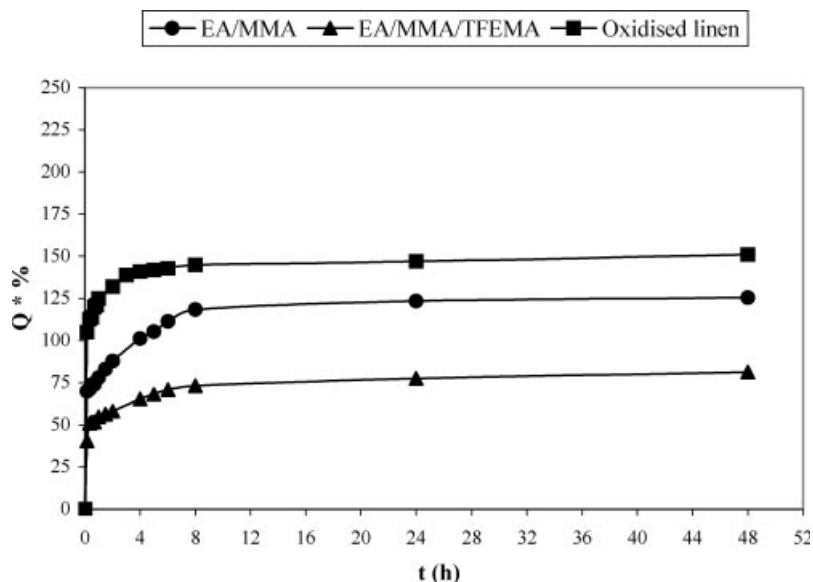


**Figure 3** Water absorption curves for cotton oxidized with  $\text{NaIO}_4$  0.4M and grafted with EA/MMA and EA/MMA/TFEMA.

the coalescence is faster than that for grafted specimens [see Fig. 2(a)]. Grafting of EA/MMA and EA/MMA/TFEMA significantly alters the surface wetting behavior of the cotton fibers, as shown in Figures 2(b–d). Water droplets are spherical and also the growing droplets retain a spherical cap shapes a long time. This is evidence of the protective effect of these grafted acrylics for cellulose-based materials, both naturally and artificially aged, due to the lower surface energy of these copolymers.

The presence of the fluorinated monomer should enhance the water repellence of the grafted cellulose; however, using ESEM observations, it is not possible to detect this improvement.

Contact angle measurement is a quantitative method for the evaluation of the wetting of a solid by a liquid, and can be coupled with ESEM observations to determine the water repellence of textiles after the grafting process.<sup>40</sup> Unfortunately, here, the viewing angle in the ESEM gives images in a wrong



**Figure 4** Water absorption curves for linen oxidized with  $\text{NaIO}_4$  0.1M and grafted with EA/MMA and EA/MMA/TFEMA.



position for contact angle measurements. Therefore, the application of Carroll's approach,<sup>41</sup> a method and an analytical expression proposed to calculate contact angles of barrel-shaped droplets on cylindrical solids, was not possible.

### Water repellence evaluation

Following on from the ESEM results, and to evaluate the wetting behavior of grafted fabrics, water absorption tests were carried out. Figures 3 and 4 show the water absorption curves for cotton and linen, respectively; by comparison between oxidized and grafted materials, any improvement of water repellence can be evaluated. It should be noted that untreated and weakly oxidized fabrics show comparable wetting behavior.

The oxidized samples absorb a large quantity of water, and in 8–10 h reach their saturation values; in particular cotton absorbs more water than linen in the same time frame. For the grafted textiles this distinction is retained, but the quantity of absorbed water is always smaller. With EA/MMA/TFEMA, a noticeable reduction of absorbed water is observed, presumably due to the presence of the fluorinated monomer.

The grafted chains in the fiber structure thus hinder the penetration and the absorption of water molecules onto cellulosic chains; the reduction of absorbed water is a signal of the protective effect given to linen and cotton by grafting polymerization. The reduced water uptake indicates a water repellence improvement due to the homogeneous presence of relatively hydrophobic acrylic chains into cellulose-based materials. This is enhanced further by the inclusion of the fluorinated monomer in the graft system.

### CONCLUSIONS

The aim of this research program is to establish the grafting method as a new technique for the consolidation and the restoration of naturally oxidized (aged) cellulose-based textiles, which belong to the field of Cultural Heritage. For the conservation of these materials, acrylic copolymers represent very useful products but some means of choosing the most appropriate copolymer composition is necessary to perform good restoration treatments.

The results here, along with a previous investigation,<sup>10</sup> indicate that EA/MMA 75/25 copolymer, and the corresponding fluorinated terpolymer, EA/MMA/TFEMA 73/24.5/2.5, can be successfully employed in a grafting polymerization reaction onto both linen and cotton. They are resistant to biological attack and they have glass transitions appropriate to the service temperature of the substrate. The mechanical resistance and the flexibility of the grafted

fabrics are improved; thus a consolidating action is achieved by the grafting process. Acrylics, due to their generally hydrophobic nature, also perform a protective function for the textiles and, by further adding a fluorinated monomer in small amounts, water repellence is noticeably improved.

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