New Polymeric Materials for Paper and Textile Conservation. I. Synthesis and Characterization of Acrylic Copolymers

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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. This area is vast and includes studies of various objects made of different materials such as wood, stone, textiles, and paper. The aim of this article is to establish the most suitable copolymer for cellulose-based-material restoration according to its properties, as evaluated by several techniques such as ^{1}H-NMR spectroscopy, size exclusion chromatography, differential scanning calorimetry, and dynamic mechanical analysis. In addition to the mechanical property evaluation, an investigation of fungal deterioration has been carried out. Because, in the literature, no complete study concerning the characterization of ethyl acrylate/methyl methacrylate and butyl acrylate/methyl methacrylate copolymers is available, a detailed and full investigation of these polymers is required before the best copolymer is selected for grafting polymerization onto cellulose. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1157–1164, 2005

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INTRODUCTION

For the preservation of historic and cultural heritage items, the use of polymeric materials for the consolidation and protection of artifacts with historical and artistic value is widely accepted.[1–3] The area of application is extensive and includes studies of various objects made of different materials, such as wood, stone, textiles, and paper. Poly(ethylene glycol)s (PEGs) are the materials most employed for wood conservation, especially in the case of waterlogged objects;[4] for other types of artifacts, acrylic polymers are often used.[5–7] Acrylics show high filmability, good adhesive properties, and moderate water repellence, and so their use makes it possible to achieve two objectives simultaneously, that is, consolidation and protection, leading to improvement of the restoration treatment. In the case of stone conservation, the consolidating polymer forms a continuous film that sticks to the interiors of the stone pores, where it partially fills cavities due to degradation to obtain a good consolidating action.

For paper and textiles, polymeric materials have been applied only in a few cases when traditional restoration methods were not sufficient to improve the mechanical resistance of the degraded artifacts. In contrast to stone conservation, for which new products and new techniques have been developed and applied,[8–10] for cellulose-based materials, only a small number of studies have been carried out.[11,12] Currently, no polymeric material exists whose properties are tailored for the conservation of paper and textiles. Moreover, the polymers that have been used so far have proved to be unsuitable, irreversibly damaging the treated objects.

In our laboratory, new acrylic products and a new technique for the conservation of paper and cellulose-based textiles have been investigated to develop a more appropriate method of intervention. We have shown that, by the grafting polymerization of acrylic monomers from the vapor phase onto cellulose chains, the mechanical resistance of degraded paper and textiles is much enhanced.[13,14] This method is advantageous because it does not alter the main features of the materials because no superficial coatings are formed on the grafted samples.

In a previous publication,[13] we reported the grafting of methyl methacrylate (MMA) onto Whatman paper, cotton, and linen as substrates; the reaction was successful but, because of the high glass-transition tem-

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perature (T_g) of the grafted poly(methyl methacrylate) (PMMA) chains, the treated materials were brittle and stiff. The grafting of ethyl acrylate (EA) improved the situation, but sometimes the substrates were sticky because of the low T_g value ($-24°C$) of poly(ethyl acrylate) (PEA).[14]

It is important to remember that a polymer has better consolidating properties when, at the service temperature, it is just above its T_g 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 of the degraded objects is achievable.[15]

On the basis of these results, the synthesis of new copolymers with characteristics suitable for cellulose consolidation is indicated, along with further research into the grafting polymerization. The main objective of this work is to establish the most suitable copolymer for cellulose-based-material restoration according to its properties, as evaluated by several techniques: ^{1}H-NMR spectroscopy, size exclusion chromatography, differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). Also, an evaluation of the mechanical properties and an investigation of fungal deterioration have been performed. Because the literature contains no complete study concerning the characterization of MMA/EA and MMA/butyl acrylate (BA) copolymers synthesized by radical polymerization carried out *in vitro*, a detailed and full investigation is required before the best copolymer is selected for grafting polymerization onto cellulose. Studies on the grafting polymerization of the optimum copolymer will be the subject of a future article.

As a starting point, a 70/30 (wt %) acrylic copolymer of ethyl methacrylate (EMA) and methyl acrylate (MA) was synthesized. Here the ratio of EMA and MA units was purposely kept similar to that of a commercially available product (Paraloid B72, Röhm and Haas, Philadelphia, PA),[16] which is currently widely employed in restoration. In addition, a series of MMA/EA copolymers with different comonomer compositions were also synthesized. The introduction of EA units led to a low-T_g material, and this made the product more efficient as a consolidant for cellulose. To assess the influence of the second comonomer, copolymers of MMA and BA were also prepared. Poly(butyl acrylate) (PBA) has a lower T_g ($-54°C$) than PEA, and so the consolidating effect of the corresponding copolymers on cellulose should be enhanced.

Since the introduction of fluorine into polymers improves chemical, thermal, and photochemical stability[17] because of the strength of the C—F bond (bond energy = 116 kcal/mol) and also induces higher hydrophobicity because of the low surface energy brought by the fluorinated groups,[18–20] a commercial fluorinated monomer, 2,2,2-trifluoroethyl methacrylate (TFEMA), was also added to the polymerizing mixture to improve the water repellence of the correspondent terpolymer.

EXPERIMENTAL

Copolymers

The monomers and solvents were commercial products from Aldrich (Milwaukee, WI). The initiator (2,2'-azobisisobutyronitrile) was purchased from Fluka (Buchs, Switerland). Monomers MMA, EMA, MA, EA, BA, and TFEMA contained an inhibitor (hydroquinone monomethyl ether), which was removed by passage through an Aldrich inhibitor remover column; the purified monomers were subsequently stored at a low temperature (4°C) and in the dark. The solvents (acetone and tetrahydrofuran) were laboratory-grade products and were used without any further purification. The copolymerizations were performed in solution at 50°C and followed the conventional mechanism of free-radical polymerization. The monomers, initiator, and solvent were mixed and placed in an oven. Previous investigations[9,21] have shown that good results are obtained with 2 wt % initiator and by the polymerization being carried out in solution (20 vol % solvent). At 50°C, the reaction could be considered complete after 48 h. At the end of the polymerization, each polymer was dissolved in acetone, and a thin film was obtained by solution casting on a glass slide.

NMR spectroscopy

^{1}H-NMR spectra were recorded in CDCl$_3$ on a Varian (Varian Associates, Palo Alto, CA) Gemini 200 spectrometer at 200 MHz, with Tetra-Methyl-Saline (TSM) as an internal standard. Chemical shifts are expressed in parts per million. The monomers and homopolymers were analyzed as references.[22] To estimate the amount of each monomer in the copolymers, the following signals were used: αCH$_3$ ($\delta = 1$ ppm) for MMA; OCH$_2$ ($\delta = 4$ ppm) for EMA, BA, and EA; OCH$_3$ ($\delta = 3.6$ ppm) for MA; and CH$_2$ ($\delta = 4.5$ ppm) for TFEMA.

Size exclusion chromatography

The sample molecular weights were determined with a modular system of a Waters (Milford, MA) 590 pump, a Waters U6K injection valve with a 200-μL sample loop, and a Waters 410 differential refractometer detector. Four PLgel (Polymer Labs, Poole, United Kingdom) columns (30 $\times$ 0.78 cm^2) in series were used; the nominal porosity of the individual columns was 500, 10^3, 10^4, or 10^5. Solutions of ~0.5% (w/v) were prepared in distilled tetrahydrofuran, which was also the chromatographic eluent. Before injection, solutions were filtered on 0.45-μm membrane syringe filters. Calibration was by polystyrene standards.

TABLE I
Molecular Weights and Polydispersities of the Copolymers

Copolymer	Feed composition (wt %)	Final composition* (wt %)[a]	M_n	M_w	M_w/M_n
EMA/MA	70/30	66/34	339,000	631,000	1.85
EMA/MA/TFEMA	68.25/29.25/2.5	66/32/2	363,000	692,000	1.89
EA/MMA	85/15	89/11	11,000	282,000	2.55
EA/MMA	75/25	78/22	78,000	224,000	2.87
EA/MMA	50/50	56/44	302,000	524,800	1.72
EA/MMA	40/60	43/57	575,000	1,020,000	1.88
EA/MMA	25/75	29/71	275,000	427,000	1.56
EA/MMA	15/85	18/82	195,000	288,000	1.48
BA/MMA	50/50	54/46	234,000	407,000	1.72
PEA	—	—	52,500	263,000	5.33
PMMA	—	—	159,000	234,000	1.46

[a] Determined by H-NMR spectroscopy.

DSC

T_g's were evaluated with a TA Instruments (Newcastle, DE) DSC 2010 differential scanning calorimeter at a heating rate of 20°C/min, and traces were recorded in the temperature range of −100 to 150°C. To eliminate any effect of the thermal history, T_g measurements were made from a second heating cycle, after the heating of the sample up to 150°C at 20°C/min, followed by quenching down to −100°C.

Mechanical analysis

DMA was carried out with 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. The samples were approximately 10 mm wide, 20 mm long, and 0.3 mm thick. Tan δ was recorded from 20 to 150°C.

Tensile measurements were performed on an Instron (Norwood, MA) tensile tester. The films were approximately 10 mm wide, 40 mm long, and 0.3 mm thick. The load cell sensitivity was 0.038 N/mV, and the samples were tested at 8 mm/min draw rate until breakage.

Biodegradation assay

The ASTM G 21-96 (2002) method was used to evaluate the capacity of fungi to grow on polymeric materials.[23] Dried films were prepared via the spreading of a solution in acetone of each copolymer on plain glass slides (7.6 cm × 2.6 cm) to obtain a thin layer. Each sample, after inoculation of *Aspergillus niger*, was placed in the center of an individual empty Petri dish and then incubated for 28 days. The samples were examined, and the growth ratings were assigned as follows: 0, no growth; 1, traces of growth (<10%); 2, light growth (10–30%); 3, medium growth (30–60%); and 4, heavy growth (60% to complete coverage).

RESULTS AND DISCUSSION

The copolymer compositions determined with ^{1}H-NMR spectroscopy are shown in Table I, and only slight differences between the feed composition and final composition can be observed for all the samples. This is not surprising because the conversion is approximately 100% and any differences are most likely due to the inherent inaccuracies of integrating broad signals.

The copolymer molecular weights are also listed in Table I; these are high even though the polymerizations were carried out in the presence of acetone, which acts as a weak chain-transfer agent. Although the polymerization conditions were kept the same in all experiments, the weight-average molecular weight (M_w) and number-average molecular weight (M_n) vary quite considerably from sample to sample. This could be due to a viscosity-dependent autoacceleration effect at high conversions.

The polydispersity indices of the copolymers are, in the main, as expected for radical polymerization.

DSC

The T_g values obtained by DSC are reported in Table II. The T_g's for the 75/25 EA/MMA and 75/25 BA/MMA copolymers are below room temperature, these copolymers are elastic, and so they can potentially be successfully used as consolidating products for flexible cellulose-based materials.

The unfluorinated copolymers 75/25 EA/MMA and 70/30 EMA/MA and the corresponding fluorinated terpolymers have comparable T_g's; therefore, the addition of a small percentage of a fluorinated monomer [poly(2,2,2-trifluoroethyl methacrylate) has a T_g of 62°C] to the polymerizing mixture does not modify T_g of the polymer to any great extent.

The main limitation of the EMA/MA copolymer (and also of Paraloid B72) is its relatively high T_g value

TABLE II
DSC and DMA Analyses Results (Evaluated at T_g)

Polymer	DSC	DMA		
	T_g (°C)	T_g (°C)	Storage modulus (MPa)	tan δ
EMA/MA	42	59	22.9	1.56
EMA/MA/TFEMA	42	58	12.0	1.58
PEA	−20	—	—	—
EA/MMA 85/15	−5	—	—	—
EA/MMA 75/25	10	21	—	—
EA/MMA/TFEMA 68.25/29.25/2.5	11	—	—	—
EA/MMA 50/50	42	52	10.1	1.62
EA/MMA 40/60	56	67	10.3	1.39
EA/MMA 25/75	71	74	7.51	1.27
EA/MMA 15/85	82	81	6.85	1.26
PMMA	104	120	6.68	1.56
PBA	−34	—	—	—
BA/MMA 75/25	−16	—	—	—
BA/MMA 50/50	35	51	2.99	1.62
BA/MMA 45/55	52	—	—	—
BA/MMA 25/75	76	—	—	—
BA/MMA 10/90	94	—	—	—

of 42°C. At their service temperatures, these are in the glassy state and, therefore being rigid and brittle, can cause embrittlement of treated substrates. It is for this reason that the copolymers EA/MMA and BA/MMA were synthesized and the effect of the composition was examined to choose the most suitable system for paper and textile conservation. In this light, the experimental T_g data obtained for the EA/MMA and BA/

MMA systems (shown in Table II) were compared with those predicted by the two theoretical equations:

$$\text{Flory–Fox}^{24}\ 1/T_g = w_1/T_{g1} + w_2/T_{g2} \qquad (1)$$

$$\text{Gordon–Taylor}^{25}\ T_g = (w_1 T_{g1} + K w_2 T_{g2})/(w_1 + K w_2) \qquad (2)$$

where w_1 and w_2 are the weight fractions of the two comonomers, 1 and 2, and T_{g1} and T_{g2} are the glass-transition temperatures of the corresponding homopolymers. K is a semiempirical parameter defined as follows:

$$K = \alpha_{l,2} - \alpha_{g,2}/\alpha_{l,1} - \alpha_{g,1} \qquad (3)$$

where $\alpha_{l,1}$ and $\alpha_{l,2}$ are the thermal expansion coefficients of the two homopolymers in the rubbery state and $\alpha_{g,1}$ and $\alpha_{g,2}$ are the thermal expansion coefficients in the glassy state.

Figure 1 shows the T_g values versus the copolymer composition for the EA/MMA system; the data are well fitted by the Gordon–Taylor formalism, with K set to unity, and so the experimental trend of T_g versus the copolymer composition is characterized by linearity in this system. The T_g data for the BA/MMA copolymer system are plotted in Figure 2, in which the behavior is compared to the Flory–Fox and Gordon–Taylor equations; the best description is obtained with the Gordon–Taylor equation with $K = 0.75$. This positive deviation of the BA/MMA system from linearity
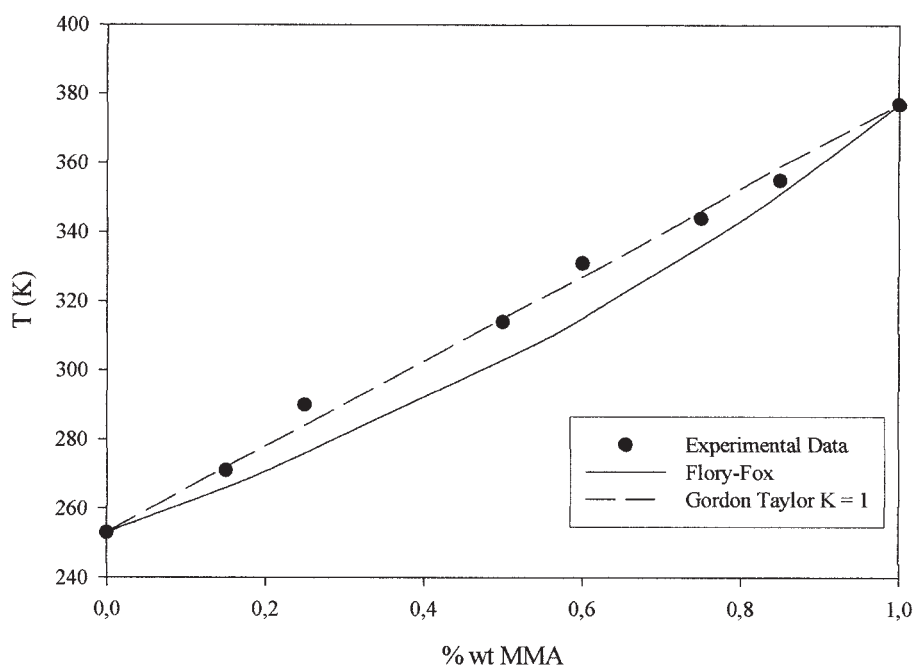

Figure 1 Experimental and calculated T_g values for the EA/MMA copolymers.
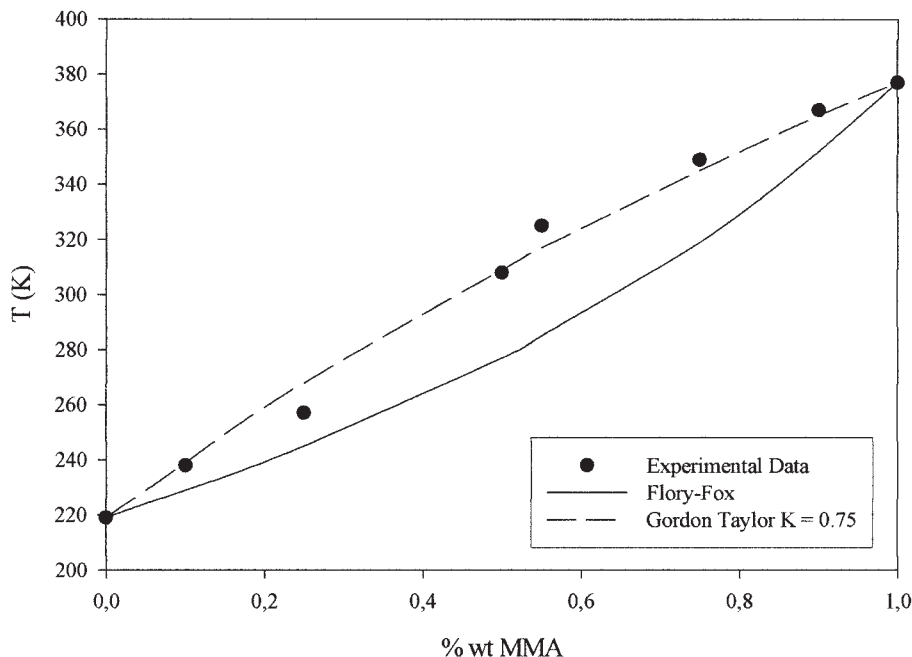
Figure 2 Experimental and calculated T_g values for the BA/MMA copolymers.

can be interpreted in terms of a strong, efficient packing of the two comonomers, compared to the situation in the respective homopolymers.

DMA

Table II reports the results of the DMA measurements; T_g is taken as the tan δ maximum. The variations of tan

δ and the storage modulus with the temperature for the EA/MMA system are plotted in Figures 3 and 4, respectively. The shape and character of the tan δ curves do not vary significantly for the copolymers, and pseudosymmetrical curves are obtained, with the single (if broad) peak indicative of a single relaxation occurring in a homogeneous system. A temperature difference is found between the T_g values from DSC
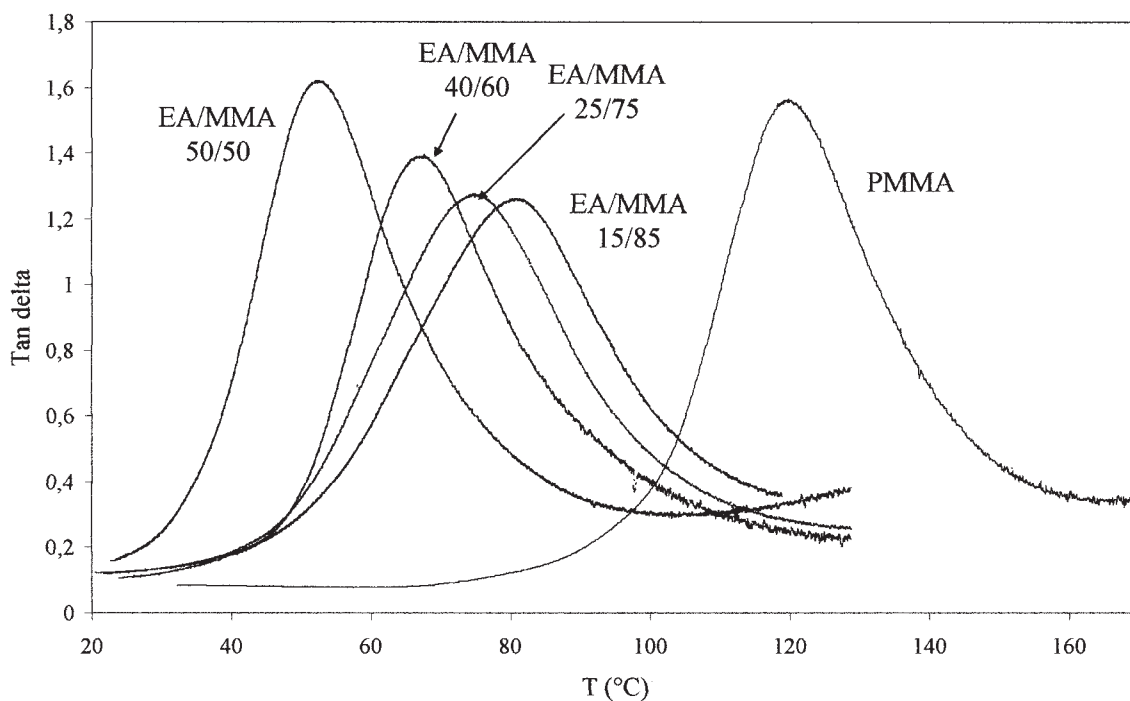

Figure 3 Tan δ versus the temperature for EA/MMA copolymers.
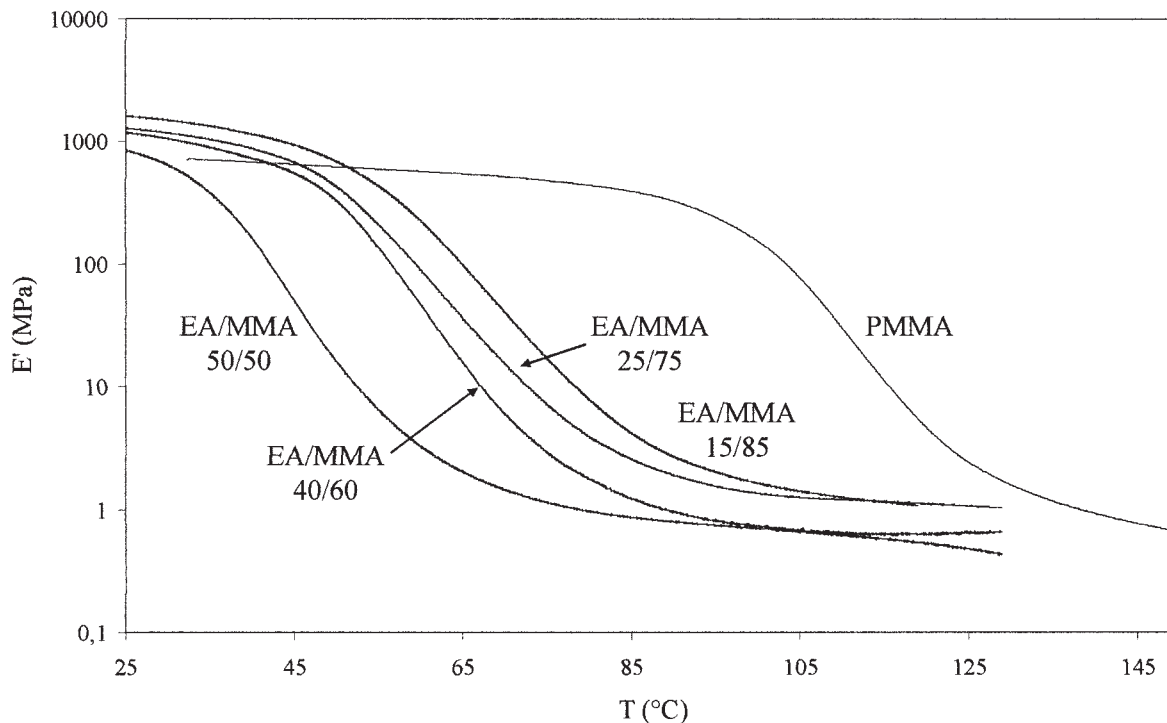
Figure 4   Storage modulus (E') versus the temperature for EA/MMA copolymers.

and DMA analyses; the T_g values obtained with DMA are slightly higher in agreement with expectations.[26]

For the 50/50 composition, the use of BA as a comonomer with MMA leads to dynamic mechanical behavior similar to that of the EA/MMA copolymer [see Fig. 5(a)]. The presence of the fluorinated monomer in the terpolymer EMA/MA/TFEMA does not modify the behavior in comparison with that of the corresponding EA/MMA copolymer [see Fig. 5(b)].

Tensile testing

The stress–strain behavior of representative copolymers was measured by tensile deformation; all samples were tested to break. The Young's modulus, stress at break, and strain at break are all collected in Table III. The data for the EMA/MA copolymer show it to be too stiff and brittle for effective use in the restoration field; this demonstrates that the corresponding commercial analogue, Paraloid B72, is also unsuitable. Concerning the MMA-based copolymers, when the MMA percentage is higher than 50%, the material is also stiff and brittle, as revealed by the values of the Young's modulus and strain at break. These data agree with the considerations deduced from the T_g values reported previously. Comparing the EA/MMA and 50/50 BA/MMA copolymers, the former is slightly more flexible; in particular, the stress and strain at break increase. Overall, reducing the MMA content in the copolymer gives a more flexible and elastic product, as required for a consolidating product.

Biodegradation assay

The optical evaluation of the fungal growth according to the ASTM practice was performed after 28 days from the inoculation by the black, filamentous fungus *A. niger*. Although the synthetic resins are not natural products, it is possible that some of them will be assimilated by microorganisms. In this way, cellulose-based materials treated with acrylic products could undergo biological attack, with a consequential biodegradation of the artifacts. It was found that the synthesized copolymers were not susceptible to fungal attack after this evaluation period. Because biodegradation is limited, the use of acrylics seems suitable in the field of paper and textile conservation.

CONCLUSIONS

For the conservation of cellulose-based materials, acrylic copolymers appear to be very useful products, and so the choice of the most appropriate copolymer is desirable to perform an optimum restoration. Any EMA/MA copolymer, similar in composition to the commercial product Paraloid B72, which is presently widely employed in restoration, is unlikely to produce best results because its T_g is higher than the normal service temperature. Such copolymers are brittle and stiff, and they are generally unsuitable to consolidate a flexible material such as cellulose.

The results here indicate that MMA/EA and MMA/BA copolymers could be successfully em-

(a)

(b)
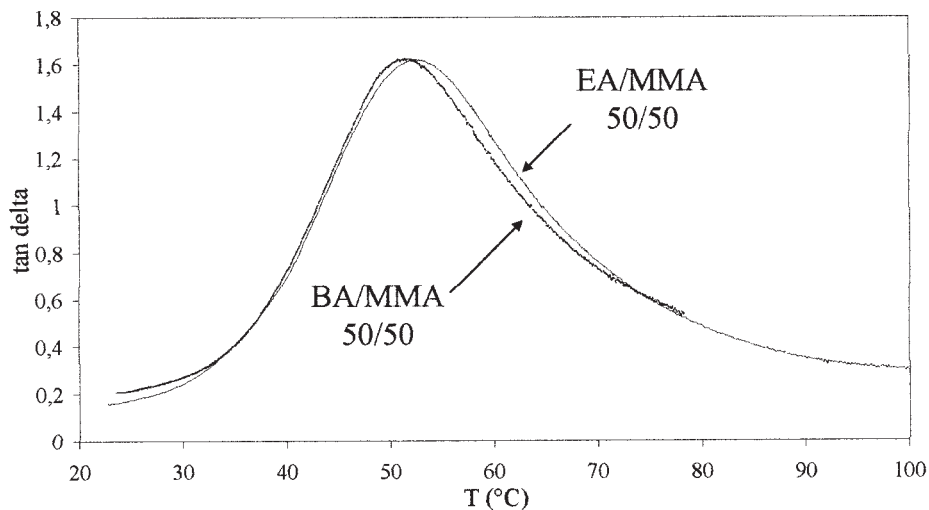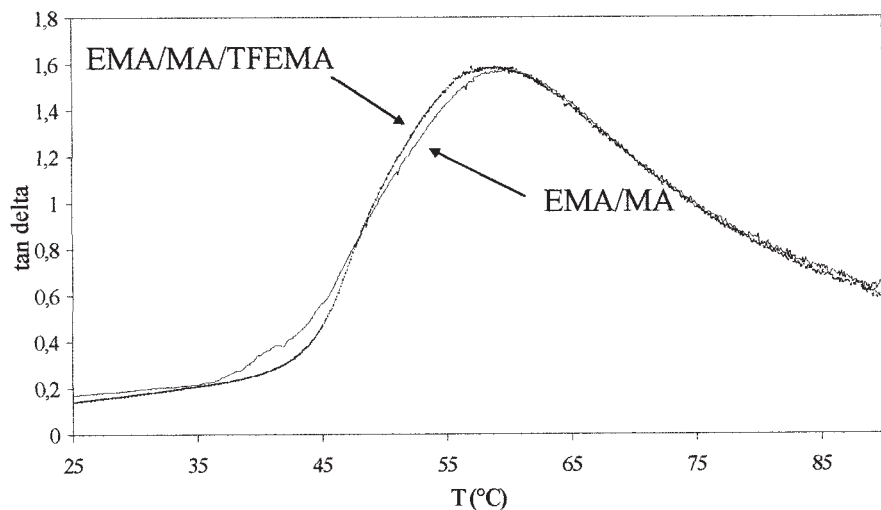
Figure 5 Tan δ versus the temperature: (a) a comparison of 50/50 EA/MMA and BA/MMA copolymers and (b) a comparison of EMA/MA and EMA/MA/TFEMA copolymers.

ployed in grafting polymerization onto cellulose. They are resistant to biological attack and, by the appropriate choice of composition, will have glass

TABLE III
Tensile Testing for the Acrylic Copolymers

Polymer	Young's modulus × 10^9 (N/m)	Strain at break (%)	Stress at break × 10^7 (N/m²)
EMA/MA	4.9 ± 1	4.7 ± 1.6	15 ± 0.1
BA/MMA 50/50	4.0 ± 0.8	28 ± 2	4.2 ± 0.3
EA/MMA 50/50	2.7 ± 0.5	103 ± 2.6	8.7 ± 0.1
EA/MMA 25/75	5.5 ± 1.1	2.5 ± 2.5	12 ± 0.2
EA/MMA 15/85	13 ± 0.7	3.2 ± 1.9	13 ± 0.1

transitions appropriate to the service temperature. This characteristic should bring about resistance to mechanical stresses in cellulose-based materials, and by the addition of a fluorinated termonomer in small amounts, the water repellence should be improved, without the modification of the characteristics of the product. The best composition, on the basis of the data described here and typical conditions of textile and paper conservation, is 25/75 MMA/EA. Future work on grafting polymerization will start with this copolymer, and once the grafting process and the best experimental conditions have been established, a 25/75 MMA/BA copolymer will also be tested. The results will be published in part II.

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