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Effectiveness of Graft Synthetic Polymers in Preventing Biodeterioration of Cellulose-Based Materials

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Summary: Synthetic polymers have been occasionally applied to the consolidation and protection of paper and cellulose-based textiles especially when traditional conservation methods were not sufficient to improve the mechanical resistance of the degraded artefacts. In this paper, the potential of the innovative technique of grafting polymerisation with synthetic polymers was investigated to prevent biodeterioration. Cotton, linen and Whatman paper were consolidated by a) coating Paraloid B72®, b) coating ethyl acrylate/methyl methacrylate (EA/MMA) preformed copolymer, and c) grafting onto cellulose chains EA and MMA monomers in the ratio 75/25. All the samples were artificially biodeteriorated to obtain biodegraded model samples of both consolidated and non-consolidated substrates, according to the ASTM G21-96(2002) "Standard Practice for Determining Resistance of Synthetic Polymeric Materials to Fungi". The consolidating effect was examined evaluating the mechanical behaviour of the grafted and coated samples, before and after the artificial biodeterioration. In addition, SEM observations were applied to monitor both the grafting level and the biodeterioration of the samples. With the grafting of acrylic monomers, the mechanical strength of cellulose-based textiles and paper was greatly improved, as well as the resistance to biological agents. Therefore, with regards to biodeterioration, the graft copolymer EA/MMA (75/25 wt) was proved to be a suitable method to help prevent possible deterioration of paper and textiles.

Keywords: acrylics; biodeterioration; cellulose-based materials; grafting polymerisation; mechanical properties; SEM

Introduction

The use of synthetic polymeric materials for the consolidation and protection of paper and cellulose-based textiles is uncommon and only a small number of studies were carried out on this topic.[1,2] Synthetic polymers were applied in a few cases, especially when traditional conservation methods were not sufficient to improve the mechanical resistance of the degraded artefacts. In these cases, the materials usually employed were commercial products, with properties not actually tailored for the conservation of cellulose-based materials.

Among the various treatments used to improve the properties of natural fibres, the synthesis of graft copolymers[3] seems a suitable method to reduce the ageing phenomena of cellulose-based materials.[2,4,5] With this innovative technique, the properties of polymers can be tailored by the chemical structure of the monomers, the length of the grafted segment and the grafting level.[6] Graft polymerisation can induce chemical changes in cellulose and the introduction of polymer chains can

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confer different structural characteristics to the raw material, for example better mechanical properties.[5,6] Acrylic monomers appear particularly suitable for graft polymerisation because of their characteristics, such as water-repellence, transparency and good filmability.[6]

In the last years, the grafting polymerisation of acrylic monomers in the vapour phase, induced by UV radiations, was investigated in Department of Chemistry and Industrial Chemistry, University of Genoa, with the aim to develop more appropriate conservation methods for cellulose-based materials. Grafting directly from the vapour phase onto cellulose results in enhanced mechanical resistance of degraded paper and textiles, without altering the typical flexibility of cellulose and, importantly, no superficial coatings are formed on the grafted samples.[7–9] Because of its low energy, UV radiation offers some 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 γ-rays or x-rays. [2,10–14] To initiate grafting, the creation of free radicals on the cellulose chain is necessary. To allow the formation of the radical sites by the UV light, photosensitive sites on the cellulose are required: these sites were formed by reaction with the oxidising agent sodium methaperiodate.[15–18] In this way the glucosidic units are oxidised to dialdehydic groups which then act as photosensitive agents: UV radiation transforms the carbonyl groups in the sites where radical polymerisation subsequently starts.

Previous studies showed that the grafting of a single kind of monomer either methyl methacrylate (MMA) or ethylacrylate (EA) are not suitable for cellulose-based materials. In the former case, due to the high glass transition temperature (Tg) of the graft poly(methyl methacrylate) (PMMA) chains, the treated materials were brittle and stiff,[7] while the samples treated with poly(ethyl acrylate) (PEA) were sticky due to the low Tg (−24 °C) of this polymer.[8] In a previous paper,[19] we selected the EA/MMA copolymer 75/25 wt % for the grafting onto cellulose-based materials, because it has a glass transition (10 °C) appropriate to the service temperature: this copolymer was also used in this work.

Biodegradability of synthetic polymeric materials depends on the chemical structures of polymeric materials, the presence of degradative microbial communities and the environmental conditions that encourage microbial growth. Our understanding of synthetic polymer biodegradation has been advanced in recent years,[20,21] but the subject is still inadequately addressed. In this study, following the ASTM G21-96(2002), an artificial biodeterioration method was performed with all the samples before and after the consolidation treatments with graft and coated synthetic polymers in order to evaluate the ability of grafting in comparison with coating at preventing biodeterioration.

Experimental

Materials

The cellulose substrates were Artemisia linen and Ghinea cotton, manufactured by Zecchi (Italy) and the Whatman filter paper by Whatman (UK). Both textiles contain about 5–6% of starch that can be removed in boiling water. 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 methaperiodate ($NaIO_4$), acetone and methanol were laboratory grade products and were used without further purification. In this study methaperiodate oxidation was used to simulate natural oxidative degradation as tested materials were new materials. For naturally aged materials this oxidation step is not required. The initiator 2,2′-azobis-isobutyronitrile (AIBN) was purchased from Fluka. Paraloid B72® was supplied by Röhm and Haas (USA). Deionised water was used throughout the work.

Grafting Reaction

The polymerisation reaction was carried out on cotton, linen and Whatman paper, oxidised with sodium metaperiodate before the grafting process. Periodate oxidation is a highly specific reaction that cleaves the C2–C3 bond of the glucosidic ring of cellulose and converts the 2,3-dihydroxyl groups into two aldehyde groups,[22] the photosensitive sites where the polymerisation starts. All the cellulose-based materials were treated with a solution of sodium methaperiodate 0.1 M for 2 hours.[8]

Cellulose samples, after drying in oven at 40 °C, were swollen in deionised water to open up the fibrous structure of cellulose and encourage homogeneous uptake of monomers during grafting.[7–9] This process lasted 10 minutes for Whatman paper and 24 h for textiles. The wet samples were placed in the quartz reaction vessel (volume 10 litres), which was evacuated for a short time so that the fabrics were still damp, then the liquid monomers mixture was loaded, vaporised, and diffused into the reactor.

As previously found by Princi et al.,[9] the best monomer to cellulose ratio is 2.5 mmol of acrylic per gram of sample, and this was used also here. Subsequently, the reaction vessel was exposed at room temperature to UV radiation using a mercury vapour 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 polymerisation was stopped after 4 hours by bringing the reactor up to room pressure.[9] Non-reacted monomer was removed by washing the fibres with a mixture methanol-water (30/70 v/v), a good solvent for acrylic monomers but not for the polymers. After this step, the sample, containing grafted cellulose and homopolymer, was filtered and brought up to constant weight.

The drawback of the graft polymerisation is the simultaneous and inevitable formation of the homopolymer; this was removed from the grafted material by extraction with acetone for 72 h at room temperature.[6,23] The percentage of synthesised polymer during grafting reaction is calculated as follows: %

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

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

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

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 polymerised monomer:

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

and the amount of homopolymer is quantified according to:

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

Traditional Consolidation Treatment with the Synthetic Polymers EA/MMA 75/25 and Paraloid B72®

The EA/MMA 75/25 preformed copolymer was synthesized in solution (20% v of acetone) at 50 °C, using 2% by weight of the initiator AIBN.[19] In order to compare traditional and innovative techniques, a treatment with Paraloid B72® was carried out. Solutions of this polymer and Paraloid B72® were prepared in acetone (3% by weight) and employed to coat paper and textiles with a brush. After 24 hours at room temperature the samples were perfectly dried.

Using the gravimetric technique the amount of polymer present in each sample was evaluated.

Artificial Biodeterioration

The ASTM G21-96(2002) method, ‘‘Standard Practice for Determining Resistance of Synthetic Polymeric Materials to Fungi’’, was used to evaluate the capacity of fungi to grow on the cellulose-based materials and synthetic polymers used for their consolidation/protection. *Aspergillusniger* van Tieghem (ATCC no. 9642), *Trichoderma virens* (Miller et al.) von Arx (ATCC no. 9645), *Chaetomium globosum* Kunze (ATCC no. 6205), *Aureobasidium pullulans* Hermanides-Nijhof (ATCC no. 15233) and *Penicillium funiculosum* Thom (ATCC no. 11797) were the test fungi used for the inoculum. The spore suspensions were aseptically centrifuged three times at 8,000 rpm and the supernatant liquids discarded in order to avoid any residue from the cultural medium. The spores obtained from each of the fungi were then diluted with sterile mineral solution. The final inoculum was a mixture of five fungal spores suspension that was sprayed using a sterilized atomizer. The inoculation was carried out three months after the polymer grafting and coating.

Each sample, after inoculation, was placed in the centre of an empty Petri dish and then incubated for 28 d (temperature 25 °C, 90% RH). Samples were examined and the growth ratings were assigned as follows: 0, no growth; 1, traces of growth (less than 10%); 2, light growth (10 to 30%); 3, medium growth (30 to 60%); 4, heavy growth (60% to complete coverage).

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).

Mechanical Analysis

Tensile measurements on yarns gathered from the grafted samples were performed on an Instron tensile tester (UK). Young's modulus (E), stress (σ) and elongation (ε) at break were evaluated at room temperature. Yarns were approximately 60–70 mm long and with a diameter of 0.20–0.25 mm. The load cell sensitivity was 5 KN and samples were tested at 20 mm/min draw rate until breakage. An average of 15 tests for type specimens was used to calculate the tensile properties.

Results and Discussion

Grafting Reaction and Comparison with the Traditional Consolidation Method

The comparison with the traditional method of intervention for paper and cellulose-based textiles was carried out applying by coating the EA/MMA preformed copolymer (synthesised in vitro) and the commercial product Paraloid B72®,[24] which is currently widely employed in conservation.

Grafting was carried out onto oxidised linen, cotton and Whatman paper, and Table 1 reports the grafting yields obtained from the monomer mixture EA/MMA 75/25 wt %. From these results it is evident that the reaction of EA/MMA 75/25 leads to higher yields for oxidised cotton in comparison with linen and Whatman paper, as already observed in previous studies.[9] In the case of linen, this effect is possibly due to the presence of lignin (2 %)[25] that could act as an inhibitor for the grafting process.[26] In all cases the percentage of homopolymer is not high, being about 20%.

Table 1.
Grafting yields for oxidised cotton (with starch), linen (with starch) and Whatman paper grafted with EA/MMA 75/25.

Sample	Grafting yield (%)	Grafting efficiency (%)	Homopolymer (%)
Cotton	55	80	20
Linen	36	75	25
Whatman paper	34	84	16

Table 2.
Polymer amount in cotton (with starch), linen (with starch) and Whatman paper after coating with Paraloid B72® and EA/MMA 75/25 preformed copolymer

Sample	Polymer amount %
Paraloid B72®	
Cotton	7
Linen	9
Whatman paper	14
EA/MMA 75/25 preformed copolymer	
Cotton	7
Linen	9
Whatman paper	14

In Table 2 the polymer amounts present in each sample after coating with Paraloid B72® and EA/MMA 75/25 are reported. It is interesting to point out that both products lead to the same results, even if, with the traditional method, the quantity of consolidating product applied to the materials is reduced in comparison with the use of grafting polymerisation. The polymer amount for Whatman paper is the highest, because it is the most porous cellulose-based material.

Artificial Biodeterioration

It is well known that cellulose-based materials can undergo biodeterioration.[27] As already said, linen and cotton contain starch. As expected, the presence of starch further enhances the attack of microbiological agents (see Table 3). To simulate as much as possible real trade products, both textiles were coated and grafted with synthetic polymers without removing the starch. Table 3 shows that there is almost no difference in coating samples with EA/MMA 75/25 and Paraloid B72®. In contrast, with regards to Whatman paper, grafting polymerization has no effect to prevent biodeterioration, but for linen and cotton the method is almost completely effective. Possibly, one reason to explain this resistance is that grafted polymers have high molecular weight while coated polymers might contain also unreacted monomers or oligomers that are more easily attacked by fungi. Indeed, as reported in a previous paper [8], M_V for the EA/MMA 75/25 grafted copolymer calculated by viscosity measurements is about 400000–500000. Considering the coated systems, Paraloid B72® has the lowest

Table 3.
Degree of fungal growth evaluated at different time (14d and 28d) during the ASTM G21-96(2002) test. REP. stands for replica. [a] yellow edges, [b] strongly yellow, [c] yellow, [d] slightly yellow

Days	Untreated Whatman paper				Whatman coated with EA/MMA 75/25		Whatman coated with B72®		Whatman grafted with EA/MMA	
	REP. 1	REP. 2			REP. 1	REP. 2	REP. 1	REP. 2	REP. 1	REP. 2
14d	0	0			0	0	0	0	0	0
28d	1[a]	1[a]			2[b]	2[b]	2[c]	2[c]	1[d]	1[d]
	Untreated cotton withouth starch		Untreated cotton with starch		Cotton with starch coated with EA/MMA 75/25		Cotton with starch coated with B72®		Cotton with starch grafted with EA/MMA	
	REP. 1	REP. 2	REP. 1	REP. 2	REP. 1	REP. 2	REP. 1	REP. 2	REP. 1	REP. 2
14d	0	0	2	2	2	3	3	3	0	0
28d	3–4	1	3	3	2	4	4	4	0–1	0–1
	Untreated linen withouth starch		Untreated linen with starch		Linen with starch coated with EA/MMA 75/25		Linen with starch coated with B72®		Linen with starch grafted with EA/MMA	
	REP. 1	REP. 2	REP. 1	REP. 2	REP. 1	REP. 2	REP. 1	REP. 2	REP. 1	REP. 2
14d	0	0	0	0	0	0	0	0	0	0
28d	0	0	1[d]	1[d]	2[a]	2[a]	2[a]	2[a]	0	0

molecular weight evaluated by GPC (Mn = 12000 and Mw = 25000), whereas the EA/MMA 75/25 preformed copolymer shows intermediate values of the molecular weight (Mn = 78000 and Mw = 224000).[19]

In addition, untreated linen with starch tends to yellow whereas grafted linen retains its original hue.

Untreated and grafted cotton before and after biodeterioration are shown in Figure 1.

Scanning Electron Microscopy

By SEM observations, it is clearly distinguishable the presence of fungi in untreated, coated and grafted materials, after 28 days of biodeterioration. In particular, Figs. 1a and 1c show Whatman paper untreated and coated with Paraloid B72® respectively; in the biodeteriorated samples (Figs. 2b and 2d), spores appear not homogeneously distributed.

Tensile Testing

The stress-strain behaviour of original, biodeteriorated, coated and grafted paper and textiles was measured by tensile deformation; all samples were tested to breaking. Young's modulus (E), stress (σ_B) and elongation (ε_B) at break for the cotton yarns are collected in Table 4. Biodeterioration induces a reduction in the stress at break and in the Young's modulus, whereas the elongation at break remains constant. By grafting with EA/MMA or by coating with Paraloid B72®, cotton becomes more flexible, as evidenced by the elongation at break values. Analogous results were obtained in the case of Whatman paper.

In comparison to cotton, the tensile properties of untreated linen yarns exhibit higher values of E and σ_B: it is well known that, among cellulose-based materials, linen shows good mechanical properties and a high resistance to stress.[28] Nevertheless, the behaviour after biodeterioration and conservative treatment is comparable to that evaluated for cotton.

The mechanical properties evaluation for each cellulose-based material show that biodeterioration reduces the stress at break (σ_B). The grafting process induces a better recovery in the mechanical resistance of paper and textiles, particularly elongation at break which increases up to values meaningful from the point of view of the mechanical behaviour. EA/MMA 75/25 is a rubber-like amorphous copolymer; therefore its choice for grafting polymerisation

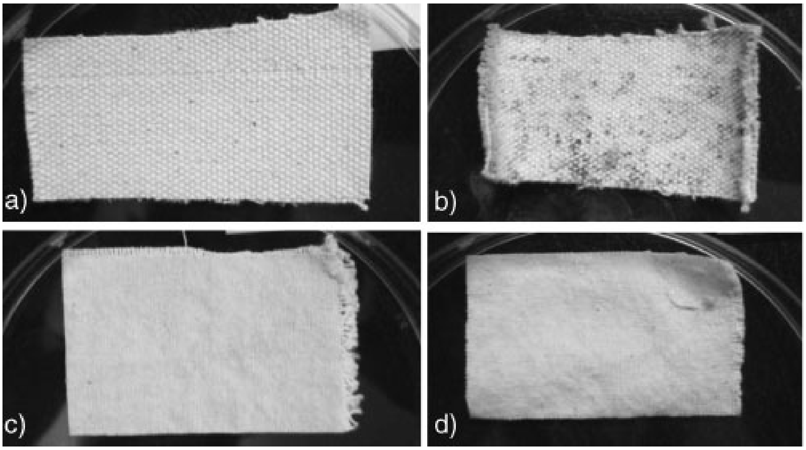

Figure 1.
Untreated cotton containing starch before (a) and after 28 days of biodeterioration (b) following the ASTM G21-96(2002) test. Cotton grafted with EA/MMA 75/25 before (c) and after 28 days of biodeterioration (d) following the ASTM G21-96(2002) test.

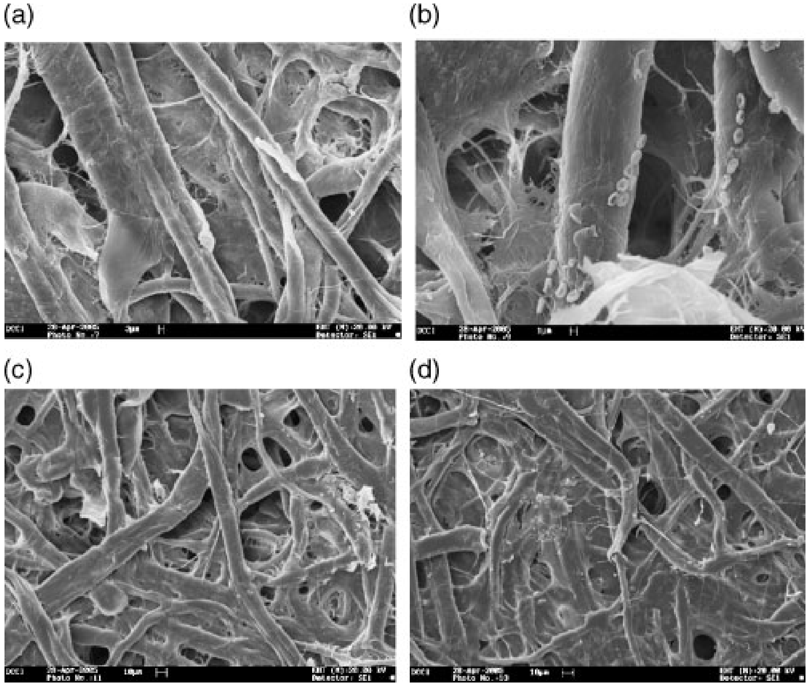

Figure 2.
SEM images for Whatman: a) Whatman (2000X), b) untreated and artificially biodeteriorated (6000X), c) coated with Paraloid B72® (1000X), d) coated with Paraloid B72® and artificially biodeteriorated (1000X)

has been suitable, in that paper and fabrics improve their typical flexibility after the treatment.

Conclusions

In our previous researches, it was proved that the grafting process does not modify the aspect of paper and fabrics; this is one of the main advantages for its future application for the conservation of objects with historical and artistic interest. On the contrary, after the coating with Paraloid B72® or preformed copolymers, i.e. EA/MMA 75/25, the cellulose-based materials appear stiff, losing their typical flexibility.

Acrylic copolymers represent very useful products for the conservation of cellulose-based materials. For a good conservation practice, it is mandatory to choose the most appropriate system, in our case EA/MMA 75/25, successfully employed in the grafting polymerisation onto paper, linen and cotton, because this copolymer has a glass transition temperature appropriate to the service temperature of the substrate. The mechanical strength and the flexibility of the grafted materials resulted improved, as well as, in the case of the

Table 4.
Tensile testing for original, biodeteriorated (28d), coated and grafted cotton: Young's Modulus (E), stress (σ) and elongation (ε) at break values.

Sample	E (GPa)	ε_B (%)	σ_B (MPa)
Untreated	0.34	27	35
Untreated biodeteriorated	0.15	26	24
Coated with Paraloid B72®	0.23	35	24
Grafted with EA/MMA	0.27	36	26

cotton and linen textiles, the resistance to biological agents. In addition, in contrast to coating, after the artificial biodeterioration grafted samples resulted not more yellow than untreated substrates. Thus, grafting polymerisation seems a suitable technique both to consolidate and prevent biodeterioration of cellulose-based materials, because it does not appreciably modify the aspect of substrates. Future research will provide other characteristics of samples before and after grafting polymerisation treatments, such as quantitative optical properties.

[1] B. J. Humphrey, *JAIC* **1986**, 25, 15.

[2] C. E. Butler, C. A. Millington, D. W. G. Clements, in "Historic Textile and Paper Materials", 2nd edition; E. F. Hansen, W. S. Ginell, S. H. Zeronian Eds., University of California (USA)1989.

[3] M. Azam Ali; M. A. Khan;K. M. Idriss Ali, G. Hinrichsen, *J. Appl. Polym. Sci.* **1998**, 70, 843.

[4] P. Gosh, Dev D . *Europ. Polym. J.* **1996**, 32, 165.

[5] F. E. Okieimen, D. E. Ogbeifun *Europ. Polym. J.* 1996, 32, 311.

[6] F. Khan, S. R. Ahnad *J. Appl. Polym. Sci.* **1997**, 65, 459.

[7] S. Margutti, S. Vicini, N. Proietti, D. Capitani, G Conio, E. Pedemonte, A. L. Segre, *Polymer* , **2002**, 43, 6185.

[8] E. Princi, S. Vicini, E. Pedemonte, G. Gentile, M. Cocca, E. Martuscelli, *European Polymer Journal*, **2006**, 42, 51.

[9] E. Princi, S. Vicini, E. Pedemonte, A. Mulas, E. Franceschi, G. Luciano, V. Trefiletti, *Thermochim. Acta*, **2005**, 425, 173.

[10] P. Cremonesi, B. Focher, L. D'Angiuro, *Cell. Chem. Technol.*, **1970**, 4, 497.

[11] P. Cremonesi, B. Focher, L. D'Angiuro, *Cell. Chem. Technol.*, **1972**, 6, 145.

[12] P. Cremonesi, B. Focher, L. D'Angiuro, *Cell. Chem. Technol.*, **1972**, 6, 277.

[13] M. L. Burstall, C. E. Butler, C. C. Mollett, *Journal of the Institute of Paper Conservation*, **1986**, 10, 95.

[14] S. Vicini, E. Princi, E. Pedemonte, *Recent Res. Devel. Macromol.* **2002**, 6, 59.

[15] J. T. Guthrie, P. D. Tune, *J. Polym. Sci., Part A: Polym. Chem.* **1991**, 29, 1302.

[16] R. Narayan, G. T. Tsao, *J. Polym. Sci., Polym. Lett. Ed.* **1984**, 22 635.

[17] A. Gandini, *J. Polym. Sci. Polym. Lett. Ed.*, **1984**, 22, 623.

[18] S. Margutti, G. Conio, P. Calvini, E. Pedemonte, *Restaurator*, **2001**, 22, 67.

[19] E. Princi, S. Vicini, E. Pedemonte, V. Arrighi, McEwen I., *J. Appl. Polym. Sci.*, **2005**, 98, 1157.

[20] F. Cappitelli, S. Vicini, P. Piaggio, P. Abbruscato, E. Princi, A. Casadevall, J. D. Nosanchuk, E. Zanardini, *Macromol. Biosci.*, **2005**, 5, 49.

[21] F. Cappitelli, E. Zanardini, C. Sorlini, *Macromol. Biosci.*, **2004**, 4, 399.

[22] U. J. Kim, S. Kuga, M. Wada, T. Okano, T. Kondo-*Biomacromol.*, **2000**, 1, 488.

[23] C. E. Brockway, *J. Polym. Sci. Part A*, **1964**, 2, 3733

[24] O. Chiantore, M. Guaita, M. Lazzari, *Int. J. Polym. Anal. Characterization*, **1996**, 2, 395.

[25] S. Vicini, E. Princi, G. Luciano, E. Franceschi, E. Pedemonte, D. Oldak, H. Kaczmarek, A. Sionkowska, *Thermochim. Acta*, **2004**, 418, 123.

[26] P. Goshy, G. Gangopadhyay, *Europ. Polym. J.* **2000**, 36, 1597

[27] F. Cappitelli, C. Sorlini, *Crit. Rev. Microbiol.*, **2005**, 31, 1–10.

[28] D. Klemm, B. Philipp, T. Heinze, U. Heinze, W. Wagenknecht, "Comprehensive Cellulose Chemistry", Wiley Ed., University of Jena Press, 1998.