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Physical–chemical characterisation of acrylic polymers grafted on cellulose

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Abstract

An oxidative reaction of cellulose with sodium metaperiodate was performed. The oxidised groups were decomposed by treatment with UV light into free macroradicals. In the presence of acrylic monomers, in the vapour phase, these reactive sites become the starting points for the graft copolymerisation of the cellulose substrate.

In this study we examined the graft yield as a function of the polymerisation time and the oxidation degree of cellulose. The grafted polymer was characterised using several analytical techniques, DSC analysis, GPC analysis, viscosity, FTIR and ^{13}C CP-MAS. Information on the morphology of grafted chains with respect to the bulk cellulose was obtained, measuring the dynamic parameters in a careful ^{13}C CP-MAS NMR study. All proposed chemical reactions, if properly conducted, do not affect the crystallinity of cellulose and introduce only a very modest amount of oligomers, therefore they seem suitable for the consolidation and protection of precious cellulose based materials, which are of historical interest. © 2002 Published by Elsevier Science Ltd.

Keywords: Grafting reaction; Cellulose modification; Acrylic grafting

1. Introduction

Cellulose is a non-branched polymer of β (14) glucose. The degree of polymerisation (DP) depends on the nature of the vegetable or animal species from which the cellulose is obtained and on the type of treatment used during the working process. The mechanical properties of a cellulose-based fibre, such as the tensile strength, are heavily dependent on its DP, by the cellulose crystalline structure present [1,2] and by the crystalline/amorphous ratio.

The main alteration of cellulose are: (i) photodegradation, (ii) acid hydrolysis, (iii) oxidation, (iv) biodegradation.

Since these phenomena are all related to each other, a full analysis of the material 'cellulose' is quite complex. In the present paper, we will consider only the oxidation process with the intent to reproduce natural oxidative ageing and to use the obtained products for a coupling reaction.

The oxidation reactions of cellulose are already widely studied and involve the primary and secondary hydroxyl groups of the pyranose ring leading to carbonyl and carboxyl groups, able to absorb UV and visible radiations. In fact both carbonyl and carboxyl groups are chromophores and their formation is responsible for the yellowing of the material. The oxidation reaction may be accompanied by the opening of the pyranose ring (Figs. 1 and 2). In both cases, the glycosidic bond becomes weaker and the eventual formation of carboxylic acids, see Fig. 2, increases the acidity of the material. Therefore, depolymerisation of cellulose (i.e. a reduction of its DP) occurs and a general worsening of physical and mechanical properties, particularly regarding the resistance to flexure.

In order to increase the mechanical properties of paper, the chemical structure of cellulose can be modified in different ways [3]:

- Replacement of the hydroxyl groups with other functional groups: usually esterification or ether formation

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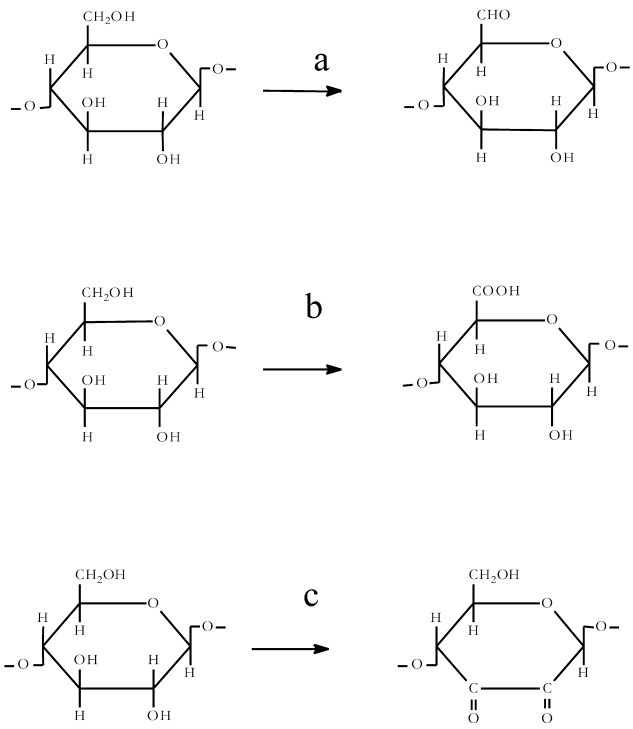

Fig. 1. Main oxidation reactions of the cellulose molecule without opening of the pyranose ring. (a) Oxidation of primary hydroxy groups into aldehyde groups. (b) Oxidation of primary hydroxy groups into carboxyl groups. (c) Oxidation of primary hydroxy groups into keto groups.

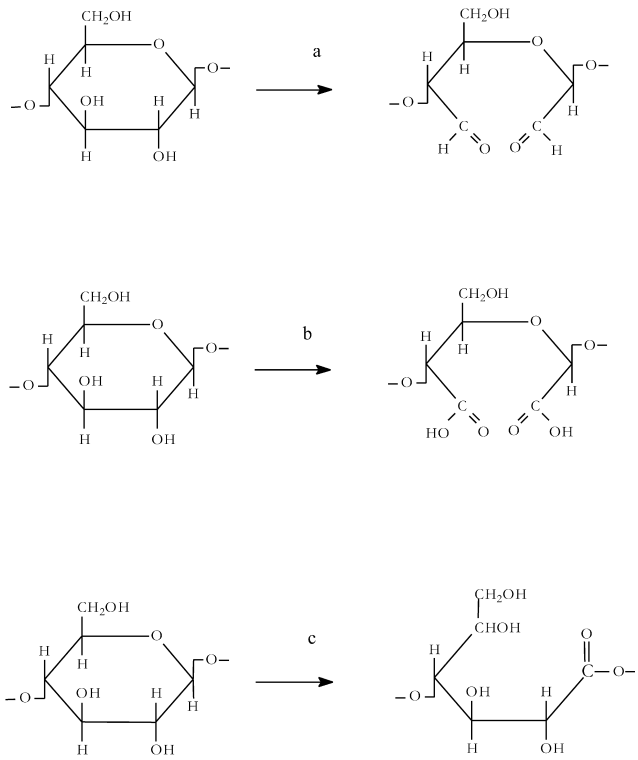

Fig. 2. Main oxidation reactions of the cellulose molecule with opening of the pyranose ring. (a) Oxidation of secondary hydroxy groups into aldehyde groups, with cleavage of the C–C bond. (b) Oxidation of secondary hydroxy groups into carboxyl groups, with cleavage of the C–C bond. (c) Oxidation of secondary hydroxy groups into keto groups, with cleavage of the C–O bond.

reactions are used. This type of treatment reduces some of the less desirable characteristics of the material such as flammability and susceptibility to microbial attack.

- Reaction with bi- or polyfunctional compounds: these reactions give cross-linking products whose global effect is the increase of the mechanical resistance of the material.
- Grafting reaction. This process binds synthetic polymers to cellulose thus improving the mechanical properties of cellulosic materials.

In this study a grafting reaction has been carried out on cellulose, using vaporised acrylic monomers: ethylacrylate (EA), methylacrylate (MA) and methylmethacrylate (MMA). Irradiating the system with ultraviolet radiation for a short time, the copolymerisation was started. UV, used for a short time, does not induce an appreciable degree of depolymerisation of cellulose [4–6].

The grafting reaction need photosensitive agents to allow the formation of radical sites on cellulose, the oxidised functional groups could be used for this aim. Carboxyl and carbonyl groups introduced by oxidation of substrate become active sites of cellulose and can be used in a grafting reaction [7–10]. In this study we present a semi-quantitative analysis of grafting reactions on cellulose and their yield as a function of grafting time.

The starting cellulosic material is simply a sheet of Whatman paper.

Before the grafting, few monomeric units had been oxidised to obtain dialdehydic groups, subsequently on these dialdehydic groups acrylic monomers were grafted. Along with the grafting reaction, we observed the presence of non-grafted homopolymer due to a homopolymerisation competitive reaction. This is an undesired effect, which reduces the effect of the grafting process and should therefore be minimised.

Since cellulose is insoluble in non-aggressive solvents, an accurate solid-state ^{13}C CP-MAS NMR study was performed, in order to obtain a quantitative analysis of the reaction yield. Therefore, the use of the solid-state NMR technique in a quantitative way will be discussed in details.

When a polymeric chain is grafted on a solid material, this chain can lay on the surface, or it can point outside, or it can find a path to the inner part of the material. All these possibilities have been carefully investigated using solid-state NMR techniques. The study of the cross-polarisation dynamic and the measurement of the spin lattice relaxation time in the rotating frame, $T_{1\rho}(^1H)$, allowed to accrue useful information on the morphology of the grafted chains in respect to the bulk cellulose.

Since the final aim of the research is the consolidation and the restoration of cellulosic manufactured objects, which belong to the field of Cultural Heritage, the obtained results suggest that the above mentioned grafting method is

applicable to old papers of historical and artistic interest, which are naturally oxidised.

2. Experimental part

2.1. Materials

The cellulose substrate was a Whatman No. 1 filter paper. This type of paper is obtained from cotton linters and can be considered as pure cellulose; its DP value is 1230. Sodium metaperiodate ($NaIO_4$ 99.8%) was obtained from Sigma-Aldrich and was used without further purification. Methylmethacrylate, (MMA), ethylacrylate, (EA) and methylacrylate, (MA) from Aldrich were used as starting materials and were purified from the polymerisation inhibitor (hydroquinone monomethylether) with an Inhibitor Remover column. Acetone, methanol, chloroform, tetrahydrofurane (THF), cuproethylendiamine (CED), sulphuric acid were laboratory grade products from Aldrich, used without further purification. Deionised water was used throughout the work.

2.2. Oxidation reaction

The oxidation of cellulose has been performed with sodium metaperiodate; a specific oxidising agent. The reaction cleaves the C2–C3 bond and involves the formation of a 2,3-dialdehyde [11,12] (Fig. 2(a)) following the mechanism of Malaprade reaction, without significant side reactions.

In every treatment the sample concentration was 1 g paper/100 ml sodium metaperiodate solution. Oxidation reactions have been carried out at 25 °C, on rectangular dry samples of the size of $1 \times 2\ cm^2$. The metaperiodate solutions were obtained dissolving the stoichiometric quantities of salt in deionised water. Cellulose samples have been introduced in closed vessels and treated with $NaIO_4$ in dark and under continuous stirring; at the end of the oxidation reaction samples have been filtered and washed with deionised water up to neutral conditions. The oxidised samples have been dried and kept in a sample holder in the dark. Several oxidations have been carried out with different time of treatment and different concentration of metaperiodate solutions.

2.3. Grafting reaction

The photoinitiated grafting reaction was carried out on Whatman No. 1 filter paper samples, which have been previously artificially oxidised.

Cellulose samples were oven dried and weighted; then brought up to 150% of their original weight by soaking in deionised water for 10 min. The polymerisation was carried out on 'wet' samples. After the absorption of water, the fibres were more accessible to the vaporised monomer, therefore being more reactive.

The cellulose sample was introduced into the reaction vessel. The reactor was connected to a vacuum pump and kept under vacuum for very short time so that the paper is still partially wet; once the pressure of 0.1 mm Hg was reached, the liquid monomer was loaded, vaporised, and diffused into the reactor. The monomer/cellulose ratio was 1.35 mmol acrylic/100 g of sample. The whole unit was then exposed to UV radiation from a metal iodide lamp: (150 W, colour temperature 3200 K) at a distance of 60 cm from the reactor surface. Since a low power lamp was used, no cooling system was required. All polymerisations were carried out at 28 °C.

The polymerisation was stopped by bringing the reactor up to room pressure. The non-reacted monomer was removed by washing the fibres with a mixture methanol–water (30/70 vol.), a good solvent for acrylic monomers only, not for the corresponding polymers. After that procedure the sample contained grafted cellulose and homopolymer; it was filtered and brought up to a constant weight (keeping under vacuum). Extraction of homopolymer was performed using acetone in a closed vessel [13] under the following conditions: sample/acetone = 1 g/100 ml; time: 50 h.

After the homopolymer had been extracted, the sample was filtered and brought up to a constant weight, keeping under vacuum.

In order to increase the grafting yield, some experiments of photoinitiated polymerisation were performed using Whatman paper samples previously oxidised and pre-irradiated with UV for 30 min. This pre-irradiation method [14], in which samples are irradiated before being brought into contact with the acrylic monomers, aimed at bringing the monomer in contact with aldehyde groups of cellulose chains which were already 'activated'. This technique has some advantages, such as the increasing of the penetration depth of the monomer, the reduction of the reaction time, and the formation of a minor amount of homopolymer.

The percentage of synthesised polymer during grafting reaction is calculated as follows

$$\%\ \text{polymer loading} = [(W_2 - W_1) \times 100]/W_1$$

being W_1 the initial weight of the sample and W_2 the dry weight of the polymerised sample before homopolymer extraction.

The quantity of grafted monomer (graft yield) was evaluated as the weight increase of the sample after the extraction of the homopolymer; it is expressed as the percentage increase of weight;

$$\%\ \text{graft yields} = [(W_3 - W_1) \times 100]/W_1$$

being W_3 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:

$$\%\ \text{grafting efficiency} = [(W_3 - W_1)/(W_2 - W_1)] \times 100$$

The amount of homopolymer is quantified according to the following relationship;

$$\%\ \text{homopolymer} = (W_H/W_2) \times 100$$

being W_H the weight of homopolymer after the extraction.

According to the relationship;

$$\%\ \text{homopolymer} = 100 - \%\ \text{grafting efficiency}$$

the percentage of monomer converted into homopolymer can be also obtained.

2.4. Separation of the grafted polymer from the cellulosic substrate

In order to characterise the grafted polymer, it was necessary to separate the acrylic polymer from the cellulose. A proposed method is the degradation of cellulose with sulphuric acid. The sample chosen for this experiment was the cellulose grafted with methylmethacrylate in the following conditions: Whatman oxidised with $NaIO_4$ 0.1 M for 2 h. Polymerisation time: 60 min after 30 min of pre-irradiation. Polymerisation pressure: 0.1 mm Hg. Ratio monomer/cellulose: 1.35 mmol/100 g.

In concentrated sulphuric acid while polymethylmethacrylate is not soluble, cellulose could be completely depolymerised; this process was performed under the following conditions: sample: grafted cellulose/H_2SO_4 (72% conc.) = 1 g/10 ml; time: 5 min.

2.5. Characterisation methods

2.5.1. Solid-state NMR

Samples were finely cut and packed into 4 mm zirconia rotors and sealed with Kel-F caps. Solid-state ^{13}C CP-MAS NMR spectra were performed at 50.13 MHz on a Bruker AMX-200 spectrometer. The spin-rate was always kept at 6 kHz. The 90° pulse width was 4 μs, the relaxation delay was 3 s. The cross-polarisation was performed applying the variable spin-lock sequence RAMP–CP-MAS [15,16], the RAMP was applied on the ^1H channel, the centre of the RAMP was set to the first matching sideband taking advantage of the faster cross-polarisation rate compared to that of the matching centreband. The contact time τ was 2 ms. Spectra were obtained using 1024 data points in the time domain, zero-filled and Fourier transformed to a size of 1024 data points.

The area of resonance was calculated using the SHAPE-2000 program which performs the spectral deconvolution [17]. The starting parameters for the deconvolution are the chemical shift, the line width and the intensity of each resonance of the spectrum. With the program, a best fit procedure is applied for obtaining the deconvoluted spectrum.

2.5.2. Quantitative NMR measurements

As well known, CP-MAS spectra are not quantitative, since the ^{13}C intensities depend on the cross-polarisation rates which may be different for different carbon atoms [18,19].

The optimisation of the cross-polarisation contact time has been afforded performing a full study of the cross-polarisation dynamic of the systems.

The cross-polarisation process depends on the dipolar interaction between the abundant spin system I (proton) and the dilute spin system S (carbon). Thus the rate of the process is strongly dependent on the number of abundant spins near dilute spin S and on their distance from S. The question rises when we wish to obtain a quantitative analysis of resonance due to carbon nuclei of different type. To bypass this problem it is necessary to investigate the cross-polarisation dynamic [20].

For simple cases, the kinetic of the cross-polarisation can be described by the equation [19];

$$\frac{S(t)}{S_0} = \frac{1}{\lambda}\left[1 - \exp\left(\frac{-\lambda t}{T_{IS}}\right)\right]\exp\left(\frac{-t}{T^*_{1\rho}(^1H)}\right)$$
$$\lambda = 1 + \frac{T_{IS}}{T_{1\rho}(^{13}C)} - \frac{T_{IS}}{T^*_{1\rho}(^1H)} \quad (1)$$

where S_0 is the 'true' area of the resonance; $T^*_{1\rho}(^1H)$ and $T_{1\rho}(^{13}C)$ are the proton and the carbon spin–lattice relaxation times in the rotating frame; T_{IS} is the cross-relaxation time between protons and carbons. With this method an approximate value $T^*_{1\rho}(^1H)$ of the proton spin–lattice relaxation in the rotating frame can be obtained.

As a function of the contact time (0.05–30 ms) different series of experiments were performed in all samples. The area of few selected resonances was reported as a function of the contact time. Fitting these experimental data to Eq. (1) the proton spin–lattice relaxation time in the rotating frame $T^*_{1\rho}(^1H)$ and S_0 were evaluated.

2.5.3. $T_{1\rho}(^1H)$ measurement

Since the spin–lattice relaxation time in the rotating frame $T_{1\rho}(^1H)$ is very important in double-resonance experiments involving cross-polarisation [20], we think it deserves some discussion.

$T_{1\rho}(^1H)$ for the abundant spin describes the rate at which a nuclear magnetisation, spin-locked in the rotating frame, approaches its thermal equilibrium value. In the spin-locking process, the magnetisation is brought into the x–y plane by a $\pi/2$ pulse, after which the phase of the radio frequency signal is changed to spin-lock the magnetisation on the y axis in the rotating frame. Since the effective magnetic field in the rotating frame B_{eff}, is orders of magnitude smaller than B_0, the rotating frame magnetisation is much larger than its thermal equilibrium value. Thus, the magnetisation decays toward the equilibrium value with the time constant $T_{1\rho}(^1H)$.

In our experiments, the effective field B_1 was 58 kHz. The variable spin-lock τ_i ranged from 0.05 to 35 ms.

For obtaining $T_{1\rho}(^1H)$ values, the intensity of the selected resonances versus the spin-lock time was reported. The obtained data were fit to the equation;

$$y_i = w \times \exp\left(-\frac{\tau_i}{T_{1\rho}(^1H)}\right) + c_0$$

being w, the weight of the exponential function and c_0, the average value of the experimental noise. Accurate measurements of this type were performed on Whatman paper, Whatman paper grafted with PMA and a sample of Whatman paper grafted with PMMA.

2.5.4. DSC analysis

A DSC analysis was performed on samples of grafted acrylic polymer separated from the cellulosic substrate in order to calculate the T_g of the grafted acrylic chains. A TA Instrument DSC Modulated 2920 was used. The samples were cycled 20 °C/min from −100 to 150 °C. In order to eliminate the effects deriving from earlier thermal histories, the second heating cycle has been always considered, after heating the sample up to 150 °C at 20°C/min and then cooling it down to −100 °C at a very high speed.

2.5.5. GPC analysis

The molecular weight of samples of grafted acrylic polymer separated from the cellulosic substrate was determined by size exclusion chromatography. Molecular weights are calculated relatively to a PMMA calibration. Nine poly(methyl methacrylate) narrow distribution standards were used to construct a calibration curve in terms of $\log(M_w)$ as a function of the elution time. The SEC analyses were performed with a Perkin–Elmer Diode Array Detector 235C and IBM computer. A set of 4 μstyragel columns with bead size of 500, 10^3, 10^4, 10^5 Å were used. HPLC grade THF was used as the eluent and the flow rate was kept at 1.0 ml/min. The samples were prepared in THF at 3 g/l.

The results are reported in terms of: M_w (weight average molecular weight), M_n (number average molecular weight) and $q = M_w/M_n$ (polydispersivity).

2.5.6. Viscosity measurements

In order to obtain the polymerisation degree of artificially oxidised cellulose, measurements of intrinsic viscosity were performed in cuproethylendiamine (CED). To avoid a fast degrading effect due to the oxygen on the polysaccharide solution, the solution has been prepared treating the dry samples with CED in a closed vessel under nitrogen and continuous stirring.

The molecular weight of the grafted polymer extracted from the cellulose substrate has been obtained by measurements of intrinsic viscosity in chloroform and THF.

Both the viscosities have been measured using the Hubbelohde viscometer. The determination of the DP and M_w can be carried out by using two equations: the first one is an empirical equation ($DP = K[\eta]^a$) and the second one is the Mark–Houwink–Sakurada equation ($[\eta] = KM^a$) where K and a are experimental constants [21].

2.5.7. FTIR measurements

The instrument we used for the infrared analyses is a FTIR Bruker IFS 66 spectrometer with a Globar type of source (silicon carbide brought up to incandescence), with a water cooling system and OPUS data processing program. Samples have been analysed with transmission measurements, i.e. by registering their absorbance.

The IR spectra of Whatman paper, oxidised Whatman paper, grafted Whatman paper and PMMA film have been carried out on KBr disk of variable depth.

3. Results and discussion

3.1. Effect of the oxidation of the samples

The oxidation of Whatman filter paper No. 1 was carried out by sodium metaperiodate ($NaIO_4$) at different concentrations: 0.01, 0.03 and 0.1 M. Different times of oxidation were also tested. Diluted solutions were slightly acid with a pH ranging from 5.4 to 5.7, whereas, for the more concentrated solution, the pH was 4.7.

For estimating the effects of the treatments on the polymerisation degree, viscosity measurements were performed; constants $K = 1.5$ and $a = 1$ were used in the empirical equation ($DP = K[\eta]^a$).

Table 1 shows viscosity and DP as a function of oxidation time. By increasing the concentration of the oxidising agent, DP decreases faster; nevertheless, the three trends converge to a common final value corresponding to the complete degradation of the paper. Since metaperiodate does not act directly on the glycosidic bond, but attacks only on the C2–C3 bond of the pyranose ring, the depolymerisation observed is due both to the effect of acidity and to the presence of aldehyde in the ring.

Owing to the high hygroscopicity of both untreated and oxidised sample, the FTIR analysis is not trivial. In fact the

Table 1
Viscosity (25 °C in CED 0.5 M) data and DP of the Whatman No. 1 filter paper oxidised by $NaIO_4$

$t_{oxidation}$ (h)	$NaIO_4$ 0.01 M		$NaIO_4$ 0.03 M		$NaIO_4$ 0.1 M	
	$[\eta]$ (dl/g)	DP	$[\eta]$ (dl/g)	DP	$[\eta]$ (dl/g)	DP
0	8.20	1230	8.20	1230	8.20	1230
1	5.93	890	3.06	460	1.60	241
2	2.60	390	1.95	293	1.23	185
3.75	2.20	330	1.66	250	1.13	170
5	2.00	300	1.60	240	1.10	165
24	1.60	250	1.42	214	1.07	160
48	1.46	240	1.40	210	1.07	160

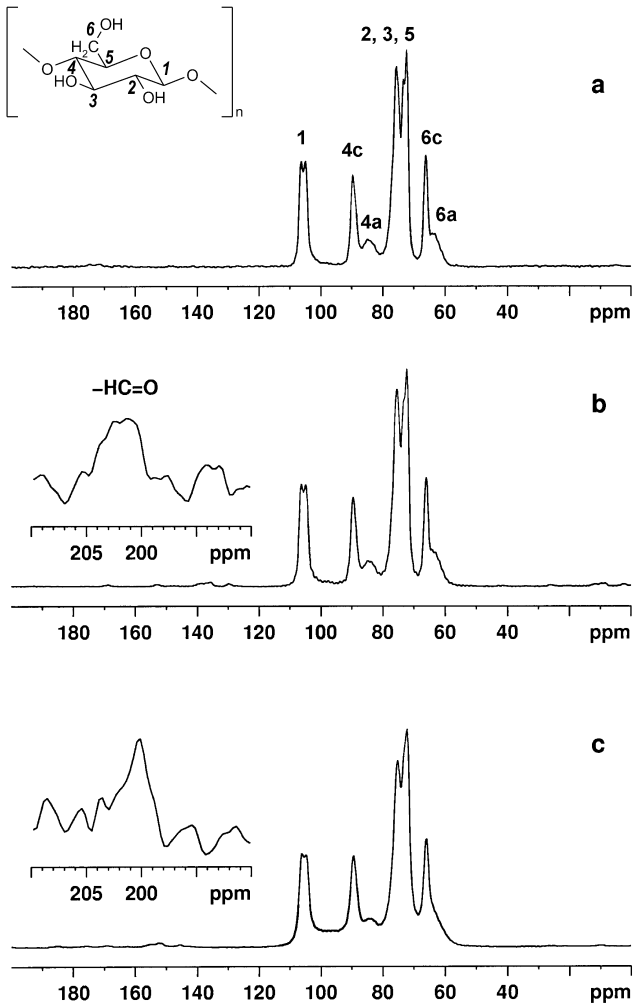

Fig. 3. ^{13}C CP-MAS NMR spectra of Whatman paper (a); Whatman paper oxidised with $NaIO_4$ for 2 h (b); Whatman paper oxidised with $NaIO_4$ for 5 days (c).

peak of the absorbed water is in the same region of carbonyl group between 1635 and 1670 cm^{-1} and sometimes it can be very broad, hiding the peak of the carbonyl groups of the cellulose.

Moreover in the oxidised samples, the identification of the functional groups is complicated because aldehyde, keto and carboxyl groups of oxy-cellulose absorb in a very narrow region of the spectrum between 1730 and 1780 cm^{-1}. The situation is even more complicated for the samples oxidised by metaperiodate, because dialdehyde cellulose can exist in partially or completely hydrated form, as hemiacetal or as hemialdale, i.e. in forms that do not present the conventional peak of the aldehydic carbonyl [22]. It is useful to compare the spectrum of the sample submitted to thermal and/or under vacuum treatment. In the spectrum of samples submitted to thermal treatments, a weak peak at about 1750 cm^{-1} is observed; this peak is due to the C=O stretching of carbonyl group, thus aldehydes in non-hydrated from are present. In the untreated sample this peak is absent [23].

In Fig. 3(a) the ^{13}C CP-MAS spectrum of the Whatman paper is shown along with the full assignment of all cellulose resonances. In Fig. 3(b), the spectrum of the Whatman paper after 2 h oxidation with $NaIO_4$ 0.1 M is shown. No apparent increase of the amorphous cellulose domain or presence of oligomers can be observed after oxidation (Fig. 3(b)). Thus the oxidation affects the cellulose surface while the bulk cellulose structure is unaffected [24,25]. The only apparent effect of the oxidation treatment is the presence of a very weak resonance at about 202 ppm, see the insert of Fig. 3(b). This resonance can be attributed to the dialdehydic groups [26]. Unfortunately, due to the transformation of aldehydic in hemiacetal species [27–30] the integral of resonance of the aldehydic group is strongly underestimated, unpairing even a very rough evaluation. Therefore, NMR confirm the presence of an aldehyde carbonyl signal previously seen in the infrared spectrum [23], however, the signal is much weaker than expected.

A prolonged oxidation treatment was attempted, carrying out the oxidation reaction for 5 days. In this case a noticeable browning of the sample occurs. The ^{13}C CP-MAS spectrum of this sample is shown in Fig. 3(c).

It is worth to note that the lengthening of the oxidation time is not convenient. In fact degradation of cellulose occurs, as shown by the presence of broad ^{13}C resonances due to oligomers in 90–100 ppm range, see Fig. 3(c). Moreover, the amorphous component of cellulose increases as shown by the growth of the signal at 84 ppm due to the carbon 4a (a = amorphous). The increase of the amorphous component is also evidenced by a general broadening of the whole cellulose spectrum.

Performing a full spectral deconvolution, it is possible to evaluate the amount of oligomers and of amorphous component as a function of the oxidation time. In Fig. 4(a) the ^{13}C CP-MAS experimental spectrum of Whatman paper oxidised for 2 h is shown, while in Fig. 4(b) the simulated spectrum is reported.

Results obtained from the deconvolution procedure show that the oxidation treatment of Whatman paper with $NaIO_4$ for 2 h does not affect the bulk structure of cellulose. In fact, only 6% of oligomer compounds are present and the amount of amorphous components is about the same as in untreated Whatman paper. Whereas after 5 days of oxidation the paper degradation is more evident. The oligomers content increases up to 25% whereas the amorphous component increases up from 40 to 50%.

3.2. Effect of the oxidation grade of the samples on grafting yields

To evaluate the dependence of the grafting yield on the concentration of sodium metaperiodate, the oxidation reaction was carried out on Whatman paper with $NaIO_4$ 0.01 M and 0.1 M for 2 h. The polymerisation reaction was

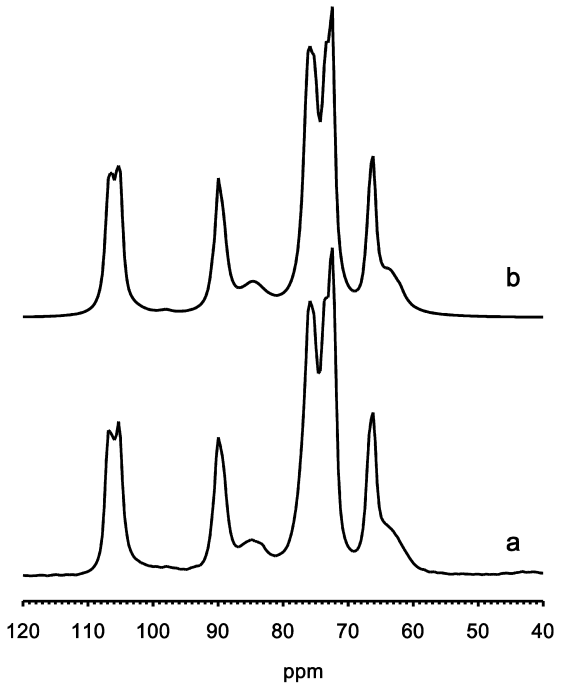

Fig. 4. (a) ^{13}C CP-MAS NMR experimental spectra of Whatman No. 1. (b) Simulated spectrum.

also carried out on an untreated Whatman sample, i.e. on a sample that had not been previously oxidised.

The results are given in Table 2. It must be pointed out that no grafting occurs on untreated Whatman paper. This observation confirms the role of the oxidised functional groups on the photosensitising process.

The data on the oxidised samples show that the grafting percentages were very different; by increasing the concentration of the oxidising agent by 10 times, the grafting percentage was about 30 times higher. Nevertheless, the efficiency of grafting was acceptable even for the samples oxidised by 0.01 M metaperiodate.

3.3. Characterisation of grafted cellulose

Both untreated and treated Whatman paper samples were submitted to FTIR analysis. The analyses were carried out after the extraction of the homopolymer from the fibres. The presence of grafted polymer chains is shown by the presence of the stretching of the acrylic synthetic polymer around 1670 cm^{-1} (peak of carboxyl group).

Table 2
Results of grafting reaction of MMA on Whatman No. 1 filter paper oxidised with different concentrations of $NaIO_4$. Oxidation time: 2 h. Polymerisation time: 60 min. Polymerisation pressure: 0.1 mm Hg. Ratio MMA/cellulose: 1.35 mmol/100 g

$NaIO_4$	% Graft yields	% Grafting efficiency
0	0	0
0.01	0.36	77
0.1	11	81.5

Samples grafted with EA, MA, MMA monomers were investigated by ^{13}C CP-MAS NMR technique.

The spectrum of the cellulose grafted with PEA sample is shown in Fig. 5(a). The 60–110 ppm region is unchanged, showing that the cellulose structure is not affected. In the spectrum we observe the resonances belonging to the EA: the methyl resonance is at 14 ppm; the broad resonance centred at about 40 ppm is due to the carbon resonance of the polymer backbone and at 176 ppm the carbonyl carbon resonance is observed. The carbon resonance due to the methylene carbon 4′, resonates at about 60 ppm and is hidden under the intense resonances of carbon 6 of cellulose. The quantitative evaluation of the amorphous/crystalline ratio and the presence of oligomers has been obtained by spectral deconvolution. For the sample grafted with EA, both the amount of oligomers and the amount of the amorphous fraction is similar to the corresponding amount calculated for the starting oxidised cellulose. Therefore, the grafting reaction does not affect the cellulose structure.

In Fig. 5(b) the spectrum of the cellulose grafted with PMA sample is reported. Resonances belonging to MA are

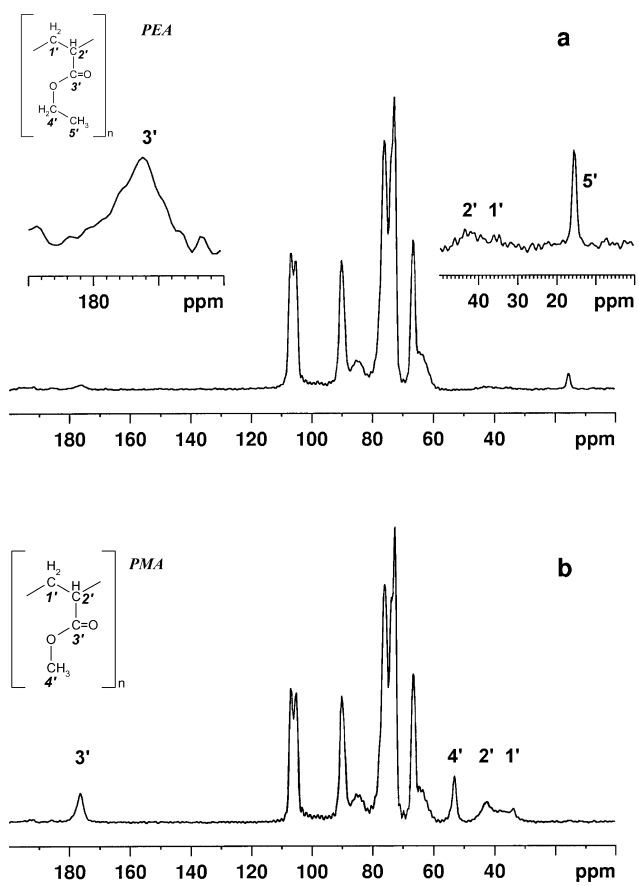

Fig. 5. ^{13}C CP-MAS NMR spectra of Whatman paper grafted with PEA (a); Whatman paper grafted with PMA (b).

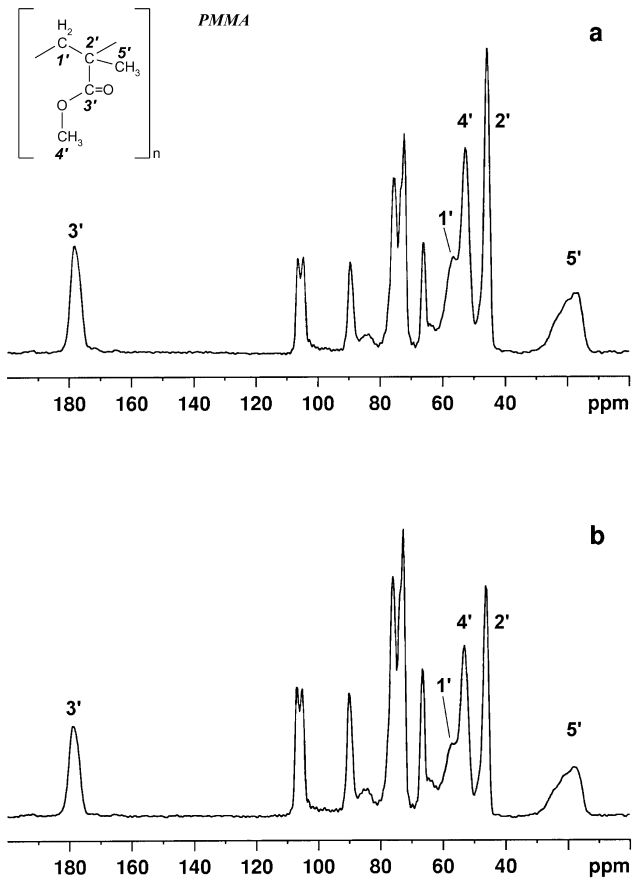

Fig. 6. ^{13}C CP-MAS NMR spectra of Whatman paper grafted with PMMA. (a) Sample WH-MMA 1: polymerisation time 5 h. (b) Sample WH-MMA 2: polymerisation time 1 h, the sample was irradiated for 30 min before the polymerisation.

well observable: the OCH_3 carbon resonance is observed at 51 ppm; the resonances due to the PMA backbone are observed at 33 and 43 ppm. Again, at 176 ppm the carbonyl carbon resonance is observed. The cellulose structure is not affected by the grafting reaction, in fact the spectral region 60–110 ppm is unchanged. Such results are confirmed by deconvolution analysis. In Fig. 6(a) and (b), the spectra of the cellulose grafted with PMMA are reported. The spectral region 60–110 ppm belonging to the cellulose does not show any changes, thus, also on these samples the grafting reaction does not damage the cellulose structure. The deconvolution analysis shows that no appreciable differences in the cellulose structure are present in respect to the Whatman paper oxidised for 2 h.

In the spectrum resonances belonging to MMA can be observed: the methyl 5′ is at 17.8 ppm, while the quaternary carbon resonates at 46.3 ppm. Again the carbon resonance due to the OCH_3 group is observed at 53.2 ppm; at 57.6 ppm the methylene carbon resonance is observed. The carbonyl carbon resonance is at 178.7 ppm.

Table 3
Results of grafting reaction of MMA on Whatman No. 1 filter paper oxidised with $NaIO_4$ 0.1 M for 2 h. Polymerisation pressure: 0.1 mm Hg. Ratio MMA/cellulose: 1.35 mmol/100 g

Polymerisation time (h)	% Graft yields	% Grafting efficiency
1	11	81.5
2	21	82
3	32	84
5	54	84.3
8	86	84
10	89	88

3.4. Effect of the polymerisation time on grafting yields

Table 3 shows the reaction yields as a function of the polymerisation time. The reproducibility of the reaction was evaluated: the error is ± 1%. As predicted, by lengthening the polymerisation time, the yields increased. After about 10 h 80–85% of the conversion of the monomer is reached and the reaction can be considered complete. Analysing the grafting efficiency, it can be observed that, raising the reaction time, the ratio between the grafted monomer and the monomer converted into homopolymer remains rather constant: the average percentage grafting efficiency is 84%. This result is interesting and demonstrates that the grafting reaction predominated on the homopolymerisation reaction.

The grafting percentage of PMMA obtained by submitting the oxidised Whatman paper to 30 min of pre-irradiation and to 1 h of polymerisation (see Table 5, column 4) was similar to the one obtained after 5-h grafting carried out on non-irradiated oxidised samples (Table 3). It is worth to note that pre-irradiation reduced the formation of the homopolymer without affecting the grafting yields. Furthermore, the reaction time was about 20% of that one necessary for not pre-irradiated samples.

Analysing the data, it became evident that it was more convenient to carry out the polymerisation on pre-irradiated samples rather than on simply oxidised samples.

The higher percentage of grafting was obtained with methylmethacrylate (MMA): the quantity of grafted copolymer was higher than that one obtained with methylacrylate (MA) and ethylacrylate (EA). In all cases the grafting reaction prevailed significantly over the homopolymerisation and the percentages of homopolymer were considerably low ranging between 15 and 7%.

The analysis of cellulose grafted with EA, MA and MMA by ^{13}C CP-MAS spectra shows that the reaction actually took place, however, the question exists of performing a quantitative analysis of the obtained compounds.

Due to the transformation of aldehydic in hemiacetal species, the error in determining the amount of dialdehyde for monomeric unit of cellulose is very large [27–30].

In the case of samples grafted with PEA, PMA and PMMA, for obtaining the area of the resonance of interest, a careful study of the cross-polarisation dynamic has been performed.

The area of resonances has been reported as a function of the contact time. In this way it is possible to obtain the area

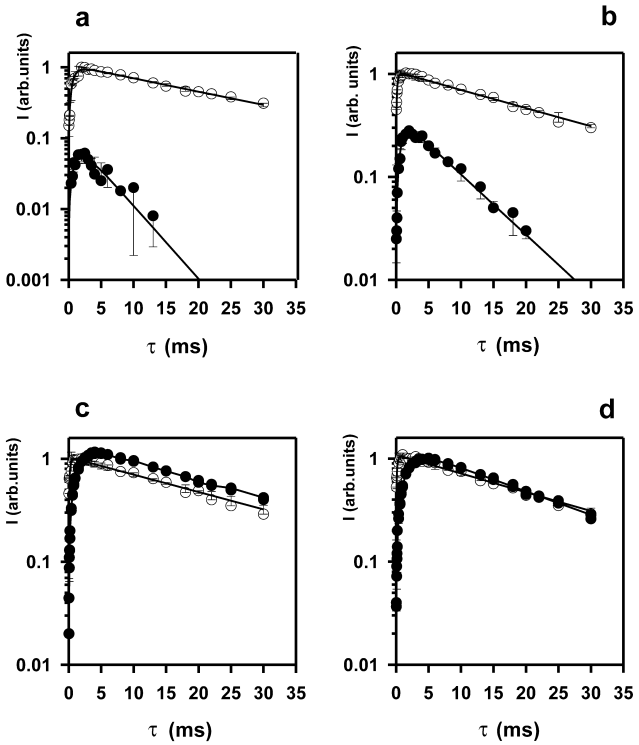

Fig. 7. Correlation between the intensity of anomeric (○) and carbonyl (•) carbon resonances of ^{13}C CP- MAS NMR spectra and the contact time τ. (a) Whatman grafted with PEA; (b) Whatman grafted with PMA; (c) Whatman grafted with PMMA, sample WH-MMA 1; (d) Whatman grafted with PMMA, sample WH-MMA 2. Lines through experimental points are obtained applying a best fit procedure to Eq. (1).

S_0 for each resonance of interest, being S_0, the extrapolated area at zero contact time, very near to the true area [19]. The obtained data were fit according to Eq. (1), see Fig. 7. Parameters obtained with the best fit procedure are reported in Table 4.

Using parameters obtained with the best fit procedure it is possible to estimate the grafting yield. In particular, the percentage of grafted monomer (graft yield) was evaluated as the ratio between the area of the carbonyl carbon resonance S_0(C=O) and the sum of areas of the anomeric carbon resonance, $S_0(C_1)$, and of the carbonyl carbon resonance S_0(C=O):

$$\text{NMR \% graft yield} = \{S_0(\text{C=O})/[S_0(\text{C=O}) + S_0(C_1)]\} \times 100$$

Results are reported in Table 5, third column. In the same table the obtained ratio has been compared with the graft yield obtained by methods described in Section 2.3. Data are in good agreement.

Table 4
Results of kinetics of the cross-polarisation and rotating frame spin lattice relaxation experiments

Sample	S_0	$T_{1\rho}^{H^*}$ (ms)	$T_{1\rho}^{H}$ (ms)
C_1			
WH	1.03 ± 0.02	24 ± 2	17 ± 2
WH-EA	1.05 ± 0.02	23 ± 2	
WH-MA	1.04 ± 0.02	25 ± 2	17 ± 2
WH-MMA 1	1.03 ± 0.02	26 ± 2	18 ± 2
WH-MMA 2	1.10 ± 0.02	24 ± 2	
C=O			
WH-EA	0.09 ± 0.01	4.2 ± 0.5	
WH-MA	0.36 ± 0.01	7.4 ± 0.5	3.5 ± 0.8
WH-MMA 1	1.40 ± 0.01	23 ± 2	15 ± 2
WH-MMA 2	1.30 ± 0.01	21 ± 2	

3.5. Morphological of the grafting: spin–lattice relaxation time in the rotating frame $T_{1\rho}(^1H)$

By performing cross-polarisation kinetics and applying Eq. (1) a rough value of proton spin–lattice relaxation time $T_{1\rho}^*(^1H)$ is obtained. As can be seen in Table 4, in the sample grafted with PMMA the same $T_{1\rho}^*(^1H)$ value for both C1 and C3′ resonances is measured. Whereas the sample grafted with PMA shows a $T_{1\rho}^*(^1H)$ value of resonance C3′ much shorter than the value measured for resonance C1.

For obtaining a precise measurement of $T_{1\rho}(^1H)$, a purposely made pulse sequence [20] must be used. Since the measurements is time consuming, we chose to measure accurate $T_{1\rho}(^1H)$ value only on three samples: Whatman paper, Whatman paper grafted with PMA and a sample of Whatman paper grafted with PMMA (see Table 4, column 4). As shown in the table, the obtained values $T_{1\rho}(^1H)$ are all shorter than the corresponding $T_{1\rho}^*(^1H)$ values.

In the sample grafted with PMMA C1 and C3′ resonances show the same $T_{1\rho}^*(^1H)$ value. Whereas the sample grafted with PMA shows a $T_{1\rho}(^1H)$ values of the resonance due to C3′ much shorter than the corresponding value measured for the resonance due to C1, see Fig. 8.

It must be pointed out that $T_{1\rho}$ (^1H) is different from $T_{1\rho}(^{13}C)$ in that $T_{1\rho}(^1H)$ is sensitive to the motion of the proton system averaged by spin diffusion over a short distance [18], while $T_{1\rho}(^{13}C)$ reflects the local motion. Thus $T_{1\rho}(^1H)$ is sensitive to macroscopic variations while $T_{1\rho}(^{13}C)$ is sensitive to site specific motions.

Since resonances C1 and C3′ are due to carbon atoms belonging to the cellulose and to the grafted polymer, respectively, using the $T_{1\rho}(^1H)$ data, information can be obtained on relative motion of the grafted polymer concerning to the bulk cellulose. In particular, it is possible to obtain information on the mobility of grafted chains in respect to the cellulose surface. In fact the grafted chains may lie on the surface becoming a whole with the surface itself or even may be able to penetrate the cellulosic material. Or the grafted chains may lie outside the cellulosic surface.

In cellulose samples grafted with PMMA, the equality, within the error, of $T_{1\rho}(^1H)$ measured on C1 and C3′ carbon resonances suggests that a spin diffusion process is fully active in equalising these two values. Thus, the grafted polymeric chain must be very close to cellulose chains, i.e.

Table 5
Results of grafting reaction of EA, MA and MMA on Whatman No. 1 filter paper oxidised with $NaIO_4$ 0.1 M. All samples, except sample WH-MMA 1, have been irradiated for 30 min before the polymerisation. Polymerisation pressure: 0.1 mm Hg. Ratio monomer/cellulose: 1.35 mmol/100 g

Sample	Polymerisation time (h)	% Graft yields by NMR methods	% Graft yields
WH-EA	1	8 ± 1	14
WH-MA	1	26 ± 1	28
WH-MMA 1	5	57 ± 1	54
WH-MMA 2	1	54 ± 1	50

lying on the surface or inside. In samples grafted with PEA or PMA, $T_{1\rho}(^1H)$ values measured on C1 and C3′ are very different, therefore, the spin diffusion process is not able to equalise these values. Then the grafted chains must lay outside the cellulose surface.

3.6. Characterisation of the grafted polymer separated from the cellulosic substrate

The grafted polymer has been separated from the cellulosic chain and characterised. The sample chosen for this experiment was the cellulose grafted with methylmethacrylate with a graft yields of 50% (Table 5).

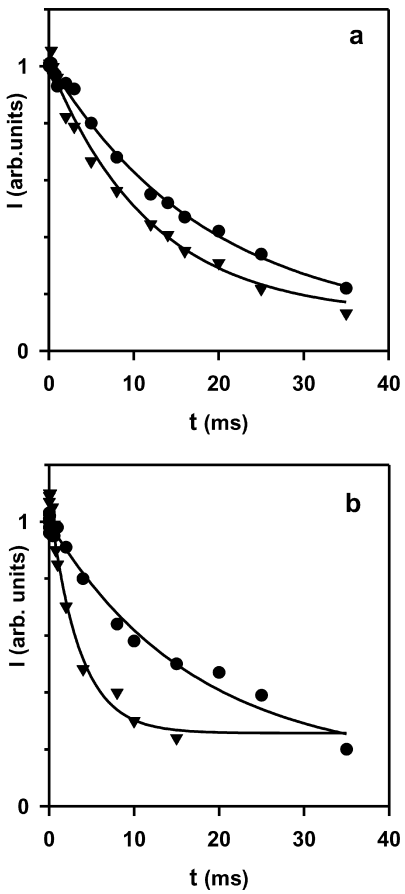

Fig. 8. The intensity of C_1 (○) and $C_{3'}$ (▼) carbon resonance is reported versus the spin lock time for cellulose grafted with PMMA (top) and cellulose grafted with PMA (bottom). Lines through experimental points are obtained fitting the data to equation: $y_i = w\exp(-\tau_i/T_{1\rho}(^1H)) + c_0$. Note that, in sample grafted with PMA, the $T_{1\rho}(^1H)$ of $C_{3'}$ resonance is much faster then the decay of C_1 resonance.

The T_g of separated polymethylmethacrylate is 108 °C, very close literature value [21].

Molecular weight of polymethylmethacrylate has been obtained by viscosity and GPC measurements. The intrinsic viscosity has been carried out in chloroform and THF at 20 and 25 °C [31–33] and the results are reported in Table 6. A good agreement is obtained between the M_v values (where $M_w > M_v > M_n$), changing solvent, temperature and thus K and a.

In Table 7, the GPC results are shown. Two set of M_n, M_w and q are reported; the data are obtained using two different calibration curves for the methylmethacrylate The two sets of values are very similar and in agreement with the viscosity results.

The study of separated polymer allows a chemical characterisation of grafted polymer. Both the T_g and the molecular weight values point to a grafted chain long enough to be considered a polymer and not an oligomer.

4. Conclusions

From the results obtained in this work the following conclusions can be drew:

1. The grafting with MMA gives the best result, with the highest number of acrylic monomers grafted on the cellulose chains: the quantity of grafted copolymer was

Table 6
Results of viscosity measures. K and a were obtained from light scattering method

T (°C)	Solvent	[η] (dl/g)	K (ml/g)	a	M_v
20	$CHCl_3$	1.75	5.5×10^{-3}	0.79	500.000
25	THF	0.97	7.5×10^{-3}	0.72	514.000

Table 7
Results of GPC measures in THF at 30 °C. K and a were obtained from light scattering method

K (ml/g)	a	M_w	M_n	q
7.5×10^{-3}	0.72	804.000	230.000	3.5
10.4×10^{-3}	0.70	807.000	224.000	3.6

higher than that with methylacrylate (MA) and ethylacrylate (EA). The monomer insertion does not alter the appearance of the treated paper; this aspect is very important when the samples are of historical and artistic interest, belonging to the field of Cultural Heritage.

2. It was more convenient to carry out the polymerisation on pre-irradiated samples rather than on simply oxidised ones.
3. In all cases the grafting reaction prevailed significantly over the homopolymerisation and the percentages of homopolymer were considerably low, ranging between 15 and 7%.
4. The quantitative evaluation of oxidation degree by ^{13}C CP-MAS NMR technique is strongly underestimated due to the transformation of aldehydic groups in hemiacetal species. The ^{13}C CP-MAS NMR technique has been used for demonstrating the grafting of PEA, PMA and PMMA on previously oxidised cellulose chains in paper. All carbon resonances due to the grafted polymers have been assigned. A study of the cross-polarisation dynamic has been performed for obtaining quantitative ^{13}C CP-MAS NMR spectra.
5. The measurement of the proton spin–lattice relaxation in the rotating frame for two properly selected resonances give information on the morphology of the grafting. In fact, in cellulose grafted with PMMA, the grafted chains lay completely on the cellulose surface or inside, while, in all other polymers, the grafted chains are free point outside to the surface.
6. A prolonged oxidation time deeply attacks the cellulose structure. This situation is never observed in ancient paper samples (which show a weak natural oxidation), even when they present a marked degradation [34]. Therefore, in order to graft the acrylic monomers, only a weak oxidation of the sample must be carried out. All reactions, if properly conducted, do not affect the degree of crystallinity of the cellulose and introduce only a very modest amount of oligomers, therefore they seem suitable for the protection of precious cellulose based materials.
7. The characterisation of grafted acrylic polymer, separated from the cellulosic chain, allowed to assert that the grafted chain, being formed by at least 2300 monomeric units, is long enough to be considered a polymer and not an oligomer.
8. As far as mechanical properties are concerned, the cellulose/polymer matrix formed should be both strong and flexible. Even if the best grafting yields is undoubtedly with PMMA, the corresponding T_g is 105 °C; therefore, when grafted to cellulose, it might produce a brittle material. A mixture of MMA/EA could be very suitable to achieve a lower T_g and so better mechanical properties [35].

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