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Poly(ethyl acrylate) surface-initiated ATRP grafting from wood pulp cellulose fibers

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ABSTRACT

Wood pulp cellulose fibers were functionalized by partial esterification of the superficial –OH groups with α-bromoisobutyryl bromide (BIBB) under mild (room temperature and THF as solvent) and harsh (85 °C and pyridine as solvent) conditions. Samples were characterized by ATR spectroscopy, EDXS, elemental analysis and SEM. Functionalization degrees was varied up to 2% mol Br/OH (by elemental analysis) by varying reaction time and method, without affecting the fiber morphology, except for the highest modification degree, where external cell-wall was partially degraded.

The BIBB-functionalized wood pulp cellulose was used as initiator for surface-initiated ATRP of ethyl acrylate in the presence or not of free-"sacrificial" initiator. Poly(ethyl acrylate) (PEA) modified fibers were characterized by ATR spectroscopy, SEM, thermogravimetric (TGA) and calorimetric (DSC) analyses, while ungrafted polymer was characterized by SEC. A direct correlation was found between the functionalization degree by BIBB and the amount of grafted polymer; products from 3% to 80% wt of grafted poly (ethyl acrylate) were obtained.

Thermal destabilization of wood pulp fibers occurred because of the BIBB functionalization, which was recovered by the successive PEA grafting. Moreover, an increase of the glass transition temperature of the grafted polymer with respect to ungrafted one was observed.

1. Introduction

In the last decades, a large number of studies has been directed toward the physical and chemical modification of polysaccharides in order to obtain new functional materials and high performance composites. Among the possible strategies, grafting polymerization, through both the grafting "from" and grafting "onto" approach, represents an appealing way to modify polymers so as to maintain the properties of the substrate polymer and add the properties of the grafted side chains(Ranby & Rodehe, 1982, chap. 17). This is of great interest for natural polymers (polysaccharides, polypeptides, polynucleic acid) which belong to our renewable resources, but occur in a few basic types and do not show versatile properties for many structural and functional applications.

Concerning cellulose fibers, graft copolymerization has several actual and potential applications in textile and paper industry such as improvement of soil release and fabric comfort (Williams & Stannett, 1976; Williams & Stannett, 1979), reduction of hydrophilicity, resistance to abrasion and heat (Walsh, Siahkolah, & Rutherford, 1969), flame retardancy (Liepins, Surles, Morosoff, & Stannett, 1977a; Liepins, Surles, Morosoff, Stannett, & Barker, 1977b; Liepins et al., 1978), antibacterial activity (Lee, Koepsel, Morley, & Matyjaszewski, 2004; Vigo, 1998). In addition cellulose fibers graft copolymers have been widely experimented in natural fibers reinforced composites in order to optimize the adhesion between the matrix and the fibers and overcome the usual problems of incompatibility between the hydrophilic natural phase and the hydrophobic synthetic phase (Bledzki & Gassan, 1999; Bledzki, Reihmane, & Gassan, 1996).

The "grafting from" process was carried out on cellulose fibers using mainly conventional free radical polymerization of vinyl monomers by generating radicals on the polymer backbone by redox systems, chain transfer processes or irradiation (Kubota & Ogiwara, 1969; Margutti et al., 2002; Oprea, Dumitriu, & Bulacovski, 1979; Ranby, 1978; Trinci, Vicini, Proietti, & Capitani, 2005). Typically these processes are characterized by low control over molecular weight and polydispersity of grafted chains, chain density on the substrate, possible degradation of the fibers. Moreover, the homopolymerization of the added monomer frequently predominates with respect to graft copolymerization.

More recently controlled/living polymerization processes have been successfully employed for cellulose graft copolymerization (Barsbay et al., 2007; Carlmark & Malmstrom, 2002; Coskun & Temuez, 2005; Daly, Evenson, Iacono, & Walker, 2001; Hafren & Cordova, 2005; Lindqvist & Malmström, 2006; Roy, Guthrie, & Perrier, 2005; Roy, Guthrie, & Perrier, 2006; Roy, Guthrie, & Perrier, 2008a; Roy, Guthrie, & Perrier, 2008b). Particularly, in surface-initiated ATRP (SI-ATRP), typically initiators are immobilized on the substrate by reacting the superficial hydroxyl groups with an

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ATRP initiator precursor (usually 2-bromoisobutyryl bromide, BIBB). Then the initiator-modified substrate is used to perform graft ATRP grafting. The SI-ATRP of acrylic and methacrylic side chains has been experimented in order to modulate filter paper (cotton linter based) surface properties, such as hydrophobic/hydrophilic character and antibacterial activity (Carlmark & Malmstrom, 2003; Lee et al., 2004). Analogous approach was followed to graft polystyrene on jute fibers to be used in fiber-reinforced PS composites (Plackett, Jankova, & Egsgaard, 2005) and to encapsulate cotton fibers with homo- and block-copolymers of hydrophobic monomers such as ethyl acrylate and styrene (Castelvetro, Geppi, Giaiacopi, & Mollica, 2007). SI-ATRP was also used to graft liquid-crystalline polymers on filter paper surface aiming to obtain addressable/responsive bio-based substrates (Westlund, Carlmark, Hult, Malmstrom, & Saez, 2007). These studies showed that by performing SI-ATRP under appropriate conditions (Fischer, 1997; Huang, Kim, Bruening, & Baker, 2002; Matyjaszewski et al., 1999) it is possible to achieve grafted chains with well-defined molecular weights, and block copolymers.

In this work, we focused on the surface-initiated ATRP grafting from wood pulp cellulose which is the most used raw material in paper industry. It is usually obtained from wood by mechanical and alkaline delignification process (Kraft process) (Roberts, 1996) with possible additional bleaching and refining stages. This substrate shows peculiar features if compared to cellulose from other sources. For instance wood pulp is generally less crystalline than cotton cellulose, mostly used for Si-ATRP experiments, and also less pure due to the presence of residual hemicellulose and lignin. Moreover the delignification process introduces new functionalities on cellulose fibers, mainly carboxylic groups (Roberts, 1996). All these features can influence the accessibility and reactivity of the substrate (Frilette, Hanle, & Mark, 1948; Oprea et al., 1979; Tasker, Badyal, & Backston, 1994), therefore its attitude to be surface modified.

In perspective, synthetic–natural hybrid materials based on wood pulp cellulose could be of interest in papermaking to influence structural and functional properties of paper products.

In our work, the possibility to modulate the amount of ATRP initiator covalently bonded to wood pulp cellulose fibers and thus the chain density was at first studied by varying the condition of the –OH esterification with BIBB. This topic was already approached by reacting filter paper with mixtures of bromoisobutyrilbromide (BIBB) and propionyl bromide (Lee et al., 2004). The latter acts indeed as a blocking agent since it does not include a functionality for ATRP initiation. Instead in our case the subsequent heterogeneous polymerization step brought to products that have various grafts chain densities and maintain different amount of unreacted hydroxyl functionalities. The free –OH groups could be available for subsequent functionalization reaction and/or hydrogen bonding in fiber felts. Secondly, the grafting of different amount of poly(ethyl acrylate), to the BIBB esterified wood pulp fibers provided a synthetic phase with hydrophobic character and low glass transition temperature (−20 to −40 °C) which can thermally stabilize the natural fibers.

2. Experimental

2.1. Materials

Wood pulp cellulose (pulp) (fiber length 2 ÷ 2.5 mm; tensile index, ISO1924/2 9.2 ÷ 9.8 km), kindly supplied by Centro Italiano Packaging (CIP), Venezia, Italy, was obtained by Kraft process and refinement (38 min) from soft wood (70% spurce, 25% pine, 5% larch). It was purified by Soxhlet extraction with acetone and tetrahydrofuran (THF) (6 h each) and dried under vacuum before use. Filter paper, Whatman #1 (WH) from cotton linter cellulose, purified as for pulp cellulose, was used as reference.

Ethyl acrylate (EA) was distilled under reduced pressure from calcium hydride (CaH_2) (100 mmHg, 50 °C) and stored under nitrogen. THF was kept on KOH overnight, then distilled from sodium (67 °C) under nitrogen atmosphere and stored over molecular sieves (3 Å). Triethylamine (Et_3N) was distilled from potassium hydroxide (KOH) under nitrogen atmosphere (78 °C). All purified solvent and chemicals were stored under nitrogen atmosphere, while all other chemicals and solvents (Aldrich or Carlo Erba) were used as received.

2.2. Instruments and characterization methods

Infrared spectra were recorded by a Perkin–Elmer Spectrum GX equipped with a Horizontal Attenuated Reflectance accessory with a ZnSe crystal (ATR) on cellulose fiber dishes obtained in a hydraulic press at room temperature. ^1H NMR spectra were recorded with a Varian 200 MHz instrument on 30 mg/mL $CDCl_3$ solutions. Thermogravimetric analysis (TGA) was carried with a Mettler Toledo TGA/SDTA 851e in nitrogen (flux 60 mL/min) in the 25 ÷ 800 °C temperature range at 10 °C/min as heating rate on 20–30 mg samples. Differential Scanning Calorimetry (DSC) measurements were performed by using a DSC 822^e-Mettler Toledo cooled by liquid nitrogen and controlled with a STARe software 6.10 version. Aluminium standard pans with 10–20 mg of sample were used for analyses that were carried out under a nitrogen atmosphere. Samples were cooled to −120 °C at 10 °C/min and after and isotherm step for 10 min were heated to 25 °C at 10 °C/min. Scanning electron microscopy analysis (SEM) was performed on gold sputtered samples using a JEOL JSM-5600 LV scanning electron microscope. Energy dispersive X-ray spectroscopy (EDXS) was performed using an Oxford EDXS system attached on the above mentioned SEM (pressure between 12 and 15 Pa). Elemental analyses (C, H) were performed by Laboratorio di Microanalisi, Facoltà di Farmacia, Università di Pisa, with a C. Erba mod. 1106 elemental analyzer. The amount of Br in BIBB modified cellulose was calculated from the C and H increase with respect to the unmodified cellulose. Molecular weight and polydispersity of poly(ethyl acrylate)s (PEA) were determined by size exclusion chromatography (SEC) on a Jasco PU-1580 apparatus equipped with 2 PLgel 5 μm Mixed-D columns eluted with $CHCl_3$ at 1 mL/min, RI JASCO 830 and UV Perkin Elmer LC-75 set at 270 nm as detectors. Monodisperse polystyrene standards were used for the calibration.

2.3. Tris(2-(dimethylamino) ethyl)amine (Me_6TREN)

It was prepared from tris(2-(aminoethyl)amine) (98%, Aldrich) by following the procedure from Matyjaszewski and co-workers (Queffelec, Gaynor, & Matyjaszewski, 2000). The crude product was purified by extraction with diethyl ether; the organic phase was dried over Na_2SO_4 and then distilled under reduced pressure (Ciampolini & Nardi, 1966) (0.5 mmHg, 68 °C) to give a pale yellow oil (81% yield), which was stored at −20 °C under nitrogen atmosphere until use.

^1H NMR (200 MHz, $CDCl_3$) δ: 2.58 (dd, 12 H), 2.36 (dd, 12H), 2.21 (s, 12H) ppm.

2.4. Immobilization of ATRP initiator on pulp cellulose

Two different methods (A, B) were adopted for the immobilization of ATRP initiator on pulp cellulose, through esterification of the –OH groups on fiber surface with α-bromoisobutyryl bromide (BIBB).

Method A was adopted from Carlmark and Malmstrom (2003). Triethylamine (66.7 mL, 0.48 mol) and a catalytic amount of 4-di-methyl aminopyridine were dissolved in 550 mL of THF. The cellulose (12 g) was immersed in the solution under nitrogen and BIBB (53 mL, 0.43 mol) was added dropwise to the heterogeneous mixture kept at 0 °C in a water/ice bath; then the temperature was raised to 25 °C. Cellulose portions were collected periodically (Table 1), washed with CH_2Cl_2 and THF, ultrasonicated in CH_2Cl_2 and THF (3 min for each solvent), Soxhlet extracted with ethanol for 8 h to completely remove any unbounded species and then dried under vacuum for 24 h. The same method was used for the modification of WH paper chosen as reference.

The pulp and WH paper cellulose that was modified under method A was named Ax or WHx, respectively, where x is the reaction time in hours.

Method B. A mixture of CH_2Cl_2 (6 mL), pyridine (8.8 mL, 109 mmol) and BIBB (13.5 mL, 109 mmol) was prepared under nitrogen atmosphere and heated at the reflux temperature (85 °C). Pulp cellulose (0.5 g) was immersed into the solution and kept therein for a period of time ranging between 2 and 10 min (Table 1). The fibers were removed from the flask, rinsed with CH_2Cl_2 and THF, washed by ultrasonication with CH_2Cl_2 and THF (3 min for each solvent), Soxhlet extracted with ethanol for 8 h and then dried under vacuum for 24 h. The pulp cellulose modified under the described procedure was named Bx where x is the reaction time in minutes.

2.5. Setting of ATRP conditions for ethyl acrylate

A CuBr/Me_6TREN stock solution was prepared from 28 mg (0.195 mmol) of CuBr, 50 μL (0.195 mmol) of Me_6TREN and 1 mL of ethyl acetate (EtOAc) previously degassed by three freeze–thaw–pump cycles. 4 mL (36.9 mmol) of EA, eventually premixed with EtOAc (0–50% wt), was degassed by three freeze–thaw–pump cycles and mixed with the catalyst solution (catalyst/initiator 0.1–1 mol/mol). Polymerization was started by the addition of 54 μL (0.37 mmol) of ethyl 2-bromopropionate (EBP), carried out under nitrogen and stopped by exposing to air and adding 10 mL of EtOAc. Copper was removed through a column of aluminum oxide and polymer was recovered by solvent evaporation.

The kinetics of EA polymerization was followed by ^1H NMR spectroscopy on samples periodically withdrawn from the solution. The ratio between the signals ascribed to the EA double bond protons (5.8–6.4 ppm) and the O–CH_2– signals of EtOAc and EA (4–4.2 ppm), which were used as references, allowed to follow the evolution of the monomer conversion with time. Similar results were obtained by using the CH_3– signal instead of the O–CH_2– as internal reference.

2.6. Surface-Initiated ATRP grafting of poly(ethyl acrylate) from cellulose

A CuBr/Me_6TREN stock solution was prepared from 28 mg of CuBr, 50 μL of Me_6TREN and 1 mL of EtOAc, thus an amount (Table 2) was added to the EA/EtOAc mixture (2/1 by volume) degassed by three freeze–thaw–pump cycles. The addition of the dried initiator-modified pulp or WH (macroinitiator) and eventually ethyl 2-bromopropionate (EBP) as free-"sacrificial" initiator started the polymerization that was carried out at 0 °C under nitrogen atmosphere and stopped by air exposition and THF addition. Polymerization time was 6 h except when differently indicated. The modified pulp fibers or WH paper were recovered by filtration, washed with CH_2Cl_2 and THF, ultrasonicated in CH_2Cl_2 and THF (3 min for each solvent), Soxhlet extracted with ethanol for 8 h and finally dried under vacuum for 24 h. The grafting percentage was expressed as relative pulp or WH weight increase.

3. Results and discussion

3.1. Initiator immobilization on wood pulp cellulose fibers

Two different experimental methods were compared to graft ATRP initiator on wood pulp cellulose through esterification of hydroxyl groups on fiber surface with α-bromoisobutyryl bromide (BIBB). In order to convert just few –OH on the surface without affecting the fiber bulk, THF was selected as the solvent in method A since it does not swell cellulose (Mantanis, Young, & Rowell, 1995). Reactions were carried out for different time (Table 1) at room temperature with a double molar amount of BIBB with respect to the cellulose –OH groups. Harsh conditions were experimented in method B: reactions were carried out for different time at 85 °C, in large excess of pyridine and BIBB with respect to the total –OH groups of pulp cellulose

ATR/FT-IR spectra of all pulp samples modified by method A did not differ from the spectra of unmodified pulp cellulose except for the presence of a new very weak peak with maximum at 1730 cm^{-1} in samples A6 (reaction time 6 h) and A21 (reaction time 21 h). The new band can be attributed to the carbonyl stretching band of α-bromoester groups, grafted to pulp as a result of the esterification of the cellulose –OH groups by BIBB. The EDXS analysis of sample A6 and A21 showed a weak but detectable signal attributed to bromine, thus confirming the BIBB grafting. The bromine and carbon peak intensities in EDXS analysis were exploited to compare the bromine content in BIBB modified pulp (Table 1), and comparable functionalization degrees were found in A6 and A21 samples (Table 1) thus indicating that no further bromination occurs after 6 h of reaction, as observed for filter paper (Carlmark & Malmstrom, 2003).

The harsh conditions experimented in method B allowed to achieve rather high degree of surface esterification as evidenced by ATR/FT-IR analysis. A well detectable carbonyl stretching band was observed with a maximum at 1730 cm^{-1} attributed to the grafted BIBB (Fig. 1). Increasing reaction time resulted in increasing carbonyl band intensity (Fig. 1) and bromine surface content, so as observed from energy dispersive X-ray spectroscopy (EDXS), thus proving the correlation between surface grafting degree and reaction time (Table 1).

No detectable morphology change with respect to unmodified cellulose was observed by SEM analysis of all modified samples

Table 1
Maximum values of BIBB immobilized on pulp cellulose fibers by esterification of hydroxyl groups, as estimated from different analysis methods

Sample	Reaction time	EDXS		SEC
		Br/OH[a] [% mol]	Br/cellulose[b] [mol/g]	Effective Ic[c] [mol/g]
Pulp	–	No bromine	No bromine	
WH	–	No bromine	No bromine	
A2	2 h	No bromine	No bromine	
A3	3 h	No bromine	No bromine	
A4	4 h	No bromine	No bromine	
A6	6 h	0.48	8.7×10^{-5}	$\geqslant 0.46 \times 10^{-5}$
A21	21 h	0.47	8.6×10^{-5}	$\geqslant 0.28 \times 10^{-5}$
B2	2 min	0.30	5.5×10^{-5}	
B5	5 min	0.52	9.5×10^{-5}	
B10-1	10 min	1.35	25×10^{-5}	
B10-2[d]	10 min	7.00	130×10^{-5}	$\geqslant 18 \times 10^{-5}$
WH21	21 h	1.63	30×10^{-5}	$\geqslant 0.96 \times 10^{-5}$

[a] Br/OH = $n_{Br} \times 100/[(n_c - n_{Br} \times 4) \times 3/6]$ where n_{Br} and n_c are the amount of bromine and carbon atoms by mole percentage, respectively, as detected by EDXS analysis.

[b] Surface bromine concentration calculated as follows: Br/cellulose = $n_{Br}/[(n_c - n_{Br} \times 4) \times 163.155/6]$.

[c] Calculated from SEC data, as described later in the text, for the experiments carried out in presence of ethyl 2-bromopropionate as free-"sacrificial" initiator.

[d] Left in the reaction mixture during the final quenching with ethanol.

Table 2
Surface initiated ATRP of ethyl acrylate from 1 g of BIBB-functionalized cellulose

Entry	Sample[a]	BIBB-functionalized cellulose	Catalyst [mmol]	Free Initiator [mmol]	EA/initiator[a] [mol/mol]	% G[b] [% wt]	$\bar{M}n_{SEC}$ of ungrafted polymer
1	B10PP	B10-2	1.28	13	100	60.6 ± 1.9	8500
2	A3PP	A3	0.45	4	100	Nd[c]	8200
3	A6PP	A6	0.45	4	100	3.7 ± 0.9	9300
4	A21PP1	A21	0.42	4	100	2.9 ± 0.9	8700
5	A21PP2	A21	0.36	2	250	2.6 ± 0.9	12000
6	A21PP3[d]	A21	0.19	2	250	5.0 ± 0.8	23300
7	WH21PP	WH21	0.40	2	250	12.7 ± 2.1[e]	13100
8	A21 P	A21	0.28	No	–	5.4 ± 0.9	–
9	B2P	B2	0.12	No	–	41.9 ± 0.7	–
10	B10P	B10-2	0.49	No	–	79.1 ± 0.3	–
11	A21PP-P[d]	A21PP1	0.001	No	–	24.1 ± 1.1	–
12	A21P-P[d]	A21P	0.001	No	–	Nd	–

[a] Double P indicates the presence of ethyl 2-bromopropionate as free initiator (check column 4) and so the formation of both grafted and ungrafted polymer.
[b] $(wt_{PEA}/wt_{Cell\text{-}g\text{-}PEA}) \times 100$.
[c] No grafted poly(ethyl acrylate) was detected by gravimetric analysis even if revealed by ATR-IR spectroscopy.
[d] Polymerisation time 21 h.
[e] Average data for two experiments performed on reference paper.

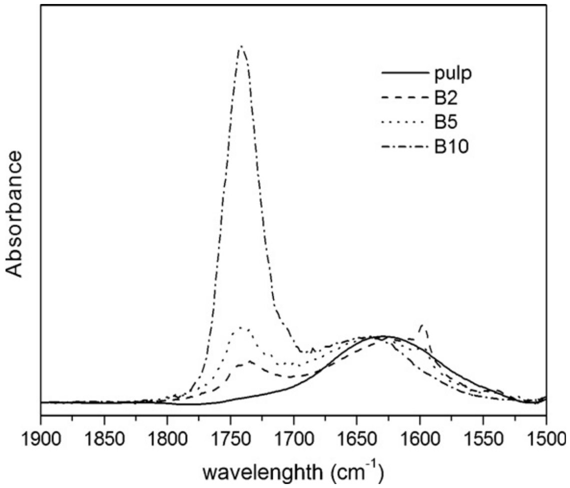

Fig. 1. Carbonyl region detail of ATR/FT-IR spectra of BIBB modified cellulose fibers by method B (reaction time evidenced).

except for B10-2 (Fig. 2a–e). This last showed degraded external cell-wall due to the hydrolysis by the HBr formed during the neutralization of BIBB with ethanol at the end of the reaction (see Section 2).

The functionalization of polysaccharides is strongly related to the concept of "accessibility" of hydroxyl groups. Actually this is referred to the capability of –OH groups to react under specific conditions (Frilette et al., 1948; Oprea et al., 1979; Tasker et al., 1994). In the present case, an evaluation of the amount of external –OH groups was performed on the basis of geometrical data (Kirk & Othmer, 1997; O'Sullivan, 1997). Wood pulp fibers were assumed to have parallelepipedal shape and to be composed by parallelepipedal fibrils and cylindrical microfibrils. The fibers side length was calculated to be 20 μm from SEM micrographs. The average dimension was assumed to be 0.2 μm for fibril side, 0.015 μm for internal microfibrils diameter, and microfibrils were assumed to be made by 36 macromolecular chains, so as reported in the literature (O'Sullivan, 1997). Under the assumption that all chains of external microfibrils are accessible the value of 0.3% mol for superficial –OH groups was estimated, that is consistent with the degrees of functionalization achieved where no external cell-wall degradation occurred.

EDXS and ATR analyses, however, do not provide quantitative values of the modification degree; therefore, elemental analysis was also exploited in a comparative way for the most modified sample (B10-2). The value of 2.0% mol (Br/OH) was obtained by elemental analysis, whereas EDXS gave 7.0% mol for the same sample. From these results we have to consider the experimental quantitative values affected by a substantial uncertainty but they can be used for comparison purposes.

In order to study the influence of the pulp feature on the modification reaction efficiency, a comparative experiment on cotton linter paper (WH) was carried out under method A for 21 h. A bromine content of 1.6% mol by EDXS (WH21, Table 1) was obtained, in good agreement with the literature value of 1.6% by ESCA (Carlmark & Malmstrom, 2003). Pulp fibers gave 0.47% mol under similar conditions thus indicating a lower attitude to surface modification of wood pulp cellulose fibers than cotton linter fibers.

Comparative structure analysis by X-ray diffraction and SEM showed small differences between the structures of the two substrates: cotton linter fibers have an higher crystallinity degree and a lower diameter than wood pulp fibers. This corresponds to higher surface area for WH paper than wood pulp with possible higher accessibility of the former (Lindqvist & Malmström, 2006).

3.2. Set up of ATRP conditions

ATRP of ethyl acrylate was carried out in homogeneous phase in order to verify the possibility to control the polymerization under mild conditions and so to achieve the maximum control over the subsequent grafting polymerization process. As already mentioned the grafting polymerization conditions were selected to avoid fiber swelling and degradation and to allow a modification on the surface, without affecting bulk properties. The procedure, adopted from the literature (Carlmark & Malmstrom, 2003), takes advantage of a highly active catalytic system (CuBr/Me6TREN) (Queffelec et al., 2000), able to work at room temperature. Ethyl acetate was chosen as solvent as it is not toxic, does not swell cellulose fiber, can wet their surface and last but not least, can be easily and completely removed by evaporation under mild conditions. Various ATRP experiments were performed at 0 °C and room temperature, varying the amount of catalyst and the amount of solvent (EtOAc). Particularly we varied the Cu(I)/initiator ratio between 1 and 0.1 and the EtOAc weight percentage between 0 and 50%. Optimum control over the polymerization process was achieved with Cu(I)/initiator = 0.1, EtOAc = 50% wt. and $T = 25$ and 0 °C. This was confirmed by SEC analysis (25 °C: $\overline{M}n_{th} = 9100$ $\overline{M}n_{SEC} = 11500$, $\overline{M}w/\overline{M}n = 1.11; 0^{\circ}C:$ $\overline{M}n_{th} = 7400$, $\overline{M}n_{SEC} = 8900$, $\overline{M}w/\overline{M}n = 1.21$). The evolution of the monomer concentration in semiloga-

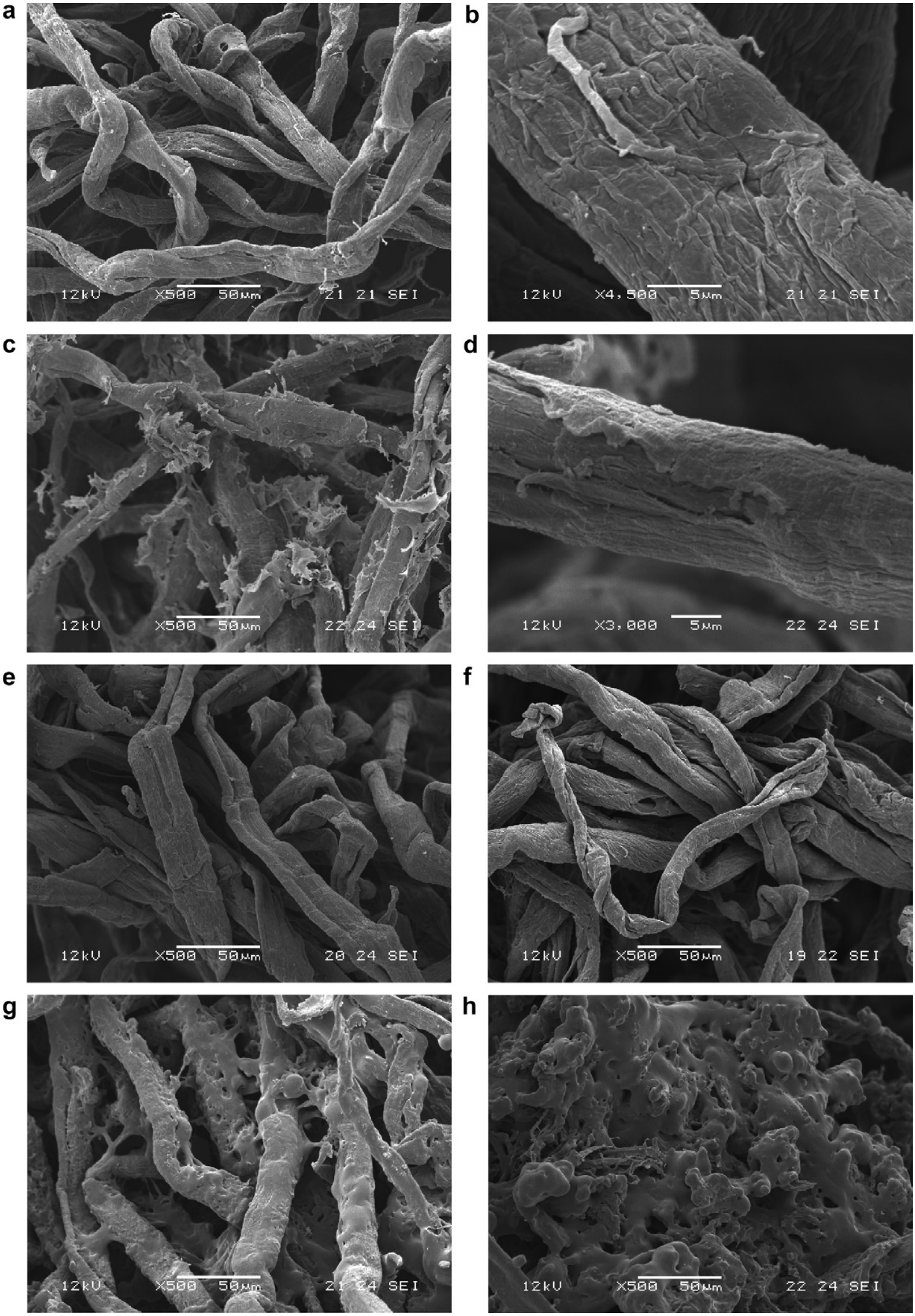

Fig. 2. SEM micrographs of wood pulp cellulose fibers: unmodified (a), unmodified at higher magnification (b); B10-2 (c) B10-2 at higher magnification (d); B2 (e); C21P (f); B2P (g); B10P (h).

rithmic plot as well as the evolution of molecular weight and polydispersity index are shown in Fig. 3 for the experiment at 0 °C. These last conditions were subsequently experimented in grafting polymerization processes (Carlmark & Malmstrom, 2003).

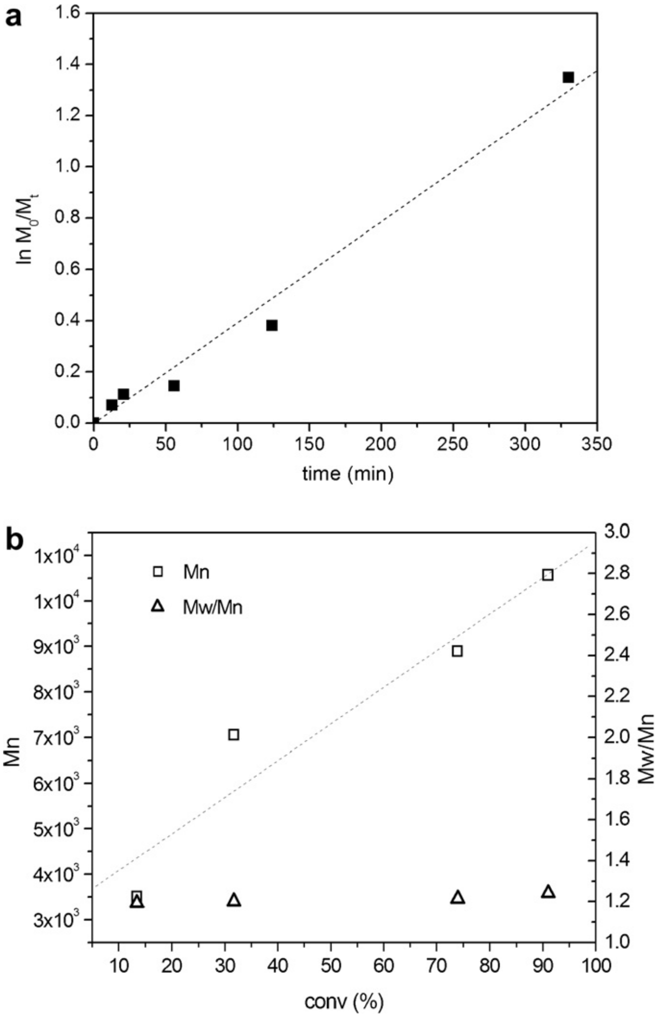

Fig. 3. Kinetic plot (a) and dependence on conversion of the molecular weight and polydispersity (b) for the polymerization of ethyl acrylate at 0 °C with (CuBr/Me$_6$TREN)/initiator = 0.1 by mol, EtOAc 50% wt, EA/initiator = 100 by mol.

3.3. Surface-initiated ATRP of ethyl acrylate from BIBB-functionalized wood pulp in the presence of free-"sacrificial" initiator

The Atom Transfer Radical Polymerization initiated from a solid surface (Carlmark & Malmstrom, 2003; Lee et al., 2004; Plackett et al., 2005) generally required the addition of a large amount of "sacrificial" free initiator to the polymerization mixture to control the process (Matyjaszewski et al., 1999) from the beginning stages. The larger amount of initiator promotes a faster building up of the necessary concentration of Cu(II) deactivator as a result of some irreversible terminations by radical coupling (Fischer, 1997; Matyjaszewski et al., 1999) thus allowing to fast keep the control over the reaction in the first reaction stage.

The wood pulp sample containing the highest amount of grafted initiator (B10-2) was used as substrate for the ethyl acrylate polymerization in the presence of free-"sacrificial" initiator (EBP) and a well detectable weight increase was observed after fibers purification (B10PP, Table 2), which indicates poly(ethyl acrylate) (PEA) grafting. A comparative experiment in the presence of unmodified pulp cellulose fibers resulted in no grafted PEA thus confirming the absence of transfer reactions. The optimum control over the polymerization from the free-"sacrificial" initiator proved the absence of significant interference of wood pulp cellulose fibers in the ATRP process: SEC analysis showed narrow polydispersity indexes (PDI) and $\overline{M}n$ values in good agreement with what expected from the initial monomer/initiator molar ratio: $\overline{M}n_{\text{teo}} = 7300$, $\overline{M}n_{\text{SEC}} = 8700$; $\overline{M}\text{w}/\overline{M}n = 1.19$.

The actual $\overline{M}n$ of grafted PEA could not be measured because it could not be effectively cleaved from the cellulose fiber without degradation. The impossibility to recover grafted PEA from cellulose surface was already reported (Castelvetro et al., 2007), either by hydrolytic demolition of the cellulose (Castelvetro et al., 2007; Margutti et al., 2002; Shen & Huang, 2004) or by selective cleavage of the cellulose–polyacrylate ester bond (Fernandez Garcia, De la Fuente, Cerrada, & Madruga, 2002; Prucker & Rühe, 1998; Thiebaud & Borredon, 1998). Therefore, the average molecular weight of the grafted chains in B10PP was tentatively estimated from the α-bromoisobutyryl ester amount value by elemental analysis and by assuming a complete initiation efficiency: PEA (% g/g cellulose)/≅ BIBB(%mol/g cellulose) 4500, while SEC analysis (referred to poly(styrene) standards) of the ungrafted polymer gave $\overline{M}n = 8500$. This finding is partially in accordance with literature for ATRP initiated from flat surfaces: the geometric constrain of the growing chains and the limited access of the active sites reduce the chain growing rate and result in a lower molecular weight of grafted polymer than ungrafted one (Matyjaszewski et al., 1999). However, in the presence of a large excess of free-"sacrificial" initiator the difference between the molecular weight of grafted and ungrafted polymer is usually smaller than observed (Bontempo et al., 2002; Ejaz, Tsuji, & Fukuda, 2001). A non complete initiation efficiency was thus suggested to explain the large difference, even if the contribution of some experimental errors can be also significant: (a) ungrafted PEA molecular weight referred to poly(styrene) standards by SEC analysis is overestimated, as confirmed by ^{1}H NMR (i.e., PEA $\overline{M}n$ 11500 by SEC analysis and 4400 by ^{1}H NMR), (b) the value of the degree of fiber modification by BIBB from elemental analysis is affected by a quite large uncertainty (maximum error 15%).

Anyhow, by assuming grafted and ungrafted polymer molecular weights as comparable (Bontempo et al., 2002; Ejaz et al., 2001), the amount of surface immobilized initiator that is effective in surface-initiated ATRP can be tentatively estimated (Br/cellulose = I_c) by the following relation:

$$\text{Br/cellulose} = I_c = \frac{\text{Wt}_{\text{grafted polimer}}}{M_{\text{n free polimer}}} \tag{1}$$

The estimated I_c for B10PP value is 18×10^{-5} mol/g that corresponds to an initiation efficiency of 53%. The wood pulp fiber surface morphology made by pores and channels whose accessibility depends on the species dimension and polarity should be responsible of the observed incomplete initiator site efficiency, whereas on others substrate, such as silicon wafers the flat and smooth surface prevent such effect.

Wood pulp cellulose modified under method A for either 3, or 6 or 21 h was also used as "macroinitiator" for the ethyl acrylate polymerization in the presence of EBP (entries 2–4 Table 2) under comparable conditions. FT-IR/ATR of all purified samples showed the presence of PEA grafted to the fiber surface (Fig. 4), while gravimetric analysis gave detectable weight increase only for samples A6PP and A21PP. A positive correlation was observed between the grafted polymer amount by weight and the α-bromoisobutyryl ester modification degree by EDXS (Table 1). The molecular weight of ungrafted polymer was comparable (for A3PP, A6PP and A21PP1, by SEC analysis), and thus it should be so for grafted one under the used hypothesis. Therefore, a positive correlation between the grafted polymer and the effective I_c amounts (see Eq. (1) and I_c values in Table 1) results for wood pulp fibers modified under method A for the ATRP initiator immobilization.

Comparative experiments of ethyl acrylate ATRP for 6 and 21 h were performed from A21 fibers in the presence of free-"sacrificial"

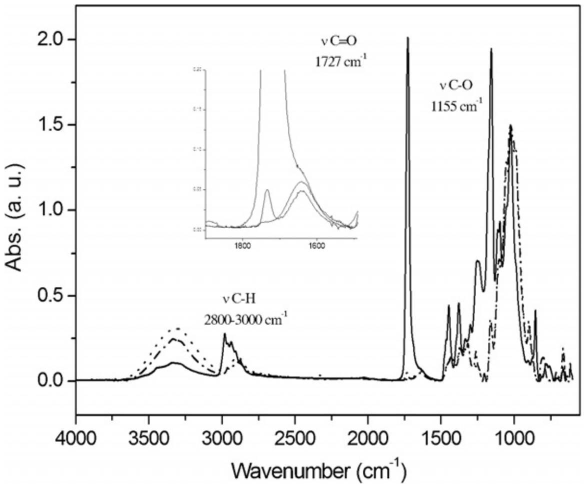

Fig. 4. Comparison among ATR/FT-IR spectra of unmodified wood pulp cellulose fibers (. . . .) and of fibers modified by PEA surface-initiated ATRP grafting: A3PP (– –) and B2P (—).

initiator (A21PP2 and A21PP3 samples, respectively of Table 2). A direct correlation was found for the polymerization time with molecular weight of the ungrafted polymer (Table 2), grafted polymer amount by weight (Table 2), and conversion degrees [% conv: 38 for A21PP2 and 86 for A21PP3], thus indicating that polymerization occurred under controlled conditions.

A duplicate experiment of ethyl acrylate ATRP from WH21 was performed in comparison with A21PP2 and similar results were obtained in term of molecular weight of the ungrafted polymer (Table 2) and conversion degree (conv(%): 41% WH21PP), while the grafted polymer amount by weight was higher in WH21PP than in A21PP2 in accordance with the lower esterification degree of the former than the latter.

3.4. Surface-initiated ATRP of ethyl acrylate from BIBB-functionalized pulp in the absence of “sacrificial” free initiator

The direct addition of a small amount of Cu(II) deactivator together with the Cu(I) catalyst has been reported to allow a control over the surface-initiated ATRP kinetic similar to that provided by the free-“sacrificial” initiator, while preventing the formation of a large fraction of ungrafted homopolymer as in the case of the addition of free-“sacrificial” initiator.

In this study, the grafting polymerization experiments were carried out with the Cu(I)Br/Me$_6$TREN catalytic system, which is one of the most reactive in ATRP due to its low redox potential (−0.30 V versus SCE Qiu, Matyjaszewski, Thouin, & Amatore, 2000). Because of this, it is also one of the most oxygen sensitive and some Cu(I) complex is usually oxidized to Cu(II) during the experiment set up by air, as evidenced by the green color of the catalyst stock solution (Queffelec et al., 2000).

In order to assess if the amount of formed deactivator was enough to allow the control over the polymerization kinetic some grafting-from experiments in the absence of free-“sacrificial” initiator were performed (entry 8–10 Table 2). The amount of catalyst used in the ATRP experiments was increased with the amount of initiator immobilized on the pulp and after purification (see Section 2) colorless fibers with increased weight were obtained while no homopolymer was detected in the washing solvents. ATR/FT-IR spectroscopy analysis (Fig. 4), showed typical bands of PEA in all samples thus indicating that grafted polymerization occurred from the surface of BIBB-functionalized wood pulp fibers under ATRP conditions i.e., without significant chain transfer to free monomer in the absence of free-“sacrificial” initiator.

However, wood pulp fibers resulted in much higher grafting percentage (%G) when the polymerization was performed without than with free-“sacrificial” initiator (EBP). For example: A21PP%G = 2.9÷5.0 versus A21 P%G = 5.4 or B10PP%G = 60.6 versus B10P%G = 79.1 (Table 2). Moreover, a self blocking polymerization experiment performed on sample A21P resulted in no weight increase while successful self blocking polymerization was achieved from sample A21PP1, obtained in the presence of free-“sacrificial” initiator (A21P-P and A21PP1-P, (Table 2). These evidences indicate that the Cu(II) amount present in the stock solution was not enough to allow good control over the polymerization process (Matyjaszewski et al., 1999).

A positive correlation was observed between the amount of the grafted polymer and the bromine content estimated by EDXS in initiator-modified wood pulp (Table 1), in the case of samples modified under the same method for different times (entry 9 and 10 Table 2). On the contrary samples reacted under different methods for the initiator immobilization (method A versus B) brought to grafted polymer amount (entry 8 Table 2) which do not correlate with the amount of immobilized initiator estimated by EDXS analysis.

The grafting efficiency seems to be mainly related to the different accessibility of initiator sites obtained by methods A or B. Actually the external cell-wall was already partially removed by the conventional refining process carried out on cellulose fibers after delignification (Fig. 2b) but the use of a significant excess of pyridine and BIBB, together with the high temperature brought to a sort of “additional refining” in the case of method B (Fig. 2c–d). The initiator sites obtained by method B are therefore more accessible and then effective, than sites obtained by method A.

The SEM micrographs (Fig. 2f–h) evidenced the presence of grafted PEA on pulp that covers non-uniformly the surface of fiber modified under method B in large amount. On the contrary, the small amount of synthetic polymer grown on C21 macroinitiator gave no apparent fiber morphology modification, as evidenced by the comparison with unmodified cellulose fibers (Fig. 2a versus f). The morphology of samples from method B can be due to a dishomogeneous initiator site distribution as not only external surface of fibers but also internal amorphous regions exposed by the above mentioned additional refining could be affected by BIBB modification.

3.5. Thermal properties of modified pulp

The thermogravimetric analysis of wood pulp cellulose samples modified by BIBB showed a reduced thermal stability (T_{onset}: temperature at which degradation starts) with respect to the unmodified pulp (Table 3). The milder conditions of method A resulted in a slight reduction of degradation temperature (Fig. 5a): the onset degradation temperature of samples A3, A6 and A21 were respectively 5, 10 and 30 °C lower than that for unmodified cellulose fibers (328 °C) with a clear correlation between reaction time and destabilization degree. Two hypotheses can be formulated to explain the observation: (1) the bonded α-bromoisobutyryl ester groups catalyze the thermal decomposition of fibers, (2) the surface area of fiber is increased by the exposition to the reaction mixture used for the esterification. However, in case of (1) a leveling off effect was expected at reaction time 6 h as observed for the grafting degree. Moreover, halogenated chemicals usually do not decrease material thermal stability. Therefore, hypothesis (2) is suggested.

Following up method B the onset degradation temperature reached 226 °C with 10 min reaction: 102 °C lower than that of unmodified fibers (Fig. 5b). In this case, the increase in the fiber superficial area was confirmed by SEM analysis (Fig. 2c), that evidenced the partial degradation of external cell-wall.

Table 3
Thermal properties by thermogravimetric analyses of modified wood pulp cellulose

Cellulose samples	T_{onset} [°C]	$T_{inflection}$ [°C]	Cell-g-PEA samples	T_{onset} [°C]	$T_{inflection}$ [°C]	$T^2_{inflection}$ [°C]	G [% wt]
Pulp	328	354	B10PP	275	297	410	75.4
WH	344	370	A3PP	326	347	–	
PEA Mn8900	325	411	A6PP	323	344	–	
A1	323	346	A21PP	314	336	–	
A3	320	343	WH21PP	231	315	398	23.3
A6	317	343	A21P	315	339		
A21	297	328	B2P	312	334	408	46.2
B2	272	302	B10P	256	298	407	87.6
B10-1	274	307	A21PP-P	329	353	407	20.8
B10-2	226	266					

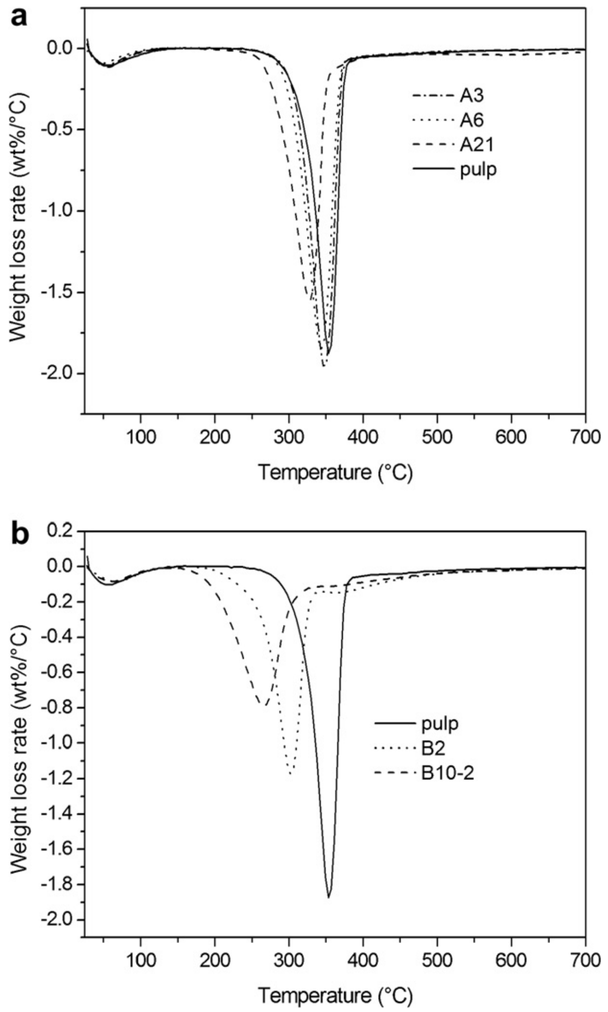

Fig. 5. Comparison of the weight loss rates from the TGA scans of unmodified cellulose fibers and fibers reacted with BIBB by method A (a) or method B (b).

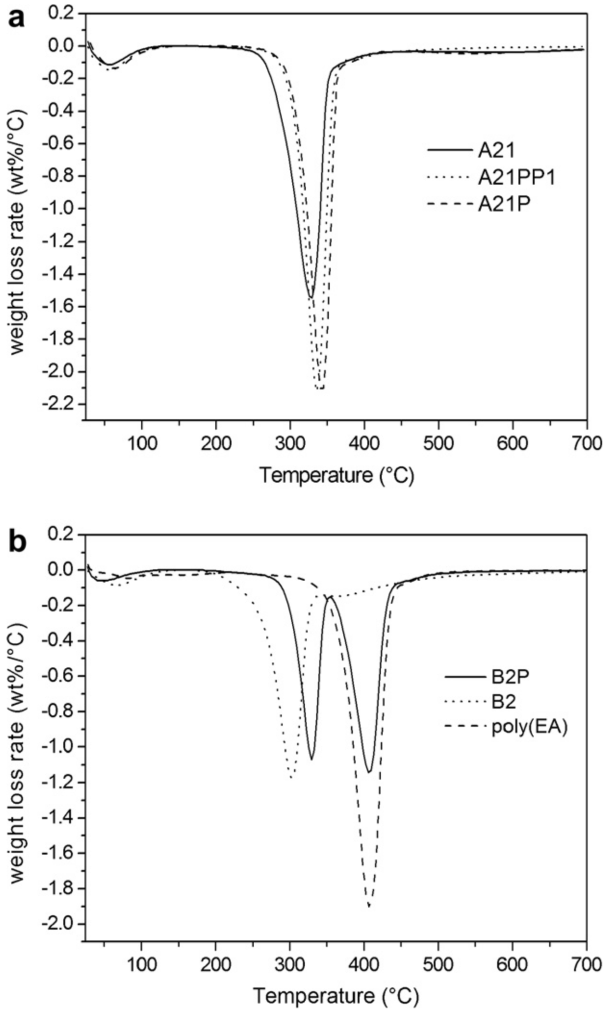

Fig. 6. Comparison of the weight loss rates from the TGA scans of (a) cellulose fibers reacted with BIBB by method A for 21 h (A21) and grafted with PEA (A21P, A21PP1); (b) cellulose fibers reacted with BIBB by method B for 2 min, grafted with PEA (B2P) and homogeneous polymerized PEA.

The loss of pulp thermal stability during the α-bromoisobutyryl ester functionalization reaction under method A is recovered by coating the fibers with PEA (Fig. 6a) and the recovering degree depends on the grafted PEA amount (see A21PP versus A21PP-P in Table 3). This thermal behavior could be due to the presence of a PEA coating on cellulose fiber surface that fill the superficial pores and channels enlarged by swelling during the reaction of esterification.

Fibers esterified under method B conditions did not recover completely the thermal stability also at high coating levels (Table 3). Therefore, it can be suggested that in the case of A samples the surface area was increased just by swelling of external microfibril, while in B samples chemical degradation was also involved.

At a polymer content higher than 24% by weight two well resolved degradative steps were observed, attributable to cellulose and PEA respectively (Fig. 6b). The weight loss associated to the latter was used to evaluate the grafted PEA (Table 3). The corresponding values are higher than those obtained on the basis of the weight increase, the latter being probably underestimated due to particle loss during washing. In any case, a part the absolute values, data from the two methods (TGA and weight increase) are qualitatively in agreement.

Calorimetric characterization by DSC showed detectable glass transition temperature in samples containing significant grafted PEA: −15.0 °C B2P; −15.0 °C B10 P, and −14.3 °C B10PP. The found values are higher than the typical value for ungrafted PEA of comparable molecular weight (PEA $\overline{M}n = 8800$, $Tg = -25.0$ °C (Andreozzi, Castelvetro, Faetti, Giordano, & Zulli, 2006). The difference can be due to the reduced mobility of the grafted PEA because of the grafting and/or the hydrogen bonding between ester groups and cellulose.

4. Conclusion

Wood pulp cellulose fibers can be modified by partial esterification of the hydroxyl group with α-bromoisobutyryl bromide (ATRP initiator) up to 2.0% by mol (by elemental analysis) by a suitable choice of the experimental conditions. In particular, the modification reaction carried out at room temperature with a double amount of α-bromoisobutyryl bromide with respect to –OH groups allows modifying just the superficial microfibrils of fibers. On the other hand, under harsh conditions (85 °C and pyridine) a higher effectiveness of the process is evident and the reaction time (in the range 1 ÷ 10 min) can be exploited to vary the functionalization degree. Moreover, the highest functionalization degree (2% by mol) was obtained with a partial degradation of the fiber cell-wall.

The initiator-modified wood pulp cellulose acted as macroinitiator for surface-initiated ATRP of ethyl acrylate in EtOAc as solvent by using $Me_6TREN/CuBr$ as catalyst. The amount of the grafted poly(ethyl acrylate) correlated with the esterification degree that was proven to be the determining step to modulate the grafted polymer chains density: thin polymer layer coating (3% wt) or up to 60% wt of poly(ethyl acrylate) can be grown on pulp cellulose fibers by leaving enough unreacted hydroxyl groups for hydrogen bonding. In the presence of free-“sacrificial” initiator the ethyl acrylate polymerization initiated from wood pulp fiber surface occurred under controlled conditions. In conclusion, wood pulp cellulose fibers from Kraft process were proven to be suitable as substrate for surface-initiated ATRP, even if less actives than cotton linter paper in the esterification reaction, thus opening the possibility to use wood pulp fibers from Kraft process for obtaining valuable materials and in particular to influence structural and functional properties of paper products.

Thermal gravimetric analysis (TGA) showed a decreased thermal stability for the α-bromoisobutyryl bromide modified cellulose with destabilization degrees which depends on the time and condition used for the esterification reaction. However, the destabilization was progressively recovered in fibers with grafted polymer.

Moreover, differential scan calorimetric analysis (DSC) showed a higher glass transition temperature for the bonded poly(ethyl acrylate) with respect to ungrafted one (−17 °C versus −25 °C) due to the reduced chain mobility of the former.

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