Surface Modification of Natural Substrates by Atom Transfer Radical Polymerization

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ABSTRACT: Surface modification of various solid polysaccharide substrates was conducted by grafting methyl acrylate (MA) and styrene via atom transfer radical polymerization (ATRP) to produce well-defined polymer grafts. The hydroxyl groups on the surfaces of the substrates were reacted with 2-bromoisobutyryl bromide followed by graft copolymerization under ATRP conditions. The studied substrates were filter paper, microcrystalline cellulose, Lyocell fibers, dialysis tubing, and chitosan films. The modified substrates were analyzed by FT-IR, water contact angle measurements, TGA, and SEM. FT-IR characterization of the grafted substrates showed significant differences between the different substrates in the amount of grafted polymer. Higher amounts of polymer seem to be possible to graft from native cellulose substrates than from regenerated cellulose substrates. To investigate whether the grafted polymers were "living" after a longer time period, a second layer of polystyrene was grafted from a filter paper modified with PMA one year ago. FT-IR characterization of the filter paper showed a peak corresponding to styrene, indicating that a block copolymer had been formed on the surface. Graft copolymerization can be used to change and tailor the surface properties of the polysaccharide substrates. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4155–4162, 2006

Key words: atom transfer radical polymerization (ATRP); surface modification; graft copolymers; polysaccharides; cellulose

INTRODUCTION

Surface modification of cellulose and other polysaccharides by graft-copolymerization of various monomers has been widely studied for several decades.[1–11] Grafting provides an important method for altering the chemical and physical properties of cellulose.[9] Cellulose is an abundant, inexpensive, biodegradable and renewable resource that is used in many important applications because of its useful properties such as the high modulus of crystalline cellulose combined with the low weight. However, for some applications, the properties of cellulose need to be improved to fit the standards of synthetic polymers. For example, when cellulose fibers are used as reinforcing agents in composites, it is crucial, and often difficult, to obtain a sufficient fiber-to-matrix adhesion. Grafting of a hydrophobic polymer to the cellulose greatly enhances the hydrophobicity of the fibers, and thus improving the adhesion to the polymer matrix.[12,13] Dimensional stability, resistance to abrasion and wear, wrinkle recovery, oil and water repellency, heat resistance, and antimicrobial activity are other examples of properties that can be improved by graft-copolymerization of cellulose.[9,14]

Grafting of cellulose has usually been conducted by a "grafting-from" technique, where radicals are generated along the cellulose backbone, followed by free radical polymerization of vinyl monomers. Using this method, it is almost impossible to control or change the molecular weight of the grafts. The molecular weight is often very high, the molecular weight distribution broad, and the end-groups unknown. If instead the cellulose is grafted via a living/controlled polymerization technique, the properties of the grafts can be accurately controlled and thereby also tailored. Grafting of cellulose via controlled polymerization methods can be accomplished by using a "grafting-to" method, where the polymers are pre-formed, usually by anionic or cationic polymerization, and thereafter coupled to the cellulosic backbone.[15–17] However, this technique yields low grafting density. Daly et al. reported the first use of a controlled radical technique to graft from cellulose, using Barton ester intermediates and nitroxy mediation.[18] Our group has previously reported the first use of atom transfer radical polymerization (ATRP) to create homopolymer grafts and block-copolymer grafts from cellulose.[19,20] Filter paper was then used as cellulosic substrate. Since then, ATRP has also been used for surface grafting of chitosan[21] and cellulose diactetate.[22] ATRP was discovered independently by Matyjaszewski[23,24] and

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Sawamoto[25] in 1995, and has since then been widely used and studied, as it is a versatile tool to create polymers with low polydispersity and controlled molecular weight. Using ATRP, it is possible to tailor the cellulose surface properties for a specific application such as antibacterial activity.[26]

Herein, we report on the grafting of methyl acrylate (MA) and styrene via ATRP from various solid polysaccharide substrates in terms of filter paper, microcrystalline cellulose, dialysis membrane, Lyocell fibers, and chitosan films.

EXPERIMENTAL

Materials

Tris(2-(dimethylamino)ethyl)amine (Me_6-TREN) was prepared similar to the procedure by Ciampolini and Nardi[27] from tris(2-aminoethyl)amine (98%, Aldrich). Methyl acrylate (MA) and styrene were passed through a column of neutral aluminum oxide prior to use. All other chemicals and solvents were used as received.

Substrates

Chitosan films and cellulose fibers in terms of filter paper, regenerated cellulose dialysis membrane, Lyocell fibers, and microcrystalline cellulose (MCC) were used as substrates.

Filter paper

Whatman No. 1 filter paper was chosen as a reference, as it had been used in earlier work. It has high cellulose content, and is a native cellulose (cellulose I) substrate.

Microcrystalline cellulose

MCC (Aldrich) is a native cellulose powder made from kraft pulp. The lignin and hemicelluloses have been removed from the pulp, and the amorphous parts of the cellulose have been hydrolyzed, yielding a highly crystalline product. The particle size is about 20 μm.

Dialysis membrane

The dialysis membrane (Spectra/Por®3, MWCO 3500) is made from regenerated cellulose. The cellulose has then been dissolved and regenerated into a substrate. During that process, the crystal form of the cellulose is changed from that of native cellulose into cellulose II or cellulose III depending on what solvent has been used.

Lyocell fibers

These regenerated fibers were kindly provided by Professor Lars Wågberg at Royal Institute of Technology, Fiber and Polymer Technology and were manufactured by Lenzing. The fibers have a diameter of 20 μm, and were supplied by the manufacturer as 4 mm pieces.

Chitosan films

Chitosan is a polysaccharide that is different from cellulose, but similar in structure and therefore included in this study. The structural difference between chitosan and cellulose is that chitosan has amino groups instead of the primary hydroxyl groups in cellulose. The films were kindly supplied by Dr. Mikael Gällstedt at Packforsk.

Immobilization of initiator on the surface

The procedure for immobilization of initiator on the surface was adopted from Carlmark and Malmström.[20] A 2×3 cm^2 piece of the filter paper, dialysis membrane, and chitosan film was used. Prior to use, the substrate was washed with acetone and tetrahydrofuran (THF) and ultrasonicated in both solvents. The hydroxyl groups on the surface were then reacted by immersing the substrate in a solution containing 2-bromoisobuturyl bromide (305 mg, 1.33 mmol, 66.3 m*M*), triethylamine (148 mg, 1.46 mmol, 73.0 m*M*), and a catalytic amount of 2-dimethyl aminopyridine (DMAP) in THF (20 mL). The reaction was allowed to proceed at room temperature on a shaking device for 4 h. The substrate was thereafter thoroughly washed with THF and ethanol and dried in a vacuum oven at 30°C.

The Lyocell fibers and the microcrystalline cellulose were reacted in a similar way as the other substrates, but varied amounts were used. 5 g of the substrates were reacted in a solution containing 2-bromoisobuturyl bromide (9.30 g, 40.5 mmol, 405 m*M*), triethylamine (4.50 g, 44.5 mmol, 445 m*M*), and a catalytic amount of DMAP in THF (100 mL). The reaction was allowed to proceed as before, and the substrates were washed as previously decribed.

Grafting of methyl acrylate from the modified substrates, general procedure with a targeted DP of 100, using sacrificial initiator

The grafting of MA from the modified substrates was performed similar to the procedure developed by Carlmark and Malmström.[19]

For the grafting reactions, 2×3 cm^2 pieces of filter paper, dialysis membrane, and chitosan films were used, and analogous 0.20 g of Lyocell fibers and mi-

crocrystalline cellulose were used. The grafting was accomplished by immersing the initiator-modified substrate into the reaction mixture containing MA (7.0 g, 81.3 mmol), Me_6-TREN (18.7 mg, 81.0 μmol), sacrificial initiator ethyl-2-bromoisobutyrate (EBiB) (127 mg, 810 μmol), and ethyl acetate (EtOAc) (3.5 g, 33% (w/w)). The flask was sealed with a rubber septum and thereafter evacuated and back-filled with Ar-gas two times. Cu(I)Br (11.7 mg, 81.0 μmol) was then added to the reaction mixture under Ar-gas flow. The flask was sealed again and evacuated and back-filled with Ar-gas one more time. All polymerizations proceeded in room temperature on a shaking device for 18 h. After the polymerization was completed, the substrates were subjected to intense washing in THF, THF:water, water, dichloromethane, methanol, and ethanol. The microcrystalline cellulose needed even more intense washing than the other substrates, and in addition to the washing, it was ultrasonicated. The bulk polymer formed from the sacrificial initiator was dissolved in THF and passed through a column of aluminum oxide to remove the copper complex. The polymer was then dried to remove solvent and remains of monomer.

Grafting of methyl acrylate from the modified substrates, general procedure without using sacrificial initiator

The same amount of initiator-modified substrates as before was used. The substrates were immersed into a reaction mixture containing MA (7.0 g, 81.3 mmol), EtOAc (3.5 g, 33% (w/w)), and Me_6-TREN (18.7 mg, 81.0 μmol). The flask was sealed with a rubber septum and thereafter evacuated and back-filled Ar-gas two times. Cu(I)Br (9.32 mg, 65.0 μmol) and $Cu(II)Br_2$ (3.62 mg, 16.0 μmol) were then added to the reaction solution under Ar-gas flow. The flask was sealed and thereafter evacuated and back-filled with Ar-gas one more time. Polymerizations were performed for 1 h and 8 h, respectively. The substrates were washed as previously described.

Grafting of styrene from the modified substrates, general procedure with a targeted DP of 100, using sacrificial initiator

The same amount of initiator-modified substrates as before was used for the polymerizations. The substrates were immersed into a reaction mixture containing styrene (10.0 g, 96.0 mmol), pentamethyldiethyltriamine (PMDETA) (166 mg, 960 μmol), the sacrificial initiator 1-phenyl ethyl bromide (178 mg, 960 μmol), and toluene (5 g, 33% (w/w)). The flask was sealed with a rubber septum and evacuated and back-filled with Ar-gas two times. Cu(I)Br (137 mg, 960 μmol) was thereafter added under Ar-gas flow and the flask was sealed again and evacuated and back-filled with Ar-gas one more time. The polymerizations were carried out at 90°C for 18 h. When filter paper, dialysis membrane or chitosan films were used as substrate, the polymerizations were carried out with the substrate hanging in a PTFE thread in the flask to prevent the substrate from being damaged by the stirring bar. The bulk polymer formed from the sacrificial initiator was dissolved in dichloromethane and passed through a column of aluminum oxide to remove the copper complex. The polymer was then precipitated in cold methanol and dried. The substrates were washed as previously described.

Grafting of styrene from modified substrates, general procedure without using sacrificial initiator

The same amount of initiator-modified substrates as before was used. The reaction mixture contained styrene (10.0 g, 96.0 mmol), PMDETA (166 mg, 960 μmol), and toluene (5 g, 33% (w/w)). Cu(I)Br (110 mg, 768 μmol) and Cu(II)Br2 (42.9 mg, 192 μmol) were added as before after two degassing cycles. Polymerizations were performed as before for 1 and 8 h. The substrates were washed as previously described.

Characterization

Infrared spectra were recorded on a Perkin–Elmer Spectrum 2000 FTIR equipped with a MKII Golden Gate, Single Reflection ATR System from Specac Ltd., London, UK. The ATR crystal was a MKII heated Diamond 45° ATR Top Plate.

Size Exclusion Chromatography (SEC), using THF (1.0 mL min^{-1}) as the mobile phase, was performed at 35°C using a Viscotek TDA model 301 equipped with two GMH_{HR}-M columns with TSK-gel (mixed bed, MW resolving range: 300–100,000) from Tosoh Biosep, a VE 5200 GPC autosampler, a VE 1121 GPC solvent pump, and a VE 5710 GPC degasser (all from Viscotek corp.). A universal calibration method was created using broad and narrow linear polystyrenes standards. Corrections for the flow rate fluctuations were made using THF as an internal standard. Viscotek Trisec 2000 version 1.0.2 software was used to process data.

Thermo Gravimetric Analysis (TGA) was performed using a Mettler Toledo TGA/SDTA851^e. Heating was performed at 10 K min^{-1}. STAR^e software, version 8.10 was used to evaluate data.

Water contact angles were measured with a Rame-Hart goniometer using MilliQ water at ambient temperature and humidity.

Scanning Electron Microscopy (SEM) was conducted on a JEOL JSM-5400. The samples were fastened on aluminum carriers with carbon tape, and

TABLE I
SEC Results for Bulk Polymers Formed during PMA-Grafting of MCC and Lyocell Fibers

Sample	Substrate	Aimed DP	Theoretical M_n	Experimental M_n	Calculated DP[a]	PDI
MCC-PMA100	MCC	100	8600	6700	77	1.15
MCC-PMA300	MCC	300	25,800	20,900	243	1.07
Lyo-PMA100	Lyocell	100	8600	6700	77	1.09
Lyo-PMA300	Lyocell	300	25,800	15,100	175	1.09

[a] The degree of polymerization was calculated from the SEC data.

sputtered with Au/Cd (60%/40%) in a Desk II from Denton Vacuum.

RESULTS AND DISCUSSION

Substrates

Several types of polysaccharide substrates were chosen for this study to explore the feasibility of the grafting. Moreover, the purpose was to investigate how differences in between the substrates (for instance, surface area) would influence the grafting.

Drying polysaccharide substrates greatly affects the surface area and properties such as swelling and solvent uptake. To reduce the differences, between samples, caused by the drying, all the substrates were dried in a vacuum oven at 30°C over night prior to modification.

Immobilization of initiator

The hydroxyl groups on the substrates were reacted with 2-bromoisobuturylbromide for 4 h, yielding covalently bound ATRP initiators on the surface, according to Carlmark and Malmström.[20] Attempts were made to analyze the modified substrates by FT-IR, but the ester group was undetectable with this method.

Polymerizations

The grafting of MA from the substrates was studied aiming at DP 100 for all the substrates. The grafting was performed by immersing the initiator-modified substrates into a reaction mixture containing monomer, ligand, copper salt, solvent and a sacrificial initiator, EBiB. Addition of sacrificial initiator allows for the possibility to tailor the graft lengths. The amount of initiating sites on the substrates is assumed to be negligible when compared with the amount of sacrificial initiator. Thus, it is possible to gain control over DP simply by controlling the monomer-to-initiator ratio. Since EBiB also initiates polymerization, a bulk polymer was formed simultaneously to the surface grafting. Analysis of the bulk polymer gives an idea of the molecular weight and polydispersity of the grafted polymer, even though the kinetics of the surface polymerization may differ somewhat from that of the bulk. On the other hand, the bulk polymer needs to be separated from the substrate, resulting in a tedious work-up process. The substrates were subjected to extensive washing and ultrasonicated in various solvents to assure removal of the bulk polymer. The grafted MCC needed even more washing than the other substrates to remove the bulk polymer.

To ensure that the polymer was covalently attached to the substrates and not just physisorbed to the surface, a blank sample was performed for every polymerization. The blank samples were not reacted with 2-bromoisobutyryl bromide, but were otherwise treated in the same way as the initiator-containing samples. The blank samples were also used to determine when sufficient washing was achieved.

To further study the possibility to control the length of the grafts on the substrates, we also aimed for a higher DP (DP = 300), on MCC and Lyocell fibers. SEC analysis of the bulk polymers for the two aimed DP's showed controlled polymerizations (Table I). The molecular weight for Lyo-PMA300 is lower than expected. This was seen even after repeating the experiment. At present, we have no unambiguous explanation for this.

TABLE II
SEC Results for Bulk Polymers Formed during PS-Grafting of MCC and Lyocell Fibers

Sample	Substrate	Aimed DP	Theoretical M_n	Experimental M_n	Calculated DP[a]	PDI
MCC-PS100	MCC	100	10,400	12,100	116	1.05
MCC-PS300	MCC	300	31,200	28,800	276	1.05
Lyo-PS100	Lyocell	100	10,400	13,100	125	1.04
Lyo-PS300	Lyocell	300	31,200	29,500	283	1.06

[a] The degree of polymerization was calculated from the SEC data.

To circumvent the problem associated with removal of the bulk polymer, grafting of MA was also performed from MCC and Lyocell fibers without using sacrificial initiator. Deactivator, in this case $CuBr_2$, was then added to achieve control over the reaction. The advantage with this method is that no bulk polymer is formed, and thus, the work-up procedure is straightforward. On the other hand, as the number of initiating sites on the substrates was unknown, the length of the grafts could only be controlled by the reaction time. Two different reaction times, 1 h and 8 h, were studied. The results from these graft copolymerizations will be discussed further on.

Corresponding polymerizations were also performed using styrene as the monomer. Styrene was chosen as it yields a very hydrophobic polymer with a high glass transition temperature, unlike PMA, which has a T_g below room temperature. As the grafting reaction with styrene proceeded at an elevated temperature (90°C), the shaking device could not be used, and it was necessary to add a magnetic stirrer to the reaction flask. The planar substrates then had to be mounted on PTFE treads in the flask to avoid being damaged by the stirrer.

The bulk polymers formed when using sacrificial initiator, 1-phenyl ethyl bromide, in the styrene reactions were analyzed by SEC (Table II). As can be seen, the molecular weights for MCC-PS100 and Lyo-PS100 are significantly higher than the theoretical values, indicating that the initiation has not worked completely or that some termination reactions have occurred early in the polymerization, causing the remaining chains to be longer. However, for the higher DPs the molecular weights are lower than the theoretical values.

If the grafting from the substrates is controlled, the bromides at the chain ends are retained and can therefore function as initiators for further polymerization. Earlier work from our group has shown that it is possible to create block-copolymer grafts from cellulose substrates.[20] To investigate whether the grafted polymers are "living" after a longer time period, a filter paper grafted with PMA one year ago was grafted with styrene. The grafting was performed without sacrificial initiator, but with addition of deactivator. The grafted filter paper was analyzed by FT-IR before and after grafting of the PS block (Fig. 1). The peak at about 700 cm^{-1} corresponds to the aromatic structure in PS and is not seen before the grafting of styrene. This indicates that the chain ends were still "living" after a time period of one year.

TABLE III
Results from Water Contact Angle Measurements on Filter Paper, Dialysis Membrane and Chitosan Films

Substrate	PMA (DP = 100)	Blank	PS (DP = 100)	Blank
Filter Paper	(76 ± 15)°	[b]	(105 ± 10)°	[b]
Dialysis membrane	62°[a]	[b]	(78 ± 2)°	[b]
Chitosan	(63 ± 1)°	53°[a]	(85 ± 5)°	(69 ± 4)°

[a] Because of deformation of the sample, only one value was obtained.
[b] Not measurable since the water was absorbed into the sample.

Characterization of grafted substrates

The hydrophobicity of the modified planar substrates (filter paper, dialysis membrane, and chitosan films) was investigated by measuring the water contact angle. As the surfaces of these substrates are rough and, furthermore, the dialysis membrane and chitosan films were deformed by the water droplet, it was very difficult to measure the water contact angle. The mea-

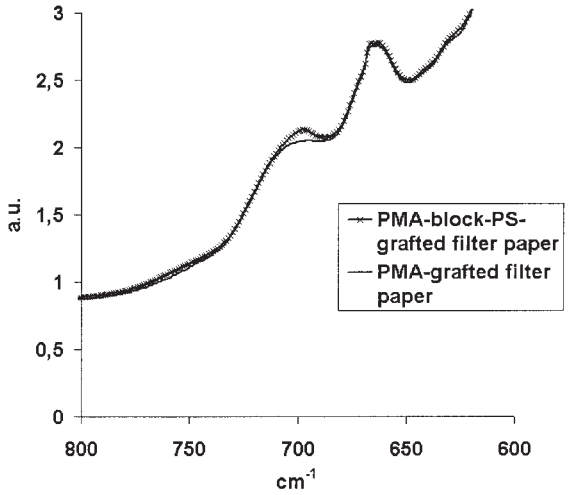

Figure 1 FT-IR spectra of PMA-grafted and PMA-*block*-PS-grafted filter paper.

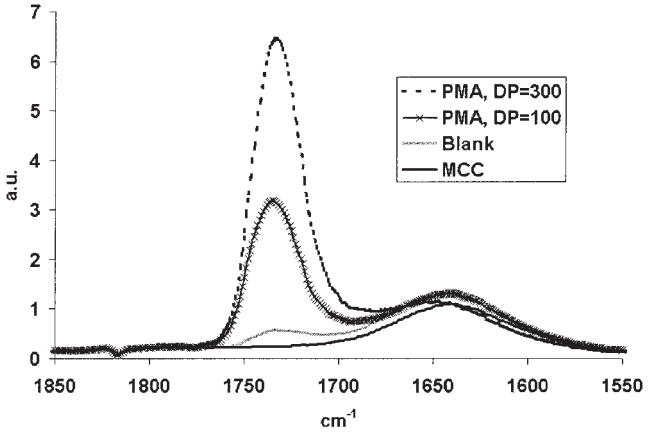

Figure 2 FT-IR spectra of MCC grafted with PMA of different DPs, compared with a blank sample and virgin MCC.

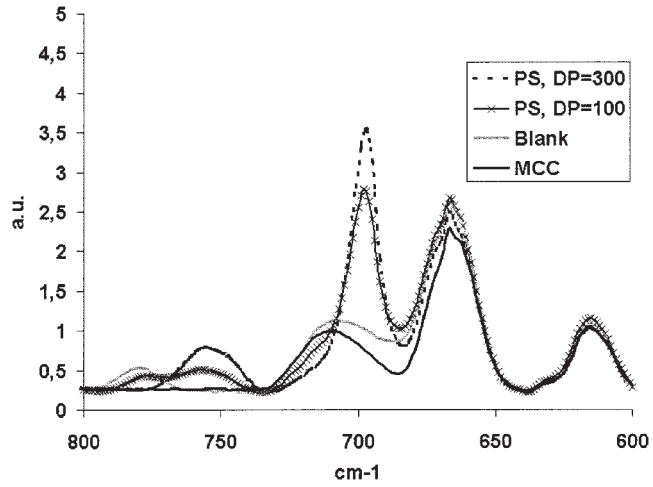

Figure 3 FT-IR spectra of MCC grafted with PS of different DPs, compared with a blank sample and virgin MCC.

surements were used to get a rough estimate of the hydrophobicity of the different samples and to make a qualitative comparison between samples, but the resulting water contact angles should not be regarded as absolute values. The results from these measurements are shown in Table III. The substrates generally become more hydrophobic after grafting, indicating that the grafting has been successful. The PS-grafts yield an even more hydrophobic surface than the PMA-grafts, which is expected, as PS is a more hydrophobic polymer than PMA.

FT-IR has proven to be a useful technique to characterize the grafted substrates. The ATR technique enables the measurements to be performed directly on the substrates, without the need to make films or tablets. All the spectra were normalized against the specific ATR crystal absorption to make comparisons possible. The grafting from filter paper is well-known and have been characterized using FT-IR in earlier

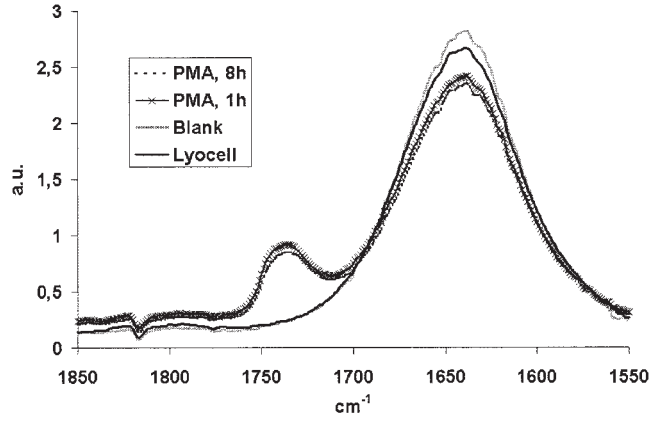

Figure 4 FT-IR spectrum of Lyocell fibers grafted with PMA at different reaction times, compared with a blank sample and virgin Lyocell fibers.

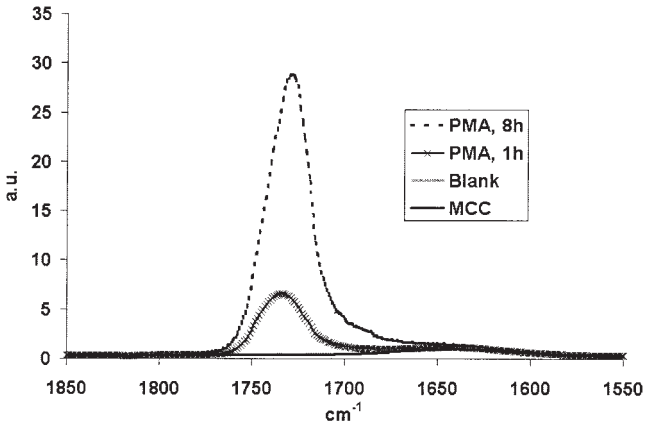

Figure 5 FT-IR spectra of MCC grafted with PMA at different reaction times, compared with a blank sample and virgin MCC.

work.[19,20] The PMA- and PS-modified MCC and Lyocell fibers were characterized with FT-IR. Figure 2 displays the FT-IR spectra of MCC grafted with MA aiming at different DP's, compared with the blank sample and virgin MCC. There is a significant increase in the carbonyl peak at 1730 cm^{-1} between DP 100 and 300. This indicates that the graft lengths can be controlled by adding sacrificial initiator, as was reported for grafting from filter paper. For the PS-grafted MCC samples, the peak at 700 cm^{-1} corresponding to the aromatic structure of styrene increase for the sample with a higher DP (Fig. 3). The FT-IR characterization of Lyocell fibers grafted with MA and styrene of different chain length shows similar results, except that the peaks are generally smaller than for the corresponding reactions on MCC. This indicates that smaller amounts of polymer are grafted from the Lyocell fibers. As the Lyocell fibers are made by extruding dissolved cellulose into fibers, they have a significantly lower surface area than MCC, which probably affects the amount of

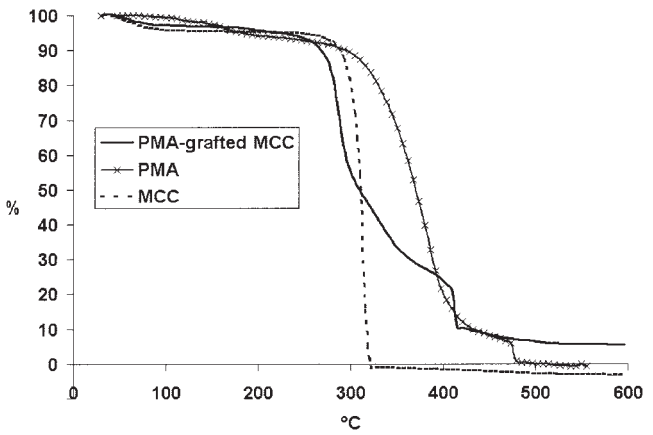

Figure 6 TGA-thermogram of PMA-grafted MCC, compared with pure PMA and virgin MCC.

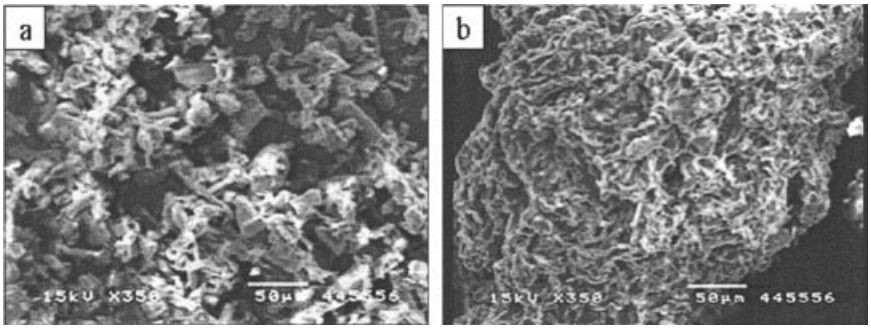

Figure 7 SEM images of (a) unmodified and (b) PMA-grafted MCC.

grafted polymer on the surface. The reactive sites are also inaccessible to some extent because of hornification of the regenerated cellulose fibers. Moreover, the low amount of grafted polymer can be explained by the fact that the Lyocell fibers aggregate into lumps during the grafting reaction, rendering the reactive sites less accessible for polymerization. The difficulties with grafting from Lyocell fibers were even more prominent when the reaction time was used to control the amount of grafted polymer. As can be seen in Figure 4, there is almost no difference in carbonyl content between the Lyocell fibers grafted with PMA for 1 h and 8 h respectively. The FT-IR spectra for the corresponding reactions on MCC show very significant differences between the two reaction times (Fig. 5).

Characterizing the modified substrates by TGA was found to be difficult. The amount of grafted polymer was in most cases to small to be detected with the analysis method. Only MCC grafted with styrene and MA for 8 h was possible to measure with the TGA. Figure 6 displays the TGA-thermogram for PMA-grafted MCC when compared with the curves for PMA and MCC, respectively. It can be seen that the thermogram for PMA-grafted MCC is a mixture of the curves for PMA and MCC, indicating that PMA is grafted onto the surface, as the results from FT-IR measurements also showed. It is also shown that grafting of MA increases the thermal stability of the MCC. These results are analogous with those for the PS-grafted MCC. As seen in Figure 6, there is a small amount of sample remaining at 600°C, which cannot originate from the organic part of the sample. Examining the TGA cup reveals a dark violet solid residue, which we assume to be the remains of the copper catalyst.

SEM was used to characterize the modified MCC and Lyocell. Figure 7 shows the SEM images of unmodified MCC and MCC grafted with MA for 8 h without sacrificial initiator. The modified MCC have aggregated into much larger particles than seen for the unmodified MCC. SEM images of unmodified Lyocell and Lyocell grafted with MA for 8 h without sacrificial initiator are shown in Figure 8. The surface of the unmodified fibers is very smooth when compared with that of the modified fibers. The modified fiber surface seems to be partly covered with polymer and looks slightly more uneven.

Comparison between all substrates

The results from the modification of MCC and Lyocell fibers indicate that the amount of grafted polymer is highly dependent on the substrate. In Figure 9, we have compared the FT-IR spectra of all the used substrates grafted with MA to an aimed DP = 100. Table IV shows the SEC results for the bulk polymers formed concurrently with the surface graftings. The highest carbonyl peaks are seen for filter paper and MCC, which are both native cellulose substrates with

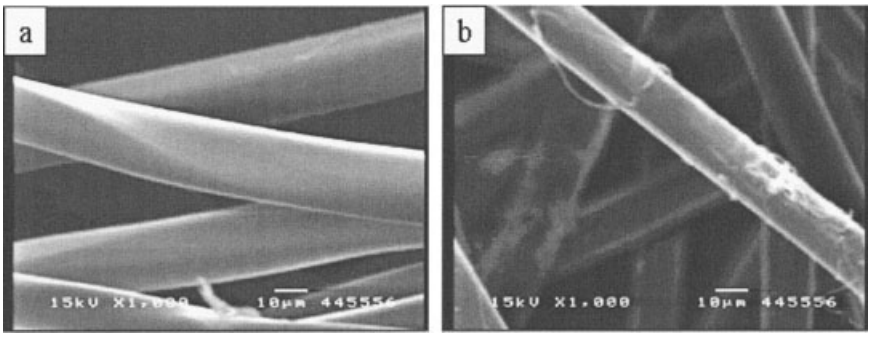

Figure 8 SEM-images of a) unmodified and b) PMA-grafted Lyocell fibers.

large surface area. The peaks are much lower for dialysis membrane and Lyocell fibers, both regenerated cellulose substrates with lower surface areas, but there is no significant difference in the molecular weight of the corresponding bulk polymers. The spectrum for the modified chitosan looks somewhat different from those of the cellulosic substrates, and therefore the baseline is different. In view of this, the carbonyl peak seems to be somewhere between the native and the regenerated cellulosic substrates, even though the surface of the chitosan films is smooth. This indicates that the amino groups that structurally separate the chitosan from cellulose are more reactive than the hydroxyl groups. On the other hand, the bulk polymer formed when grafting from chitosan shows a higher molecular weight than the bulk polymers corresponding to the other substrates, which could explain at least some of the increased amount of grafted polymer in that sample.

In an ongoing project, we are currently investigating the use of the surface modified substrates in various composites.

CONCLUSIONS

The grafting of MA and styrene from various cellulosic and chitosan substrates have been successful. There are considerable differences in the amount of grafted polymer between the different substrates. Higher amounts of polymer seem to be possible to graft from native cellulose substrates than from regenerated cellulose substrates. This is probably a result of the difference in surface area between these substrates, and an effect of the hornification of the regenerated cellulose substrates. A comparatively high amount of polymer is grafted from chitosan, indicating that the amino groups are more reactive than the hydroxyl groups.

The grafting polymerizations are controlled and the chain ends are also shown to be living after a time period as long as one year. Graft copolymerization from polysaccharide substrates offers the possibility of changing and tailoring the surface properties of the substrates.

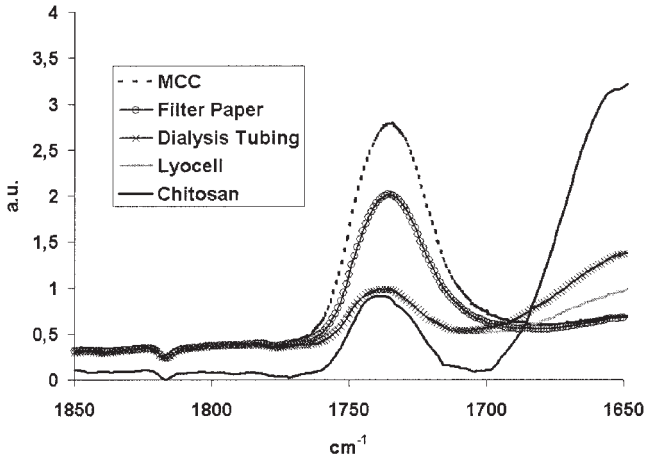

Figure 9 FT-IR spectra of substrates grafted with PMA to an aimed DP of 100.

TABLE IV
SEC Results for Bulk Polymers Formed during PMA-Grafting of All the Substrates

Substrate	Aimed DP	Theoretical M_n	Calculated M_n	Calculated DP[a]	PDI
Filter Paper	100	8600	6600	76	1.10
Chitosan	100	8600	7800	90	1.03
Dialysis membrane	100	8600	6700	77	1.02
MCC	100	8600	6700	77	1.15
Lyocell	100	8600	6700	77	1.08

[a] The degree of polymerization was calculated from the SEC data.

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