Grafting of Cellulose Fibers with Poly(ϵ-caprolactone) and Poly(L-lactic acid) via Ring-Opening Polymerization

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In this study, ring-opening polymerization (ROP) of ϵ-caprolactone (ϵ-CL) and L-lactide (L-LA) has been performed from cellulose fibers. The hydroxyl groups on cellulose act as initiators in the polymerization, and the polymers are covalently bonded to the cellulose fiber. As an attempt to introduce more available hydroxyl groups on the surface, and thereby obtain higher grafting efficiency in the ROP of ϵ-CL and L-LA, unmodified paper was modified with xyloglucan-bis(methylol)-2-methylpropanamide (XG-bis-MPA) and 2,2-bis(methylol)propionic acid (bis-MPA), respectively. The grafted substrates were characterized via Fourier transform infrared spectroscopy (FTIR), contact angle measurement, atomic force microscopy, and enzymatic degradation. The results showed a successful grafting of poly(ϵ-caprolactone) (PCL) and poly(L-lactic acid) (PLLA) from the cellulose fiber surfaces. Furthermore, the results showed an improved grafting efficiency after activation of the cellulose surface with bis-MPA, and showed that the amount of grafted polymer could be controlled by the ratio of added free initiator to monomer.

Introduction

Environmental awareness and the demand for green technology have led to a rapidly increasing interest in biocomposites. In true biocomposites, both the reinforcing material, e.g., a natural fiber, and the matrix are biodegradable.[1] Since biocomposites have the potential to replace present petrochemical-based materials, they represent an important element of future waste disposal strategies.

Cellulose is the most abundant organic compound in nature, as well as an inexpensive, biodegradable, and renewable resource. Cellulose consists of linear polymers of β-(1→4)-D-glucose units and constitutes the main load-bearing component of natural fibers. The use of natural fibers such as flax, jute, and wood fiber,[2,3] instead of traditional reinforcement materials, such as glass fibers, carbon, and talc, provides several advantages including low density, low cost, good specific mechanical properties, reduced tool wear, and biodegradability.[4]

Poly(ϵ-caprolactone) (PCL) and poly(L-lactic acid) (PLLA) are biodegradable polymers that are potential candidates as matrixes in biocomposites.[1,2,5,6] Ring-opening polymerization (ROP) is a versatile technique for the synthesis of polymers from cyclic monomers, such as lactones and lactides, resulting in polymers with controlled molecular weight and molecular weight distribution.[7,8] ROP of ϵ-CL and L-LA with stannous 2-ethylhexanoate ($Sn(Oct)_2$) catalyst and an alcohol initiator is well-known.[9,10] PCL is a tough, crystalline polymer with a melting point (T_m) of 60 °C, glass transition temperature (T_g) of −60 °C, and good compatibility with many polymers and organic compounds. PLLA is a hard, highly crystalline, and transparent polymer with T_m of 170−180 °C, and T_g of 53 °C.[2,5]

Despite several advantages of using cellulose fibers as reinforcement in biocomposites, there are some limitations. The most important restraint is the poor compatibility between the hydrophilic fiber and the hydrophobic polymer matrix.[11,12] Hence, the fiber−matrix interface is usually the weakest point in a biocomposite, which makes the performance of the final composite limited by fiber pull-out rather than fiber break.[11] Thus, the full strength of the cellulose fiber as reinforcing material is not utilized, the optimal properties of the biocomposite are not obtained, and the full commercial potential is therefore not achieved.

To improve the compatibility between the fiber and the polymer matrix, the reinforcing fiber can be physically or chemically modified. One effective method for chemical modification of cellulose substrates is to grow polymers directly off the surface, using the "grafting-from" approach.[3] By this approach, polymers have been successfully grafted from cellulose and cellulose derivatives using a wide variety of polymerization techniques.[4,13,14] On the other hand, the ROP technique has been used frequently to graft biopolymers from other substrates than cellulose, such as starch, silica nanoparticles, gold surfaces, and hydroxyapatite surfaces.[15−19] Furthermore, various preparation methods have been developed to fabricate biocomposites by blending a biopolymer matrix with a biofiber or conventional biomaterial filler.[20] In some of these biocomposites, one of the components has been modified in order to improve the interfacial adhesion.[21−23]

Several studies have been conducted on the PCL and PLLA modification of soluble cellulose and its derivates.[24−29] However, only a limited number of studies have addressed covalent modification with either PCL or PLLA of solid cellulose substrates, e.g., cellulose fibers or fiber networks such as paper. Oishi et al.[30] and Hadano et al.[31] demonstrated the grafting of PCL and PLLA, respectively, to waste pulp and waste pulp modified with succinic anhydride and maleic anhydride. Fur-

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thermore, it was shown that acetylated and deacetylated waste pulp can be grafted with PLLA.[32] Córdova et al. studied grafting of unmodified paper and cotton with PCL, using an organic acid as catalyst.[33]

The aim of this study was to attempt grafting of biopolymers directly from the surface of solid cellulose substrates. The better compatibility achieved in this way, between hydrophobic polymer matrixes and cellulosic fibers, should improve the mechanical properties of biocomposites. The biopolymers used were PCL and PLLA, which were grafted by ring-opening polymerization from Whatman no. 1 filter paper representing a model cellulose surface. Composite materials will be prepared in a continuation of this project.

Experimental Section

Materials. ϵ-Caprolactone (ϵ-CL) was dried over CaH_2, distilled under reduced pressure, and stored under argon atmosphere. L-Lactide (L-LA) was recrystallized from dry toluene. Toluene was distilled prior to use. Filter paper, Whatman 1, was used as cellulose substrate, and was dried in a vacuum oven at 50 °C for 24 h prior to use. Benzyl alcohol, tin octoate ($SnOct_2$), 2,2-bis(methylol)propionic acid (bis-MPA), tetrahydrofurane (THF), methanol (MeOH), pyridine, 4-dimethyl(aminopyridine) (DMAP), dichloromethane (DCM), and dimethylformamide (DMF) were used as received. Celluclast, a culture filtrate containing a mix of different endo- and exocellulases, was obtained from Novozyme, Denmark. Acetonide-protected 2,2-bis(methylol)propionic anhydride and benzyl ester protected bis-MPA was synthesized according to procedures described elsewhere.[34] The xyloglucan-bis-MPA (XG-bis-MPA) was prepared by xyloglucan endotransglycosylases (XET)-mediated incorporation of xyloglucan oligosaccharides-bis-MPA (XGO-bis-MPA) into XG.[35] Synthesis of XGO-bis-MPA is described in the Supporting Information.

Characterization. Nuclear magnetic resonance (NMR) spectra were recorded at 400 MHz on a Bruker AM 400 using $CDCl_3$ as solvent. Remains of the non-deuterated solvent signal were used as an internal standard.

Size exclusion chromatography (SEC) was performed on PCL using a TDA model 301 equipped with one or two GMH_{HR}-M columns with TSK-gel (Tosoh Biosep), a VE 5200 GPC autosampler, a VE 1121 GPC solvent pump, and a VE 5710 GPC degasser from Viscotek Corp. THF was used as the mobile phase (1.0 mL min^{-1}). The measurement was performed at 35 °C. The SEC apparatus was calibrated with linear polystyrenes standards, and toluene was used as flow rate marker.

SEC on PLLA was performed on a Waters 717 plus autosampler and a Waters model 510 apparatus equipped with two PLgel 10 μm mixed-B columns, 300 × 7.5 mm, and with $CHCl_3$ as solvent. Calibration was made with linear polystyrene standards.

Fourier transform infrared spectroscopy (FTIR) was conducted on a Perkin-Elmer Spectrum 2000 FTIR equipped with a MKII Golden Gate, single reflection ATR system from Specac Ltd., London, U.K.

In the contact angle (CA) measurement, a 10 μL droplet of deionized water was applied onto the cellulose surface with a syringe. Digital images were taken after 10 s with a Sanyo VCC4100 color video CCD camera, equipped with a Cosmicar 25 mm 1:1.4 lens and a 20 mm spacer for increased optical magnification. The contact angles were calculated with Optimas 6.2 software from Optimas Corporation. The contact angle on each sample was measured at four different points with three different readings per droplet; the average value and standard deviation from the measurement is reported. The measurement was performed under ambient conditions.

The enzymatic degradation of cellulose was conducted with a culture filtrate (5 μL) in an acetic acid buffer (10 mL, pH ~5) at 40 °C. After hydrolysis, the free cellulose fibers where dispersed in water, centrifuged, and the solution was decanted off. From the dry weight of the remaining sample, the mass balance was calculated.

Atomic force microscopy (AFM) was performed using a Nanoscope III-a system (Digital Instruments, Santa Barbara, CA) equipped with a J-type vertical engage piezoelectric scanner operating in tapping mode in air. Silicon AFM probes from Nanosensors were used throughout the study (l = 125 μm, force constant ≈ 42 N/m, resonance frequency ≈ 320 kHz).

Grafting of Cellulose Substrates via Ring-Opening Polymerization of ϵ-CL and l-LA. A typical procedure for the grafting of PCL from filter paper (DP 125) was as follows: Predried paper, 2 × 3 cm^2, was put into a flame-dried flask with a magnetic stirrer. The initiator, benzyl alcohol (38.9 mg; 0.36 mmol) or benzyl ester protected bis-MPA (40.5 mg; 0.18 mmol), was added to the reaction flask. The flask was sealed with a rubber septum and degassed by three vacuum/argon cycles. Thereafter, ϵ-CL (5.15 g; 45.1 mmol) and toluene (15 mL) were added to the reaction flask with a syringe under argon. The flask was immersed in an oil bath and heated to 95 °C. A catalytic amount of $Sn(Oct)_2$ (2 wt % of the monomer) was added to the reaction mixture under argon, and the flask was then flushed for 15 min with argon. The polymerization was allowed to proceed for 18−20 h, and the conversion of the monomer was estimated with ^{1}H NMR.

Grafting of PLLA from filter paper follows the same procedure as described above, with the exception that L-LA is added to the flask together with the initiator and the filter paper, i.e., before the vacuum/argon cycles.

The nongrafted polymer, formed in bulk, was purified by precipitation using THF as solvent for PCL and $CHCl_3$ as solvent for PLLA; methanol was used as nonsolvent. To remove the adsorbed but not chemically bonded polymer, the grafted filter paper was washed with a good solvent, for 24 h, using Soxhlet extraction. To check the washing procedure, unmodified paper was immersed into a polymer solution and left for 24 h; the paper was then washed via Soxhlet extraction for 24 h. Thereafter, the FTIR analysis showed no presence of polymer, which confirms the efficiency of the washing procedure. The grafted cellulose substrates were analyzed with FTIR, AFM, CA measurement, and enzymatic degradation. The ungrafted, free polymer was analyzed with ^{1}H NMR and SEC.

Activation of Cellulose Substrate with bis-MPA. Filter paper, 2 × 3 cm^2, was washed with acetone and dried in a vacuum oven at 50 °C for 24 h prior to use. Acetonide-protected bis-MPA anhydride (2.0 g; 6.1 mmol), pyridine (39 mg; 0.5 mmol), DMAP (2.3 g; 19 mmol), DCM (2.5 mL), and DMF (5.5 mL) were added to a 50 mL flask. After complete dissolution, the filter paper was immersed in the reaction mixture. The modification reaction was left to proceed for 3 days at room temperature on a shaking table. Thereafter, the filter paper was washed with DCM and dried in a vacuum oven at 50 °C. Subsequent deprotection of the acetonide-protected bis-MPA filter paper was carried out with H^+ DOWEX resin in MeOH at 50 °C for 24 h. The deprotected bis-MPA modified filter paper was then repeatedly washed with DCM and dried. The success of the modification and the subsequent deprotection were confirmed via FTIR analysis.

Activation of Cellulose Substrate with XG-bis-MPA. *XET-Mediated Synthesis of XG-bis-MPA.* A sample (200 mL total volume) containing a mixture of XG (1 g/L, M_w 4.5 × 10^5, PDI = 1.5), XGO-bis-MPA (0.5 g/L), and XET (400 units) in sodium acetate buffer (20 mM, pH 5.5) was incubated at 30 °C for 60 min. The reaction was terminated by heating (80 °C, 10 min), and the denatured XET was removed by centrifugation at 12 000 g for 20 min. Then, 500 mL of ethanol was added to precipitate XG-bis-MPA, with the free XGO-bis-MPA in the supernatant. After filtration over a Whatman GF/A glass microfiber filter, the precipitated XG-bis-MPA was dried under vacuum, redissolved in water, and lyophilized (yield: 231 mg). The XG-bis-MPA produced in this manner had a M_w value of 1.16 × 10^4 (PDI = 1.7).

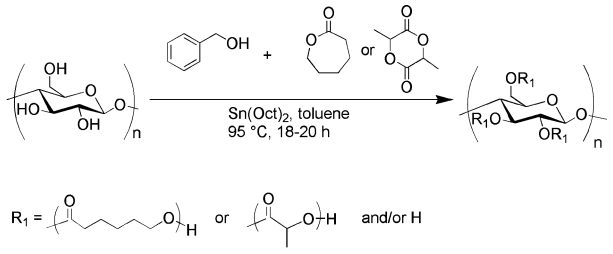
Immobilization of XG-bis-MPA onto Cellulose Filter Papers. Seven Whatman no. 1 filter paper disks (diameter 1.5 cm, total mass 0.1 g) were immersed in 20 mL of an aqueous solution containing 20 mg of XG-bis-MPA in glass vials and incubated at 20 °C with orbital shaking

Table 1. Characterization of Free PCL and PLLA Formed during the Grafting ROP

sample	cellulose substrate	polymer	graft length	theoretical MW[c]	M_n NMR[c,d]	M_n SEC[c]	PDI[e]
1	unmodified[a]	PCL	short	14400	17200	14800	1.8
2	unmodified[a]	PCL	long	34300	23700	20100	1.6
3	unmodified[a]	PLLA	short	18100	32900	22900	1.1
4	unmodified[a]	PLLA	long	43300	42300	24700	1.2
5	bis-MPA modified[b]	PCL	short	28700	21900	18500	1.5
6	bis-MPA modified[b]	PCL	long	68600	39000	23100	1.7
7	bis-MPA modified[b]	PLLA	short	36200	38500	37800	1.2
8	bis-MPA modified[b]	PLLA	long	86600	107000	44200	1.3
9	XG-bis-MPA modified[b]	PCL	short	28700	15500	8600	1.5
10	XG-bis-MPA modified[b]	PCL	long	68600	24200	12500	1.8
11	XG-bis-MPA modified[b]	PLLA	short	36200	26700	30500	1.3
12	XG-bis-MPA modified[b]	PLLA	long	86600	50900	29000	1.3

[a] Coinitiator: benzyl alcohol. [b] Coinitiator: benzyl ester protected bis-MPA. [c] (g mol^{-1}). [d] Estimated from the degree of polymerization (DP) with ^{1}H NMR. DP for PCL was calculated from the signals at 4.05 ($-CH_2O-$, repeating unit) and 3.62 ($-CH_2OH$, end group). The signals at 5.17 ($-CH(CH_3)O-$, repeating unit) and 4.34 ($-CH(CH_3)O-$, end group) were used for estimation of DP for PLLA.[40] [e] Determined by SEC.

Scheme 1. Ring-Opening Polymerization of ϵ-CL or L-LA from Unmodified Cellulose Substrate Using Benzyl Alcohol as Free Initiator



for 24 h. The XG-bis-MPA adsorbed onto the cellulose was measured by the loss of XG-bis-MPA from the solution according to the colorimetric method of Kooiman[36] as follows: 100 μL of the solution was withdrawn and mixed with 100 μL of water, 0.8 mL of 20% (w/v) Na_2SO_4, and 0.2 mL of triiodide solution (0.5% I_2 + 1% KI). The amount of bound XG-bis-MPA was calculated from the difference in adsorption at 620 nm of the solutions before and after the binding reaction using a standard curve derived from XG-bis-MPA solutions of increasing concentrations versus a blank where water replaced the XG-bis-MPA solutions. 11 mg XG-bis-MPA was immobilized onto 0.1 g cellulose filter papers.

Results and Discussion

The use of biocomposites is presently limited due to poor adhesion between the hydrophobic matrix and the hydrophilic reinforcement material, giving rise to poor mechanical properties. The aim of this study was to improve the compatibility between the components in the biocomposite, i.e., the hydrophilic cellulose fiber and the hydrophobic polymer matrix, via chemical grafting of biodegradable polymers to cellulose substrates.

Grafting of Cellulose Substrate via Ring-Opening Polymerization of ϵ-CL and L-LA. Whatman no. 1 filter paper with very high cellulose content (>98%) was chosen as the substrate for chemical grafting out of biodegradable polymers. ROP of ϵ-CL and L-LA, respectively, was performed from the paper surface, resulting in PCL and PLLA grafted papers. The "grafting from" approach was used in the modification of cellulose substrates with PCL and PLLA (Scheme 1). High conversions, 98−100%, were obtained in all polymerizations.

The hydroxyl groups on cellulose act as initiators for the polymerization, and the ratio of monomer to initiating groups determines the degree of polymerization (DP) of the polymer chains. However, the number of initiating OH groups on the cellulose substrates is not known, and therefore, to enable control over the polymerization, a soluble coinitiator, benzyl alcohol or benzyl ester protected bis-MPA, was added to the polymerization system. Both these compounds have been reported to be effective initiators for ROP of lactones and lactides in the presence of $Sn(Oct)_2$.[37,38] The cellulose substrates were grafted with different graft lengths, i.e., DP 300 and DP 125, which was controlled by the ratio of added free initiator to monomer.

Free PCL and PLLA formed during the grafting reaction from unmodified cellulose were analyzed with ^{1}H NMR and SEC (Table 1 entries 1−4). Most likely, the reactivity of the hydroxyl groups on the coinitiator, as well as the primary and secondary hydroxyl groups on cellulose, are different. Thus, the obtained DP of the free polymer will not be the same as the DP for the grafted polymer. Therefore, the molecular weight estimated with ^{1}H NMR and SEC will not correspond to the length of the polymer grafts. The table also shows that the estimated molecular weight values are much lower than the theoretical values. This could be expected, since the latter values only were based on the addition of coinitiator to monomer, without taking the initiating hydroxyl groups on the cellulose surface into consideration. Furthermore, the true molecular weight of the free polymers is even lower than the values estimated with SEC using PS standards.[39] This results in an even higher discrepancy between the theoretical molecular weight and the molecular weights estimated via ^{1}H NMR, compared to the molecular weights estimated with SEC.

The grafted filter paper was thoroughly washed by Soxhlet extraction in order to remove adsorbed polymer from the surface prior to characterization with FTIR, contact angle measurement, AFM, and enzymatic degradation.

FTIR spectroscopy was used to characterize cellulose surfaces grafted with polymer. All spectra were normalized against a specific ATR crystal adsorption, this to enable comparison between the polymer-grafted cellulose substrates.[13,14] The FTIR spectrum of unmodified cellulose paper grafted with PCL shows a small adsorption peak from the carbonyl group at 1729 cm^{-1}, which confirms the presence of polymer (Figure 1 curve 2). Similar results were obtained for PLLA-grafted cellulose, in which a carbonyl peak was seen at 1760 cm^{-1} confirming the presence of polymer (Figure 2 curve 4).

Hence, successful modifications of unmodified cellulose with PCL and PLLA were verified with FTIR analysis. However, a higher grafting efficiency is desirable in order to improve the compatibility between the hydrophilic cellulose fiber and the hydrophobic polymer matrix, thus enhancing the mechanical properties of the final biocomposite.

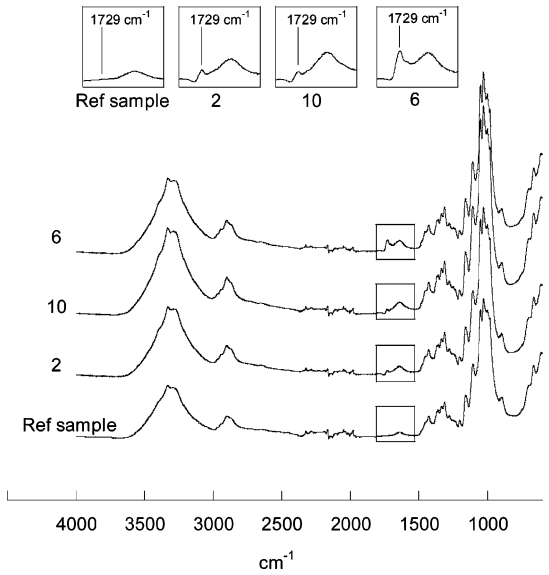


Figure 1. FTIR spectra of unmodified reference paper and papers grafted with long grafts: unmodified paper-*g*-PCL (2), XG-bis-MPA modified paper-*g*-PCL (10), and bis-MPA modified paper-*g*-PCL (6). (Numbers refer to the sample entries in Table 1.)

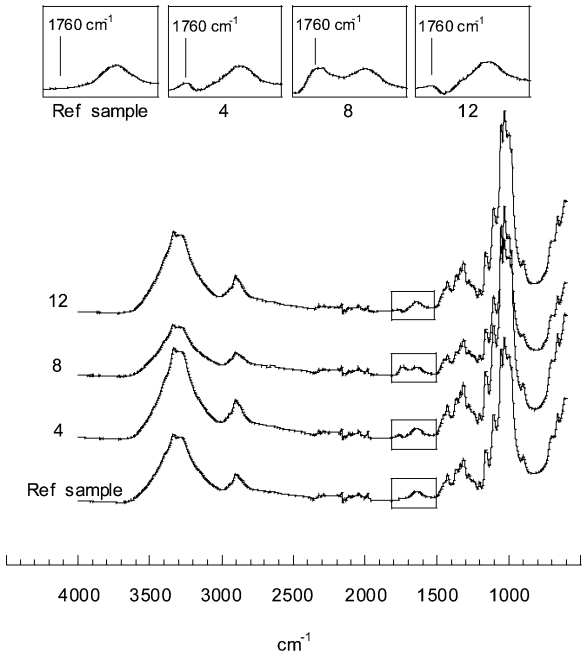


Figure 2. FTIR spectra of unmodified reference paper and papers grafted with long grafts: unmodified paper-*g*-PLLA (4), bis-MPA modified paper-*g*-PLLA (8), and XG-bis-MPA modified paper-*g*-PLLA (12). (Numbers refer to the sample entries in Table 1.)

Activation of Cellulose Substrate with bis-MPA or XG-bis-MPA and Subsequent Grafting with PCL or PLLA via Ring-Opening Polymerization. The number of available hydroxyl groups on the cellulose surface determines the grafting efficiency. As an attempt to introduce more available hydroxyl groups on the surface, and thereby to obtain higher grafting efficiency in the ROP of ϵ-CL and L-LA, the cellulose substrate was modified with bis-MPA and XG-bis-MPA (Schemes 2 and 3, respectively). Bis-MPA was chosen due to the facile process of ROP from the hydroxyl groups on the bis-MPA moiety, resulting in controlled molecular weight and low polydispersity.[38] In the activation step, the bis-MPA moiety is covalently bonded to the cellulose surface via the reaction of an acetonide-protected bis-MPA anhydride and subsequent deprotection.[34] XG-bis-MPA is strongly adsorbed to the cellulose surface, and the modification takes place without fiber degradation or change in the fiber structure.[35,41]

The modification of cellulose with acetonide-protected bis-MPA is visualized in the FTIR spectrum through the appearance of a carbonyl peak at 1730 cm^{-1} and a peak at 828 cm^{-1} originating from the cyclic acetal (Figure 3 curve B). Subsequent deprotection of bis-MPA modified cellulose is shown by the disappearance of the cyclic acetal peak while the carbonyl peak remains (Figure 3 curve C).

High conversions, 97−100%, were obtained in the ROP of ϵ-CL or L-LA from bis-MPA and XG-bis-MPA activated substrates. Free PCL and PLLA, formed during the grafting reactions of paper preactivated with bis-MPA and XG-bis-MPA, were analyzed with ^{1}H NMR and SEC (Table 1 entries 5−12).

A comparison between the different cellulose substrates grafted with PCL shows that the bis-MPA modified filter paper resulted in the strongest carbonyl adsorption at 1729 cm^{-1} (Figure 1). This implies that the largest amount of PCL was grafted from the bis-MPA activated cellulose surface. It was also demonstrated that no significant difference was obtained with PCL grafting from XG-bis-MPA modified paper, in comparison to grafting from unmodified paper. The more efficient grafting of PCL from the bis-MPA activated filter paper may be due to the different reactivity of the hydroxyl groups on unmodified cellulose and XG-bis-MPA activated cellulose, compared to the bis-MPA activated cellulose. It could also be a result of the increased number of hydroxyl groups introduced to the surface, after the bis-MPA modification, via the bis-MPA diol. Moreover, it may be due to less steric hindrance, since the bis-MPA moiety acts as a spacer from the cellulose surface, allowing the monomer to react more easily with the hydroxyl groups on bis-MPA. PLLA-grafted paper followed the same trend. Thus, the strongest adsorption at 1760 cm^{-1} was obtained for PLLA grafted from bis-MPA activated paper; the adsorptions for PLLA-grafted XG-bis-MPA modified paper and grafted unmodified paper were about the same, Figure 2.

FTIR spectra of bis-MPA activated paper, grafted with long and short grafts of PCL, show a higher adsorption at 1729 cm^{-1} for paper with long grafts (Figure 4). Thus, the length of the grafts can be controlled by the feed ratio of monomer to free initiator. Similar results were obtained for PLLA-grafted cellulose, for which a longer graft length results in a stronger adsorption peak at 1760 cm^{-1}.

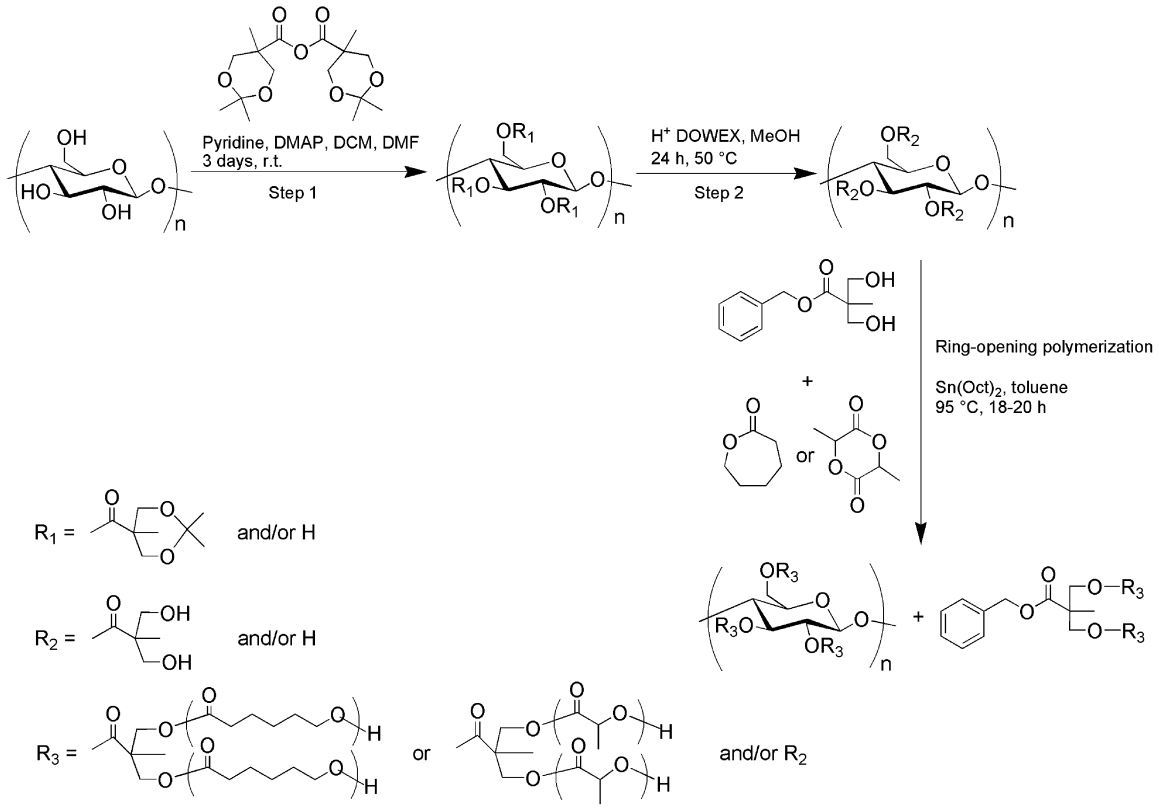
As discussed earlier, the obtained DP of the free polymer estimated with ^{1}H NMR and SEC (Table 1) will not be the same as the DP for the grafted polymer. However, samples with higher molecular weight of the free polymer also show a stronger adsorption peak in the corresponding FTIR spectrum of the grafted substrate.

Surface Characterization of Cellulose Substrate Grafted with PCL and PLLA. Contact angle (CA) measurements were used to estimate the change in hydrophobicity of the grafted substrates compared to unmodified cellulose paper, and a distinct difference in hydrophobicity was observed. When a droplet was placed on the surface of the ungrafted cellulose substrate, it was rapidly adsorbed, whereas the droplet on the grafted filter paper remained on the surface for a much longer time (Figure 5).

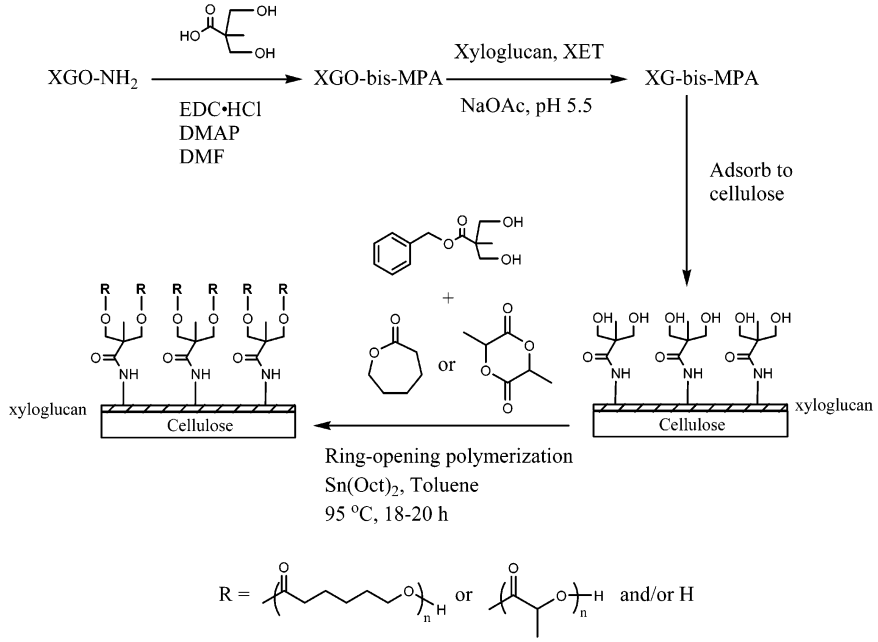
Hence, an increase in contact angle was observed for both PCL- and PLLA-grafted cellulose substrates in comparison to unmodified substrates, showing the more hydrophobic nature of the polymer-modified substrates (Table 2).

The contact angle values obtained were generally higher in comparison to the values found in the literature, although the

Scheme 2. Modification of Cellulose with Protected bis-MPA (Step 1) and Deprotection to bis-MPA Activated Cellulose (Step 2), and Subsequent Ring-Opening Polymerization of ϵ-CL or L-LA with Benzyl-Protected bis-MPA as Free Initiator



Scheme 3. Modification Reaction of Cellulose with XG-bis-MPA and Subsequent Ring-Opening Polymerization of ϵ-CL or L-LA with Benzyl-Protected bis-MPA as Free Initiator



values in the literature differ a lot depending on the sample preparation and the measurement method.[42] In this study, the contact angles are used as a rough measure to follow the changes in surface hydophobicity due to grafting. However, since filter paper is a porous substrate with a rough surface, the contact angles are difficult to estimate and should therefore be considered only as an indication for the change in hydophobicity, and not as an absolute value of the contact angle. A significant difference in hydophobicity was observed between the different cellulose substrates. The PCL-grafted paper activated with bis-MPA showed the highest values, which indicates that more polymer is present on the surface. This is corroborated by FTIR spectra which show that the most efficient grafting of PCL is obtained from bis-MPA activated filter paper. However, the PLLA-grafted cellulose substrate did not follow the same trend: No significant difference in contact angle was observed between the different substrates, which is possibly explained by a more hydrophobic character of PLLA as compared to PCL. It was also demonstrated that the contact angle is dependent on the graft length; this was most evident in the case of paper

Table 2. Contact Angle for PCL and PLLA Grafted Cellulose Substrates

cellulose substrate	contact angle[a] (°) PCL short grafts	contact angle[a] (°) PCL long grafts	contact angle[a] (°) PLLA short grafts	contact angle[a] (°) PLLA long grafts
unmodified	95 (±4)	99 (±3)	107 (±5)	112 (±3)
bis-MPA modified	103 (±5)	105 (±3)	108 (±4)	111 (±6)
XG-bis-MPA modified	84 (±4)	96 (±6)	104 (±6)	110 (±5)

[a] Standard deviation is shown in parentheses.

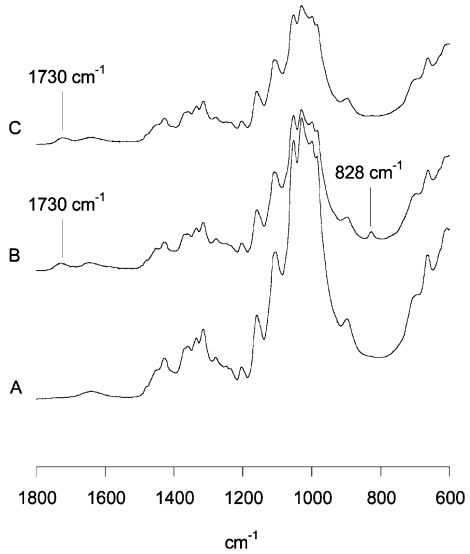


Figure 3. FTIR spectra of unmodified paper (A), paper modified with acetonide protected bis-MPA (B), and deprotected bis-MPA modified paper (C).

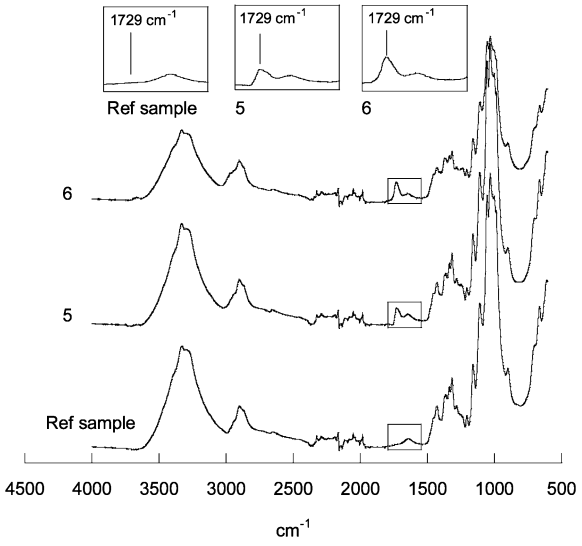


Figure 4. FTIR spectra of unmodified reference paper, bis-MPA modified papers grafted with PCL short grafts (5) and PCL long grafts (6). (Numbers refer to the sample entries in Table 1.)

activated with XG-bis-MPA and grafted with PCL, for which the contact angle increased from 84° to 96°, when the graft lengths were increased.

Atomic force microscopy was used to investigate the changes in surface morphology after grafting. Figure 6 visualizes a large difference in the structure of the unmodified paper compared to the grafted papers. The latter has a less-defined fibrillar structure and much smoother surface indicating that the surface has been covered with a quite thick polymer layer. The root-mean-square roughness (rms), which reflects the surface morphology, was calculated for the different surfaces and is shown in Figure 6.

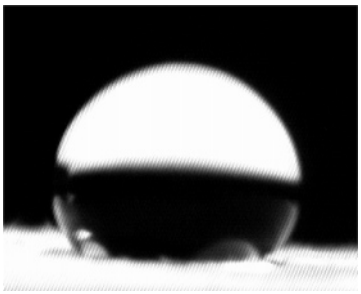


Figure 5. A water droplet deposited on the surface of bis-MPA activated cellulose substrate modified with short grafts of PCL, showing its hydrophobic nature, for the estimation of the contact angle.

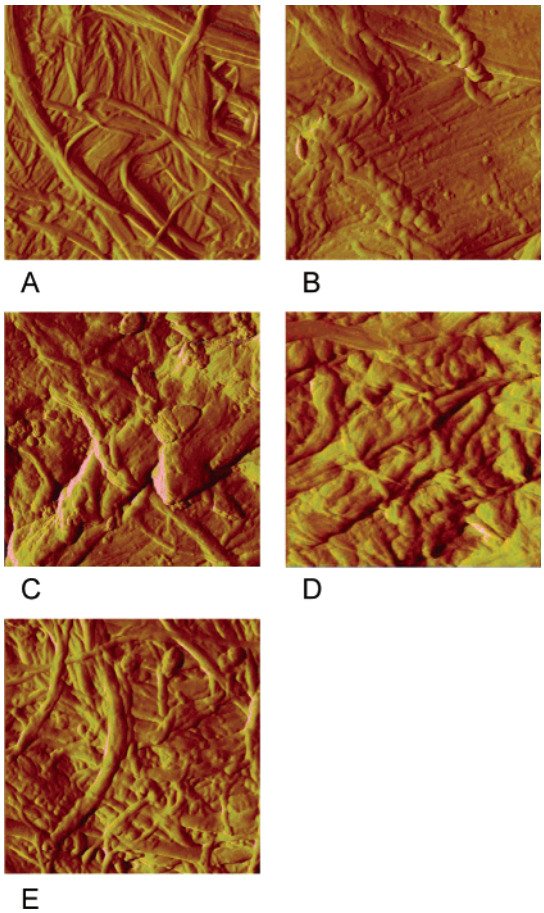


Figure 6. AFM images: (A) unmodified paper (rms 208 nm), (B) bis-MPA modified paper grafted with PCL (rms 135 nm), (C) bis-MPA modified paper grafted with PLLA (rms 194 nm), (D) XG-bis-MPA modified paper (rms 177 nm), and (E) XG-bis-MPA modified paper grafted with PCL (rms 111 nm). All images are 5 × 5 μm^2.

In comparison to unmodified paper, a decrease in rms values was obtained for PCL- and PLLA-grafted bis-MPA paper with 35% and 7%, respectively. In the case of ungrafted XG-bis-MPA modified paper, the rms value was lower than for unmodified paper. Hence, in the premodification of filter paper with XG-bis-MPA, the polysaccharide coats the surface, leveling

Table 3. Enzymatic Treatment of Cellulose Substrates: Unmodified Paper, Bis-MPA Activated Paper, Bis-MPA Treated Paper, Unmodified Paper Grafted with Polymer, and Premodified Paper[a]

	grafted polymer				grafted polymer			
cellulose substrate	short grafts	24 h	48 h	7 days	long grafts	24 h	48 h	7 days
unmodified	none	−	−	−				
bis-MPA modified	none	+	+	+				
chemically treated[b]	none	−	−	−				
unmodified	PCL	±	−	−	PCL	+	±	−
bis-MPA modified	PCL	+	+	+	PCL	+	+	+
XG-bis-MPA modified	PCL	−	−	−	PCL	−	−	−
unmodified	PLLA	+	+	−	PLLA	+	+	−
bis-MPA modified	PLLA	+	+	+	PLLA	+	+	+
XG-bis-MPA modified	PLLA	−	−	−	PLLA	±	−	−

[a] i.e., XG-bis-MPA and bis-MPA, grafted with polymer. Not disintegrated (+), disintegrated (−), and partially disintegrated (±). [b] Chemically treated, according to the bis-MPA modification without the acetonide protected bis-MPA anhydride.

out the surface morphology. In subsequent grafting, the surface becomes even smoother, and a 37% decrease of the rms value is obtained.

To investigate how well the polymer grafts cover the cellulose surface, the grafted substrates were exposed to enzymatic degradation in a mixture of different endo- and exocellulases. The grafted substrates, and an unmodified reference substrate, were immersed into a solution of cellulases at 40 °C. The results are summarized in Table 3. To investigate if the enzymatic degradation is affected by the chemical modification during the bis-MPA activation, bis-MPA activated substrate and a substrate that was chemically treated according to the bis-MPA modification—without the acetonide protected bis-MPA anhydride—were exposed to enzymatic treatment.

Table 3 shows that, after 24 h of enzymatic treatment, the ungrafted reference paper and paper treated according to the bis-MPA modification, as well as the polymer grafted XG-bis-MPA papers, were completely disintegrated into fiber dispersions. This suggests that the enzymes easily access the cellulose surface and initialize the degradation. Thus, subjecting the paper to the same reaction conditions as during the bis-MPA activation, without actually attaching the bis-MPA moiety, does not seem to affect the enzymatic degradation of the substrates. The degradation of grafted XG-bis-MPA papers could be expected, since XG is readily digested by cellulases.[43] As a consequence, the polymer attached to the cellulose surface via XG is solubilized from the surface. The hydrolysis with endocellulase is proposed to cleave the bonds in the middle of the cellulose chain, with a higher activity in the more disordered sites of the cellulose.[44] Exocellulases, on the other hand, degrade the cellulose from the chain end and can degrade even highly crystalline cellulose.[44] When the polymer was grafted directly from unmodified paper, the PCL with short grafts was partially disintegrated after 24 h, whereas the PCL with long grafts showed no tendency to disintegrate after 1 week of enzymatic treatment. Thus, a more efficient grafting of PCL from the cellulose substrate, i.e., longer grafts, prevents the enzymes from reaching the surface to defibrillate and solubilize the cellulose. Unmodified substrates modified with both long and short grafts of PLLA were intact after 24 h. Hence, the short PLLA grafts render a coating sufficient enough to delay cellulose degradation. Subjecting these substrates to 1 week of further enzymatic treatment, however, causes formation of fiber dispersions. Both bis-MPA activated paper and polymer-grafted bis-MPA activated papers were intact after 1 week of enzymatic treatment and showed no tendency to separate into free fibers. The high enzyme resistance of these papers may be due to the high degree of surface coverage obtained with the bis-MPA moieties. Bis-MPA activation renders higher grafting efficiency of the ROP, as confirmed with FTIR and contact angle measurements, as well as an improvement of the protection against enzymatic degradation; consequently, the grafted bis-MPA substrates also have a high persistence toward the degradation.

Furthermore, a mass balance of the enzymatic treated papers, forming free fibers, confirmed that they were not only subjected to disintegration but also to degradation, as the total mass of the solid sample decreased after the treatment; for instance, the weight loss of XG-bis-MPA activated paper grafted with long grafts of PCL was estimated to be 30%.

Conclusions

In this study, the biopolymers PCL and PLLA were successfully grafted from unmodified filter paper and paper preactivated with XG-bis-MPA and bis-MPA, respectively. The highest grafting efficiency was obtained with bis-MPA activated paper, giving the most promising results regarding the compatibility improvement between the components in biocomposites, thus improving the mechanical properties. It was also shown that the amount of grafted polymer can be controlled via the addition of free initiator to monomer. The more hydrophobic nature of the grafted papers, compared to unmodified papers, was confirmed through contact angle measurement. AFM was used to study the change in surface morphology due to grafting. A less-defined fibrillar structure and much smoother surface was obtained after grafting, indicating that the surface has been covered with polymer. Enzymatic treatment of the grafted papers with a mixture of cellulases showed that an efficient grafting with PCL or PLLA protects the papers from degradation and defibrillation. The activation of the cellulose surface with bis-MPA moieties gives a high level of protection against enzymatic degradation. As a consequence, the grafting bis-MPA substrates also have a high persistence toward the degradation.

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Supporting Information Available. The general method for the synthesis of XGO-bis-MPA. Molecular structure of XGO-NH_2 and XGO-bis-MPA. ^{1}H NMR and MS spectra of XGO-NH_2 and XGO-bis-MPA, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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