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Synthesis of Polycaprolactone-Grafted Microfibrillated Cellulose for Use in Novel Bionanocomposites—Influence of the Graft Length on the Mechanical Properties

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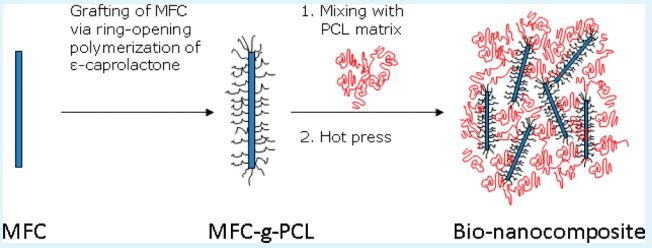
ABSTRACT: In the present work, microfibrillated cellulose (MFC) made from bleached sulfite softwood dissolving pulp was utilized to reinforce a poly(ε-caprolactone) (PCL) biopolymer matrix. To improve the dispersibility of the hydrophilic MFC in the nonpolar matrix and the interfacial adhesion in the composite material, we covalently grafted the MFC with PCL via ring-opening polymerization (ROP) of ε-caprolactone (ε-CL). To be able to investigate the effect of the PCL graft length on the mechanical properties of the composite material, we performed ROP to different molecular weights of the grafts. Bionanocomposites containing 0, 3, and 10 wt % MFC were prepared via hot pressing using both unmodified and PCL grafted MFC (MFC-g-PCL) as reinforcement. PCL grafting resulted in improved dispersion of the MFC in a nonpolar solvent and in the PCL matrix. The mechanical testing of the biocomposites showed an improvement in the mechanical properties for the PCL grafted MFC in comparison to ungrafted MFC. It was also shown that there was an impact on the mechanical properties with respect to the PCL graft lengths, and the strongest biocomposites were obtained after reinforcement with MFC grafted with the longest PCL graft length.



KEYWORDS: biocomposites, microfibrillated cellulose, polycaprolactone, grafting from, graft length, hot pressing, bionanocomposites

INTRODUCTION

Over the last decades, there has been an increasing interest in the development of novel composite materials based on biodegradable and renewable materials. Because cellulose is an abundant, renewable, and biodegradable resource, it is advantageous to utilize different types of cellulosic fibers as reinforcement in such biocomposites. Cellulose fibers and fibrils also have mechanical properties that make them desirable as reinforcing components in novel low-density and high strength materials.

The use of nanosized cellulose as reinforcement has been reviewed by Samir et al.[1] and Siqueira et al.[2] The main benefits associated with these nanosized fillers are the improvements in thermal, optical, and mechanical properties, even at relatively low filler contents.[3,4] Siqueira et al. investigated nanocomposites reinforced with either cellulose whiskers or microfibrillated cellulose (MFC), and reported that the MFC fibrils increased the tensile modulus compared to whiskers and the difference was proposed to be due to the possibility of MFC to form entanglements.[2]

Microfibrillated cellulose was originally developed by Turbak et al.[5] in the 1980s by high-pressure homogenization of water suspensions of wood pulp. This method was, however, very energy demanding and there were issues with clogging of the homogenizer. Recently, this method has been further developed. If the cellulose is pretreated prior to the homogenization, it is possible to produce a better dispersed MFC and decrease the energy consumption during the production. One such pretreatment involves the use of enzymes,[6] another is carboxymethylation. MFC from carboxymethylated cellulose was first produced by Wågberg et al.[7] By carboxymethylation of the wood pulp, charges are introduced in the fiber wall. The increased charge density causes the fibers to swell and thus facilitates the homogenization. Characterization of carboxymethylated MFC produced by a similar method have shown that the fibrils have a diameter of 5 to 15 nm and a length of more than 1 μm.[8]

To fully utilize the potential of nanocellulose as reinforcement in composite materials, the hydrophilic character of cellulose should be altered to make it more compatible with organic solvents and nonpolar polymer matrices. This improves both the incorporation of cellulose into the composite materials, which results in more homogeneous composites, and the interfacial adhesion in the final composite. Previously, surface modification of different celluloses has been accomplished via both chemical and physical modification using low-molecular-weight compounds and polymers.[9−15] Covalent grafting of polymers can be accomplished either via a "grafting-to" approach, in which preformed polymers are attached to the surface, or via a "grafting-from" approach, where polymers are grown directly from the surface. The latter method is superior in the synthesis of polymer grafts with high grafting density in combination with high

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molecular weight.[16,17] These properties have been shown to be desirable in the improvement of the interfacial adhesion between two immiscible components in a composite material.[18−20]

To produce novel sustainable materials based on MFC, i.e., bionanocomposites, the polymer matrix should also be biodegradable.[21] One interesting and commonly used polymer for such applications is poly(ε-caprolactone) (PCL).[21,22] PCL is a semicrystalline polymer with a glass transition temperature around −60 °C and a melting temperature around 60 °C. However, PCL is a ductile polymer and is therefore most often used in combination with other polymers or with different reinforcing fillers.

In the past decade, several studies have focused on the grafting of a biodegradable, hydrophobic polymer on nanosized cellulose using either the "grafting-to" or the "grafting-from" approach.[23−26] Some of the authors to this article have previously reported polycaprolactone (PCL) grafting of MFC using the "grafting-from" technique.[27] It was shown that the grafting of PCL from the MFC surface greatly improved the dispersibility in organic solvents, and that the length of the polymer grafts can be varied by the addition of a sacrificial initiator. A similar approach was used by Habibi et al. to graft PCL from cellulose nanocrystals that subsequently were used in nanocomposites prepared by a solvent casting procedure.[24] Chen et al. have reported that the amount of PCL grafted from a microcrystalline cellulose surface can be varied utilizing microwave irradiation, and the PCL-grafted cellulose was subsequently used to prepare thermoformable bionanocomposites with good mechanical strength.[25] Also, Lin et al. used microwave-assisted ROP to graft PCL from nanosized cellulose; the incorporation of the grafted cellulose into a poly (lactic acid) matrix resulted in significantly improved mechanical performance of a PLA-based material.[28]

The effect of the graft length on the mechanical properties of cellulose bionanocomposite materials, via the grafting-from approach, is still poorly investigated. Therefore, the aim of this study was to graft PCL from the surface of microfibrillated cellulose (MFC-g-PCL) via ring-opening polymerization (ROP) of ε-caprolactone (ε-CL), according to a similar method previously described in the literature.[27] In order to evaluate the impact of the length of the grafts on the mechanical properties of a MFC-g-PCL biocomposite, MFC-g-PCL samples with three different graft lengths of PCL were prepared. Biocomposites composed of unmodified MFC, or MFC-g-PCL, in a PCL matrix were produced via hot pressing. The final cellulose contents of the composites were 0, 3, and 10 wt %, respectively.

EXPERIMENTAL SECTION

Materials. ε-Caprolactone (ε-CL), acetone, toluene, benzyl alcohol, tin octoate ($SnOct_2$), tetrahydrofuran (THF), methanol (MeOH), and polycaprolactone (PCL, Aldrich, 80 000 g/mol) were used as received. The pulp used for the production of the MFC was never dried, bleached, sulfite softwood dissolving pulp (Domsjö Dissolving Plus, Domsjö Fabriker AB, Domsjö, Sweden). The pulp was first subjected to a carboxymethylation pretreatment using a method previously described.[8] The final degree of substitution (DS) of the treated fibers was 0.089 as determined by conductometric titration.[29] The pretreated pulp in Na^+ form was then homogenized using a Microfluidizer (Microfluidizer M-110EH, Microfluidics Corp., USA) according to the same method.[8] The MFC suspension (2 wt %) was solvent exchanged to acetone by repeated centrifugation (two times) and filtration (four times) on a Büchner funnel using a Munktell filter paper, grade 3, followed by redispersion. Thereafter, the MFC acetone suspension was solvent exchanged to toluene by five times filtration on a glass filter pore 4, and redispersion in the pure solvent.

Grafting of ε-Caprolactone from MFC Using "Grafting-from" Approach. The MFC in toluene suspension (1.0 g in 250 mL) was poured into a round-bottomed flask together with ε-CL (99 g) under rapid stirring for 24 h. Free initiator, benzyl alcohol (1.87 g, 0.63 g, or 0.16 g), was added to the system. Assuming that the amount of available cellulose hydroxyl groups is the same in the reactions, the free initiator regulates the graft length by competing for the ε-CL monomer. By varying the ratio of free initiator to monomer, the molecular weight of the grafts was varied to produce MFC-g-PCL with three different target graft lengths, here referred to as MFC-g-PCL_short, _medium, and _long. To remove the majority of the remaining water, we distilled off 50 mL of solvent at 120 °C. Thereafter, the flasks were sealed with rubber septa and degassed by 3 vacuum/argon cycles. After cooling the flasks to 110 °C, the catalyst, $Sn(Oct)_2$ (2 wt % of the monomer), was added to the reaction mixture under argon flow. The flasks were then flushed for 15 min with argon. The polymerizations were allowed to proceed for 3−5 h, and the conversion of the monomer was estimated with ^{1}H NMR.

After the polymerization, the reaction mixture was dispersed in THF, the PCL grafted MFC (MFC-g-PCL) was separated from free PCL in the solution by filtration. The free PCL was then precipitated using cold MeOH, dried, and analyzed with ^{1}H NMR and SEC. In order to remove nongrafted PCL the MFC-g-PCL was thoroughly washed, first by dispersion in THF for 24 h and then filtrated to remove dissolved PCL. Second, the MFC-g-PCL was washed via Soxhlet extraction in THF for 24 h. Then the final product was dried in a vacuum for 24 h.

Preparation of MFC-g-PCL Composites. Bionanocomposites were prepared with different MFC contents (0, 3, and 10 wt %) using unmodified MFC as well as MFC-g-PCL with varying PCL graft lengths. The unmodified MFC was solvent exchanged from water to acetone, then to toluene and THF. First, the PCL matrix (80 000 g/mol) and the unmodified MFC or MFC-g-PCL was dispersed separately in THF. The PCL solution and the MFC dispersion were mixed under rapid stirring for 3 h, sonicated in a bath for 30 min and finally the solvent was removed by rotary evaporation, after which the blends were dried in vacuum oven for 24 h, at 50 °C. Bionanocomposites were prepared by hot pressing the blends at 120 °C, at 2 min 1 unit pressure and then 5 min at 4 unit pressure into thin composite films (thickness ∼130−200 μm).

Characterization of the MFC-g-PCL Bionanocomposite Materials. Nuclear magnetic resonance (NMR) spectra were recorded at 400 MHz on a Bruker AM 400 using $CDCl_3$ as solvent. The molecular weight of the PCL was estimated from the NMR spectra by calculating the ratio of the signals at 4.05 ($-CH_2O-$, PCL repeating unit) and 3.63 ($-CH_2OH$, PCL graft end group).

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 measurements were performed at 35 °C. The SEC apparatus was calibrated with linear polystyrene standards, and toluene was used as a flow rate marker.

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

Differential scanning calorimetry (DSC) measurements were performed from −85 to 100 °C, with cooling and heating rates of 10 °C/min. The degree of crystallization (X_c) was calculated from the melting transition according to: $X_c = \Delta H_m / (w\Delta H^\circ_{100})$, where ΔH_m is the heat of fusion of the sample, w is the weight fraction of PCL, and ΔH°_{100} is the heat of crystallization for a 100% crystalline PCL, the value used was 136 J/g.[30]

Scheme 1. Ring-Opening Polymerization of ε-Caprolactone from MFC with Benzyl Alcohol As a Co-Initiator

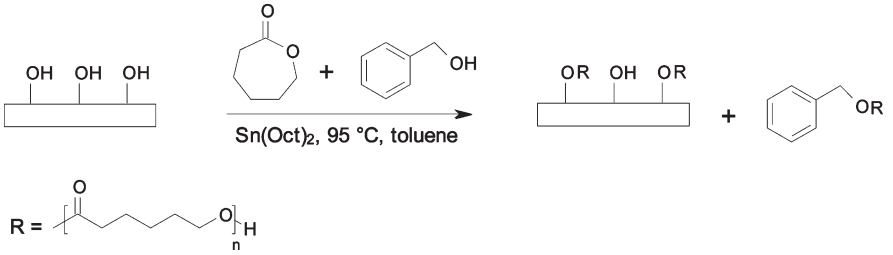

Table 1. Results from Characterization of Free PCL and MFC-g-PCL with Different Target Graft Lengths

		M_n (g/mol)			DSC		
		free PCL		MFC-g-PCL	MFC-g-PCL		
	PCL content in grafted MFC-g-PCL[a] (wt %)	NMR	SEC	NMR	T_g (°C)	T_m (°C)	X_c (%)
MFC-g-PCL_short	22	6300	8100 (PDI[b] 1.4)	700	−59	33	20
MFC-g-PCL_medium	70	11400	16400 (PDI[b] 1.3)	1100	−61	52	39
MFC-g-PCL_long	78	13300	26800 (PDI[b] 1.5)	2200	−60	56	45

[a] PCL content in the MFC-g-PCL samples based on the initial mass of MFC added to the reaction and the mass of the resulting MFC-g-PCL. [b] PDI is the polydispersity index.

Dynamic vapor sorption (DVS) measurements were performed using a DVS from Surface Measurement Systems Ltd. The measurements were performed at about 32.5 °C. Each sample was first dried in the DVS until constant weight was obtained. The relative humidity (RH) was then increased from 0 to 90% in steps of 10% and the sample weight was recorded after stabilization at each level of humidity. The moisture uptake was calculated by dividing the mass gain with the dry weight.

Tensile tests of bionanocomposites were performed on an Instron Testing Instrument 5566 with a load cell of 100 N and cross head speed of 10 mm/min. The relative humidity was kept at 50% and the temperature at 23 °C. The composites were conditioned in this environment for at least 48 h prior to testing. The gap distance was 15 mm and the sample thickness and width were calculated from an average of five values. Four specimens were used to characterize each sample.

Dynamic mechanical analysis (DMA) was performed on a TA Instruments Q800 in tensile mode. Rectangular pieces, about 4 mm wide and 130−205 μm thick, were cut from the samples. The sample thickness and width was calculated from an average of five values, and three to five specimens were used to characterize each sample. The gap distance was about 10 mm. The measurements were carried out at a constant frequency of 1 Hz, amplitude of 15 μm, and a heating rate of 2 °C min^{-1}. Temperature scans were performed at temperatures from −80 to 100 °C.

The cellulose content of the MFC-g-PCL samples was calculated from the amount of the initially used microfibrillated cellulose and the weight of the final MFC-g-PCL product obtained after thorough washing and drying.

RESULTS AND DISCUSSION

Analysis of MFC-g-PCL. PCL grafted MFC (MFC-g-PCL) was synthesized via ROP of ε-CL from the MFC surface to three different target graft lengths according to Scheme 1. Some of the authors have previously shown that the addition of free initiator is an efficient approach in order to vary the molecular weight of PCL grafted from the cellulose surface.[27] This is also in agreement with previously published results for ROP of ε-CL from functionalized gold film.[31]

Table 1 reports the result from the characterization of free PCL formed in bulk during the ROP, and of the PCL grafts that are covalently attached to the MFC surface. As expected, the molecular weight of the free PCL increases when the ratio of competing initiator to monomer is decreased. Although several attempts have been made to estimate the absolute molecular weights of grafted polymer, none has so far been successful. Nevertheless, in well dispersed suspensions of the MFC-g-PCL it was possible to detect the grafted PCL by solvent ^{1}H NMR, and the estimated molecular weights were 700, 1100, and 2200 g/mol for the short, medium and long PCL grafts respectively. The molecular weight for the PCL grafts obtained with this method will largely underestimate the actual molecular weights, since parts of the polymer grafts closest to the MFC surface will not be detectable; however, it verifies previous results showing that the length of the grafted polymer is varied by changing the ratio of free initiator to monomer.[27]

The thermograms from the DSC-analysis exhibits transitions both at −60 °C and between 33 and 56 °C, which can be ascribed to the glass transition temperature (T_g) and the melting temperature of the crystalline parts of PCL. As can be seen, the melting temperature (T_m) and the degree of crystallinity (X_c) increased with longer graft lengths on MFC. This is suggested to be due to the formation of more perfect crystalline structures with higher molecular weight of the grafts, because the short grafts have more restricted mobility.

FTIR spectroscopy results for the MFC-g-PCL shows an increase in the intensity of the PCL carbonyl group signal (1730 cm^{-1}) with increased grafting (Figure 1). The signal at 3200−3400 cm^{-1} can be ascribed to cellulose OH-groups, the decrease in this signal also indicates that more and more PCL is grafted to the surface. This is in agreement with the results from NMR analysis of the free PCL and the MFC-g-PCL (Table 1).

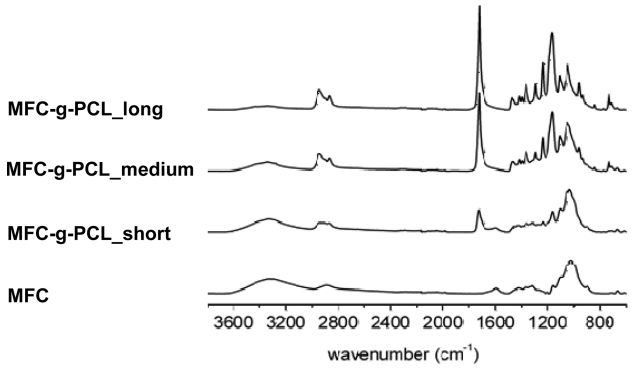

Figure 1. FTIR spectra of unmodified MFC and MFC-g-PCL with increasing graft lengths.

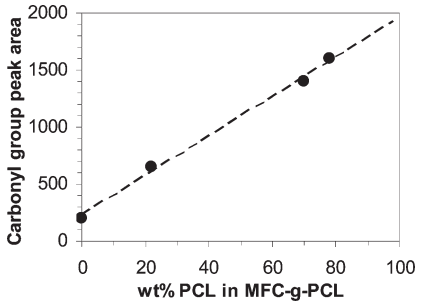

Figure 2. Area of the peak corresponding to the PCL carbonyl group signal plotted against the PCL content in the MFC-g-PCL samples as calculated from the initial mass of MFC added to the reaction and the mass of the resulting MFC-g-PCL.

The peak area of the FTIR spectroscopy PCL carbonyl group signal (1730 cm^{-1}) was plotted against the PCL content in the MFC-g-PCL samples as calculated from the initial mass of MFC added to the reaction and the mass of the resulting MFC-g-PCL (Figure 2, Table 1). There is a linear correlation between the carbonyl signal peak area and the gravimetrically determined PCL content in the MFC-g-PCL samples. Hence, the gravimetric method for determining the PCL weight content in the MFC-g-PCL samples is supported. Thus, as can be determined from the characterization of the grafted material, varying the ratio of monomer to free initiator efficiently increases the amount of PCL grafted to the MFC surface as well as the molecular weight of the PCL grafts.

Moisture sorption tests were performed to study the hygroscopic behavior of the MFC-g-PCL samples. The moisture sorption for all modified MFC-g-PCL samples is lower than expected based on the MFC content in the samples when compared to the pure MFC (Figure 3). The moisture uptake in cellulose composite material depends on the number of available cellulose hydroxyl groups. Hydrophobic modifications of MFC, such as PCL grafting, reduces the hydrophilic character by blocking surface hydroxyl groups and hence reduces the moisture uptake.[15] The molecular weight of the PCL grafts as determined by the NMR analysis of the free PCL, and the gravimetrically determined PCL content in the MFC-g-PCL samples were used to estimate the number of moles of PCL grafts in the samples. The result was plotted against the moles of adsorbed water (Figure 4). As the PCL grafting was increased in the MFC-g-PCL samples, the water sorption is decreased. From

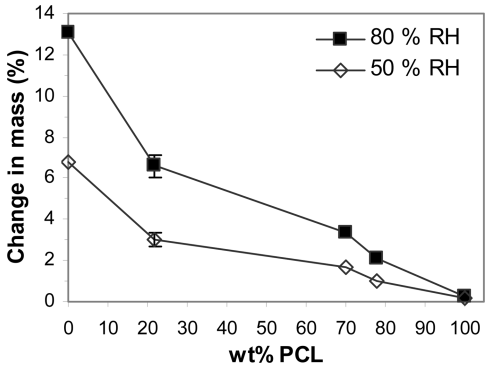

Figure 3. Mass increase as a function of PCL content in modified MFC-g-PCL samples of different graft lengths (relative PCL contents) at 50 and 80% relative humidity (left). The sample containing 22 wt % PCL was analyzed in triplicate; the bars indicate the maximum deviation from the mean value.

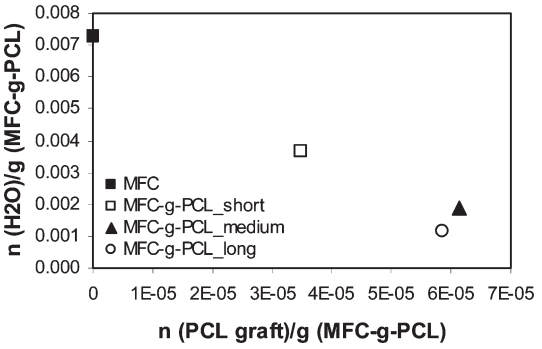

Figure 4. Number of moles of PCL graft versus moles of adsorbed H_2O at 80% RH for pure MFC and MFC-g-PCL with different graft lengths.

Figures 3 and 4 it can also be noted that the decrease in water sorption is slightly lower than expected for the medium compared to the long grafts sample. This could perhaps be due to differences in the amount of low molecular weight grafts in the two samples.

The hydrophilic character of unmodified MFC makes dispersion in a nonpolar organic solvent difficult and drying of MFC will cause an irreversible formation of strong aggregates.[2] It has previously been shown that grafting of PCL from MFC effectively enables the dispersion of MFC in organic solvents.[27] Similar results have also been reported in the literature for different covalent modifications of nanosized cellulose.[2,15,32] Homogenous dispersion of MFC in an organic solvent, or nonpolar matrix, is crucial in the preparation of biocomposites with high performance. The dispersibility of the samples in THF is shown in Figure 5. As can be seen, unmodified solvent exchanged (never dried) MFC could not be homogeneously dispersed in THF, whereas the dried MFC-g-PCL samples were easily dispersed. In addition, the impact of the graft length on the stability of the suspensions could be seen. The ungrafted MFC exhibited poor dispersibility and started to settle immediately at rest. The MFC-g-PCL with short PCL grafts displayed a better dispersibility than unmodified MFC, but did not provide a stable suspension over time. The two MFC-g-PCL samples with longer grafts exhibited a significantly improved dispersibility in THF and required a longer time to settle.

The sample with medium graft lengths, however, showed slightly better stability than the longest grafted sample, perhaps due to variation in the grafting.

Analysis of MFC-g-PCL Bionanocomposite Materials. Table 2 shows the results from the DSC analysis of the bionanocomposite materials. There are differences in crystallinity between the different bionanocomposite samples but the variation is quite small.

Mechanical Properties of MFC-g-PCL Bionanocomposites. Tensile tests were performed to evaluate the mechanical properties of the bionanocomposites, and the results are summarized in Table 3. Typical stress−strain curves for PCL based composites reinforced with 3 wt % MFC are shown in Figure 6. The pure PCL is a ductile polymer material that undergoes large deformation before break. The addition of MFC had a reinforcing effect in all composites, increasing the E-modulus of the composites to ∼230−330 MPa from an E-modulus of about 190 MPa for the pure PCL film. However, there is a different mechanical behavior for composites containing unmodified MFC in comparison to MFC-g-PCL. At 3 wt % MFC loading, the unmodified MFC composites showed increased E-modulus, whereas the maximum

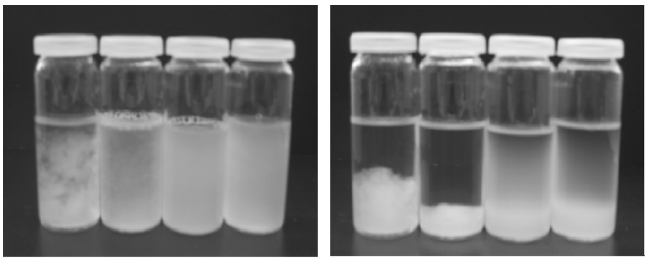

Figure 5. Dispersion of unmodified, never dried MFC and MFC-g-PCL_short, _medium, and _long (from left to right) in THF. All vials contain the same amount of MFC on dry basis. Photographs are taken just after agitation (left) and after 30 min of rest (right).

Table 2. Results from Characterization of Biocomposite Materials Containing Modified MFC-g-PCL with Different Graft Lengths

		DSC (MFC-g-PCL)		
composite sample	MFC content (wt%)	T_g (°C)	T_m (°C)	X_c (%)
PCL (reference)		−63.7	56.4	51.8
unmodified MFC/PCL	3	−59.8	58.3	52.5
MFC-g-PCL_short/PCL	3	−59.8	57.9	52.2
MFC-g-PCL_medium/PCL	3	−63.1	58.5	53.0
MFC-g-PCL_long/PCL	3	−63.7	56.5	55.0
unmodified MFC/PCL	10	−63.3	57.5	50.0
MFC-g-PCL_short/PCL	10	−61.3	57.3	53.2
MFC-g-PCL_medium/PCL	10	−61.5	57.3	51.8
MFC-g-PCL_long/PCL	10	−61.1	57.8	55.2

Table 3. Mechanical Data from the Tensile Tests of Biocomposite Materials Reinforced with MFC and Modified MFC-g-PCL with Different PCL Graft Lengths

		tensile test		
composite	MFC content (wt %)	σ_{max} (MPa)	$\varepsilon_{\sigma,max}$ (%)	E (MPa)
PCL (reference)		22 ± 4.3	880 ± 200	190 ± 18
unmodified MFC/PCL	3	17 ± 0.1	16.1 ± 2.5	256 ± 24
MFC-g-PCL_short/PCL	3	21 ± 1.2	690 ± 71	229 ± 16
MFC-g-PCL_medium/PCL	3	20 ± 2.5	435 ± 270	257 ± 14
MFC-g-PCL_long/PCL	3	22 ± 2.3	495 ± 150	230 ± 3.4
unmodified MFC/PCL	10	18 ± 1.1	13.2 ± 3.2	260 ± 42
MFC-g-PCL_short/PCL	10	20 ± 0.2	16.9 ± 2.3	287 ± 34
MFC-g-PCL1_medium/PCL	10	24 ± 0.8	21.2 ± 4.4	276 ± 24
MFC-g-PCL_long/PCL	10	27 ± 0.7	18.3 ± 1.2	326 ± 29

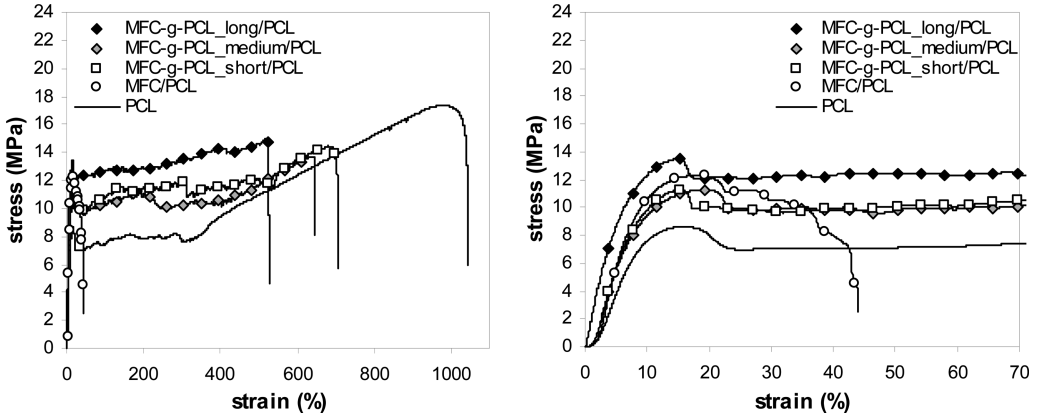

Figure 6. Typical stress−strain curves for PCL based composites reinforced with 3 wt % MFC. Full scale (left) and zoomed area (right).

strength and especially the elongation at break were drastically decreased. The modified MFC-g-PCL composites also resulted in higher modulus, but, contrary to the unmodified MFC composite, the ductility was much better preserved. This is suggested to be due to a better compatibility and an improved dispersion of the modified MFC-g-PCL in the PCL matrix resulting in fewer defects compared to the unmodified MFC/PCL composite. The results are in accordance with other studies that have used surface modification of nanocellulose to improve the performance of PCL composites.[2,24] There was also a difference in the yield strength for MFC-g-PCL/PCL composites with 3 wt % MFC, and after the yield point the plastic deformation progresses at different stress levels. These levels increase with the graft length, where the MFC-g-PCL_long/PCL composite exhibits the highest value and the unmodified MFC/PCL composite the lowest. Finally, strain hardening and fracture of the composites occurs.

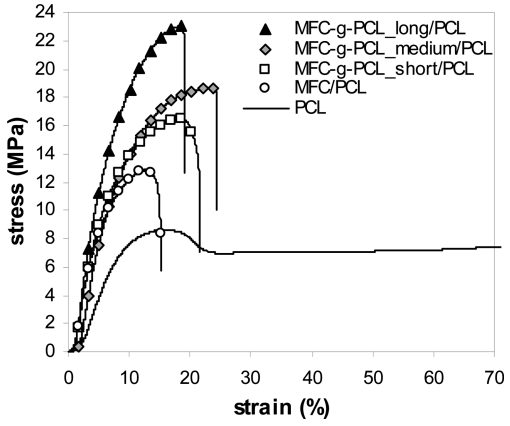

Figure 7. Typical stress−strain curves for PCL based composites reinforced with 10 wt % MFC.

The composites reinforced with 10 wt % MFC display a different mechanical behavior, Figure 7. At 10 wt % MFC loading all composites were brittle material with drastically decreased strain at break. Thus, the ductile properties of the PCL composites were lost for all composites reinforced with 10 wt % MFC. At 10 wt % MFC reinforcement, increased graft length of the MFC-g-PCL improved the tensile strength whereas the stiffness was not significantly improved. Overall the MFC-g-PCL_long/PCL composite exhibited the best mechanical properties. The improved tensile strength may be due to an improved interfacial adhesion with longer graft lengths, which results in a better stress transfer from the matrix to the MFC reinforcement when a load is applied to the material. Improved dispersion of the modified

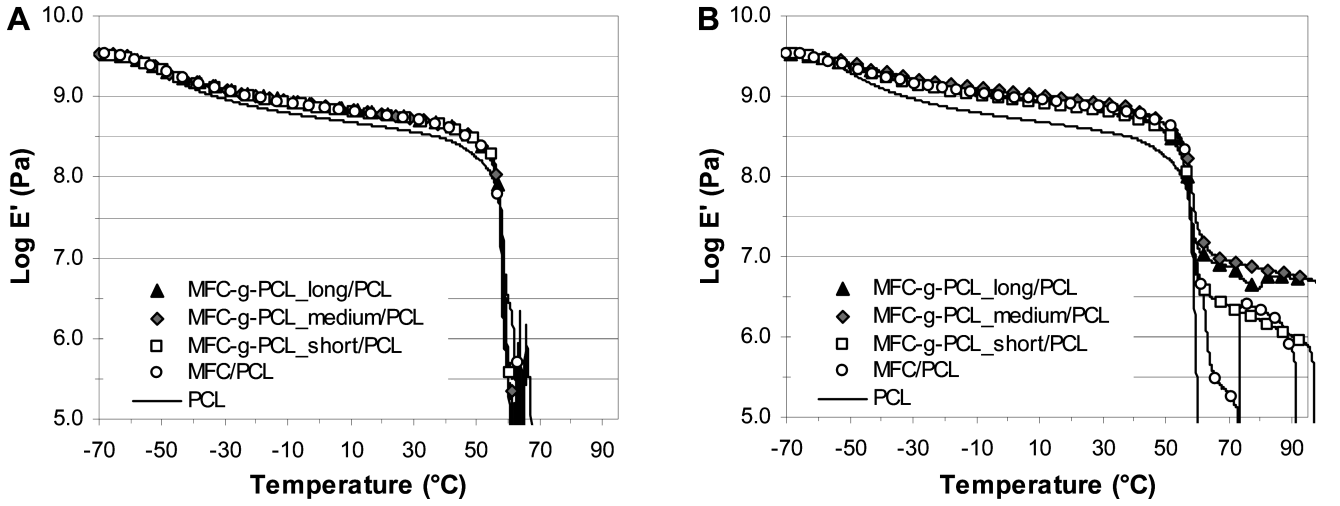

Figure 8. Logarithm of the normalized storage modulus E' versus temperature for PCL bionanocomposites prepared from neat PCL, PCL/MFC, and MFC-g-PCL_short/PCL, MFC-g-PCL_medium/PCL, and MFC-g-PCL_long/PCL reinforced with 3 wt % (A) and 10 wt % (B) MFC.

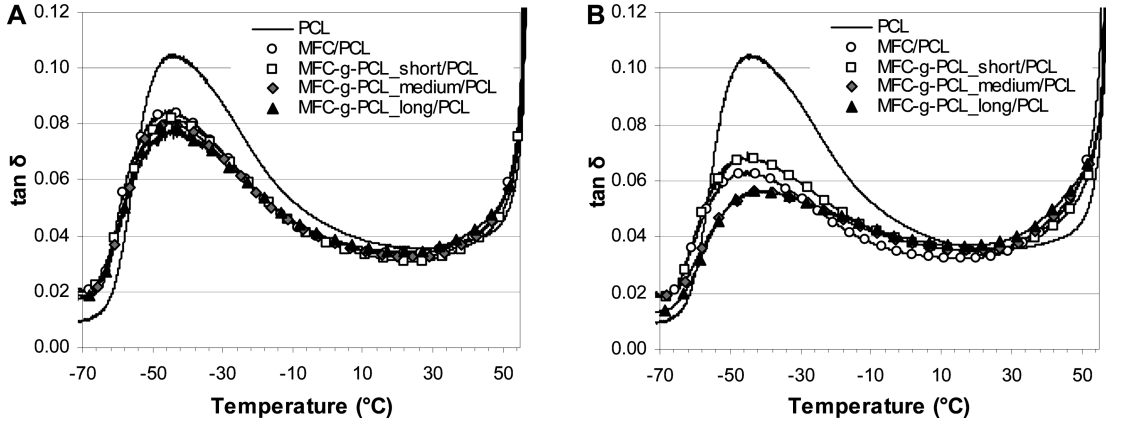

Figure 9. Tan δ versus temperature curves for the bionanocomposites reinforced with 3 wt % (A) and 10 wt % (B) MFC.

MFC within the PCL matrix and decreased moisture uptake also will increase the mechanical performance of the composites. However, the current data cannot distinguish between these three factors.

The MFC-g-PCL films with different MFC contents, 3 wt % and 10 wt %, were analyzed with DMA. Figure 8 shows the normalized storage modulus (E′) as a function of temperature. At low temperatures the polymer is in its glassy state and the modulus is fairly constant for all samples. A change occurs when the temperature approaches −60 °C which corresponds to the glass transition temperature (T_g) for PCL. The modulus rapidly decreases as the amorphous regions of PCL changes from a glassy to a rubbery state. The decrease is relatively small due to the semicrystalline nature of PCL. An increase of the MFC content in the composites from 3 wt % to 10 wt % increases the storage modulus in the rubbery region between T_g and the melting temperature, T_m, in agreement with the results from the tensile test.

At temperatures above 50 °C the crystalline regions of PCL begins to melt, causing a drastic drop in the storage modulus. However, for the samples reinforced with 10 wt % modified MFC some of the modulus is preserved even at high temperatures above the PCL melting temperature, 60 °C. The modulus after the melting point of the matrix is larger for the samples reinforced with modified MFC with the two longer graft lengths. The MFC with the two longest graft lengths had a good dispersion in THF (Figure 5). A good dispersion in THF would lead to a better dispersion of the grafted MFC within the PCL matrix which leads to the formation of a continuous MFC network. The preservation of modulus above T_m indicates that there is a network of MFC carrying some strength. The storage modulus for the bionanocomposite containing unmodified MFC showed large deviations in modulus probably due to heterogeneity in the sample. The 3 wt % samples became too soft above T_m to be analyzed.

Figure 9 shows the development of tan δ versus temperature for the different samples. As the MFC content is increased from 3 to 10 wt %, the amorphous polymer becomes more and more restricted leading to a decrease in the magnitude of the tan δ peak. In general there is no significant shift in T_g as determined from the tan δ peak but there seem to be a small shift toward higher temperature for the bionanocomposites reinforced with 10 wt % MFC with the two longer graft lengths. A shift in the tan δ peak toward higher temperatures could indicate that the adhesion between the matrix and the MFC is improved with increasing graft length.

CONCLUSIONS

Microfibrillated cellulose was successfully grafted with different lengths of PCL using ring-opening polymerization, resulting in MFC-g-PCL with a cellulose content of 78, 30, and 22 wt %. Biocomposite materials based on a PCL matrix reinforced with MFC were prepared by blending and then hot pressing of both unmodified MFC as well as MFC-g-PCL with increasing target graft length.

To make a bionanocomposite material with a good reinforcing ability the characteristic dimensions of MFC must be preserved throughout the grafting procedure. Great improvement of the dispersibility of the MFC in organic solvent was seen after PCL grafting, and it was shown that longer graft lengths significantly improved the stability of the suspensions.

Mechanical tests showed that an incorporation of MFC reinforced the PCL polymer, and the effect of polymer grafting was distinct. At low MFC load (3 wt %) the PCL grafts much better preserved the ductility of PCL in comparison to ungrafted MFC. At high MFC load (10 wt %), increasing graft lengths gradually improved the strength of the biocomposites, and the strongest biocomposites were obtained with high MFC load (10 wt %) and with the longest graft length.

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