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Paper-sheet biocomposites based on wood pulp grafted with poly(ε-caprolactone)

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ABSTRACT: Kraft pulp fibers were used as substrates for the grafting of poly(ε-caprolactone) (PCL) from available hydroxyl groups through ring-opening polymerization, targeting three different chain lengths (degree of polymerization): 120, 240, and 480. In a paper-making process, paper-sheet biocomposites composed of grafted fibers and neat pulp fibers were prepared. The paper sheets possessed both the appearance and the tactility of ordinary paper sheets. Additionally, the sheets were homogenous, suggesting that PCL-grafted fibers and neat fibers were compatible, as demonstrated by both Fourier transform infrared spectroscopy microscopy and through dye-labeling of the PCL-grafted fibers. Finally, it was shown that the paper-sheet biocomposites could be hot-pressed into laminate structures without the addition of any matrix polymer; the adhesive joint produced could even be stronger than the papers themselves. This apparent and sufficient adhesion between the layers was thought to be due to chain entanglements and/or co-crystallization of adjacent grafted PCL chains within the different paper sheets. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42039.

KEYWORDS: biomaterials; cellulose and other wood products; composites; grafting; ring-opening polymerization

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INTRODUCTION

With the growing environmental concerns during recent years, bio-based materials have gained significant attention, and the demand for environment-friendly products is increasing. The market is constantly looking for new "green" materials that can be used in packaging and composite applications, for example, to replace conventional materials not originating from renewable sources.

In line with this development, cellulose-based elements, such as cellulose fibers, fibrils, or crystals[1–7] have attracted interest as alternatives to fossil fuel-based fibers. Cellulose, which is the most abundant biopolymer in the world,[8] is a biodegradable and inexpensive polysaccharide. Traditionally, pulp fibers, derived from cellulose, have been used in large-scale products such as paper and cardboard. More recently, fibrils, of smaller size, have been used in more sophisticated applications, taking maximum advantage of cellulose's attractive properties such as high modulus combined with a low specific weight.[9,10] This has been demonstrated in the work of Sehaqui *et al.* where they prepared paper biocomposites with high cellulose content based on wood fibers and cellulose nanofibrils (CNF),[11] and by Nyström *et al.* who prepared conducting papers based on CNF and polypyrrole.[12] Paper-based materials possessing properties not found in ordinary paper sheets, but with the appearance of ordinary paper sheets and paper-feel are of interest within packaging applications, for example, where the perceived feeling of the packaging is an important factor.

To take advantage of the inherent properties of cellulose in a composite material, the cellulose constituent often has to be surface-modified to obtain sufficient interfacial adhesion between polar fibers and non-polar matrices. One way to modify cellulose, or other polysaccharides, is to graft a polymer from or onto its surface.[13–17] Modification of cellulose *via* grafting has been widely studied with various monomers using conventional radical polymerization,[18–20] and also controlled polymerization techniques, such as atom transfer radical polymerization (ATRP),[21–23] ring-opening polymerization (ROP),[24–27] and reversible addition-fragmentation chain transfer polymerization (RAFT).[28,29] Further, for biocomposite applications, it is desirable to graft biodegradable monomers, such as lactones[30] and lactides.[31]

In this study, bleached never-dried cellulose fibers retrieved from the kraft process,[32] with a cellulose content of approximately 75%,[33] were modified by surface-initiated ring-opening

Additional Supporting Information may be found in the online version of this article.

polymerization (SI-ROP) of a cyclic, biodegradable lactone, ε-caprolactone (ε-CL), to introduce a thermoplastic component. The grafting was performed according to an approach that has been reported for high-cellulose content substrates previously.[34–36] The kraft pulp was solvent-exchanged from water, to acetone, to toluene to perform the polymerization that cannot be performed in the presence of water. Additionally, neither the monomer nor the formed polymer is soluble in water. An alternative route for removal of water from the fibers, and transfer into toluene, could have been oven-drying with subsequent immersion in toluene. However, complete drying of the fibers may cause hornification, that is, decreased flexibility and increased brittleness of the fibers.[37] The effect of the surface modification was evaluated by mixing polymer-grafted pulp with neat kraft pulp and subsequent forming into paper-sheet biocomposites, using a Rapid-Köthen sheet former. Different ratios of modified-to-unmodified pulp were evaluated, targeting biocomposites with as high content of fibers as possible. A similar approach was used by Rezai and Warner who grafted kraft pulp fibers using free-radical polymerization of different acrylates followed by sheet formation into composites.[20] In addition, our aim was to introduce thermoplastic properties to the paper to allow for subsequent thermal processing, while at the same time preserving both appearance and paper-feel of a neat paper sheet. To our best knowledge, this combination has not been achieved before, and was obtained through a combination of straight-forward polymer chemistry and a conventional paper-making process.

EXPERIMENTAL

Materials and Methods

ε-Caprolactone (ε-CL, 98%, Aldrich), benzyl alcohol (Merck, 98%), tin octoate ($Sn(Oct)_2$, 95%, Aldrich), 4-(dimethyloamino)pyridine (DMAP, 99+%, Aldrich), pyridine (analytical grade, Prolabo), 2-[4-(2-Chloro-4-nitrophenylazo)-*N*-ethylphenylamino]ethanol (disperse red 13 (DR13), 95%, Aldrich), succinic anhydride (SA, 99+%, Aldrich), *N*,*N*′-dicyclohexylcarbodiimide (DCC, 99%, Acros organics), toluene (HPLC grade, Fischer Scientific), acetone (technical, Prolabo), methanol (MeOH, Merck), dichloromethane (DCM, Merck), tetrahydrofurane (THF, Merck), and chloroform (HPLC grade, Fischer Scientific) were all used as received. DR13 anhydride[38] was kindly supplied by Surinthra Mongkhontreerat and used as received.

The cellulose fibers used were industrial, never-dried kraft pulp (30 wt % dry content, denoted F) kindly supplied by Södra Cell AB and Korsnäs AB, Sweden. The average size of the fibers was approximately 35 μm in diameter and 1 mm in length.

Characterization

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AM 400 using deuterated chloroform ($CDCl_3$) as solvent. The solvent signal was used as the internal standard.

Size exclusion chromatography (SEC) was performed using a Verotech PL-GPC 50 Plus system equipped with a PL-RI detector and two Mixed-D columns (Varian). Chloroform (1.0 mL/min, 30°C) was used as the mobile phase with toluene used as flow-rate marker. The SEC apparatus was calibrated with linear polystyrene standards with low $Đ_M$ and molecular weights ranging from 580 to 400,000 g/mol.

The thermal degradation of the polymer and modified pulp fibers was analyzed with thermogravimetic analysis (TGA, Mettler Toledo). Samples were heated from 40 to 650°C at 10°C/min in N_2 atmosphere.

Differential scanning calorimetry (DSC) was performed on the paper-sheet biocomposites using a Mettler Toledo DSC 820 equipment. The heating and cooling rates were 10°C/min in the temperature range of −65 to 100°C performed in two cycles under N_2 atmosphere, where data were extracted from the second heating.

Fourier transform infrared spectroscopy (FTIR) was performed on a Perkin-Elmer Spectrum 2000 FTIR equipped with a MKII Golden Gate™, single reflection ATR System from Specac, London, UK. The ATR-crystal was a MKII heated Diamond 45°C ATR Top Plate.

FTIR images were recorded in attenuated total reflectance mode on a Spectrum Spotlight 400 FTIR microscope connected to a Spectrum 100 FTIR spectrometer (Perkin-Elmer). The area of interest was scanned in ATR image mode by a 16-point dual-array liquid-N_2-cooled MCT detector. Samples were area-mapped in the *x*, and *y* direction resulting in the assembly of a chemical image of 400 × 300 μm^2 with a pixel resolution of 1.56 × 1.56 μm^2 and 8 cm^{-1} spectral resolution between 4000 and 750 cm^{-1}.

The hydrophobic and oleophilic character were investigated through static contact-angle measurements on a KSV instrument CAM 200 equipped with a Basler A602f camera using 5 μL droplets of either MilliQ water (hydrophobicity) or rapeseed oil (oleophilicity). Measurements were performed in triplicate at ambient temperature and contact angles determined with CAM software.

Optical microscopy was performed on a Leica DM IRM optical microscope.

Scanning electron microscopy (SEM) was conducted to study the morphology of the modified fibers using a Hitachi S-4800 with an acceleration voltage of 1.5 kV. The samples were attached on metal studs with carbon tape, and sputtered with 8 nm Au/Pd in a Cressington 208HR sputter-coater unit. To study peeling of laminated paper-sheet biocomposites, a tabletop Hitachi TM-1000 SEM with an acceleration voltage of 15 kV was used.

Paper-sheet biocomposites containing 10, 50, or 90% modified fibers were cut in size 40 × 10 mm^2 and hot pressed (Fontijne Presses) together between Teflon sheets at five different temperatures ranging from 50 to 120°C. During the pressing, performed for 3 min, the force was increased from 50 to 200 kN. Subsequently, the formed laminates were allowed to cool down to ambient temperature under 200 kN pressure. The papers pressed together at 120°C were the ones used for peel tests.

T-type peel tests of hot-pressed papers were performed according to a modified version of ASTM 1876 standard. The peel

Table I. The Length of the Polymer Grafts, DP, Was Varied Using Different Amounts of ε-CL and $Sn(Oct)_2$ (2 wt % with Respect to ε-CL) in the Polymerizations

Sample	DP_{theor}[a]	ε-CL
FgS	120	0.10 kg, 0.90 mol
FgM	240	0.21 kg, 1.8 mol
FgL	480	0.41 kg, 3.6 mol

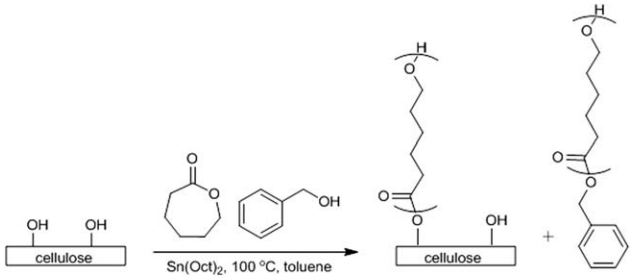
The loading of fibers (0.020 kg) and amount of benzyl alcohol (0.63 g, 6.0 mmol) were kept constant.
[a] Based on 80% monomer conversion.

tests were performed in triplicate with an Instron 4411 with a speed of 10 mm/min with a load cell of 50 N. Prior to testing, the specimens were conditioned at 25°C, 50% relative humidity for 96 h.

Tensile tests of the paper-sheet biocomposites, according to ISO 1924-3 standard, were conducted by Stora Enso AB, Sweden.

Grafting of Poly(ε-caprolactone) from Kraft Pulp Fibers *via* Ring-Opening Polymerization

Never-dried kraft pulp fibers were modified through grafting of ε-CL. The targeted degree of polymerization was adjusted by the addition of a fixed amount of a sacrificial initiator, benzyl alcohol, to a fixed amount of kraft pulp, while varying the amount of ε-CL (Table I). Three different lengths of poly(ε-caprolactone) (PCL) were targeted: DP120, DP240 and DP480, denoted *Fiber-g-Short* (FgS), *Fiber-g-Medium* (FgM), and *Fiber-g-Long* (FgL), respectively. A typical procedure for grafting follows and is illustrated in Scheme 1. Kraft pulp fibers were solvent-exchanged from water to toluene *via* acetone according to a procedure adopted from Lönnberg *et al.*[7] Kraft pulp fibers (0.020 kg) were immersed in acetone (0.20 L), and then dispersed through ultrasonication (10 min) followed by magnetic stirring (30 min) and the acetone was removed through filtration. This procedure was repeated four times. Thereafter, the fibers were solvent-exchanged from acetone to toluene following the same procedure five times. The solvent-exchanged kraft-pulp fibers (0.020 kg dry weight), ε-CL (Table I), and toluene (0.12 L) were charged into a round-bottomed flask. The flask was connected to distillation equipment, immersed in an oil bath pre-heated to 130°C, and approximately half of the volume of toluene was allowed to distill off. The flask was then equipped with a rubber septum and 3 cycles of evacuation and back-filling of argon were performed. The flask was allowed to cool to room temperature before introducing benzyl alcohol (0.63 g, 6.0 mmol) under argon flow, and the flask was immersed in an oil bath pre-heated to 100°C. The catalyst, $Sn(Oct)_2$ (2 wt % of the monomer), was added under argon flow, and the reaction was allowed to proceed for 4–5 h, stirring under argon atmosphere until a monomer conversion of 80% was reached, as monitored by NMR spectroscopy. The reaction was quenched by retracting the flask from the oil bath and adding THF. The fibers were then extensively washed with THF in a glass filter funnel to remove non-grafted, free, PCL. To ensure that no trace amounts of free PCL remained, the fibers were subsequently subjected to Soxhlet extraction with THF overnight. Soxhlet extraction is known to be an efficient washing procedure to remove unbound and physically adsorbed polymer from cellulose substrates leaving only covalently grafted polymer.[39] After extraction, the fibers were dried at reduced pressure at 50°C for 2 h. The grafted fibers; FgS, FgM, and FgL, were analyzed with TGA, DSC, and FTIR. The filtrate from the washing was concentrated and precipitated into cold MeOH (−78°C). The free PCLs, denoted *PCL(s)*, *PCL(m)*, and *PCL(l)*, were dried at reduced pressure at 50°C overnight, and analyzed with ^{1}H-NMR, SEC, and TGA.



Scheme 1. Grafting of ε-caprolactone from kraft pulp using benzyl alcohol as a sacrificial initiator.

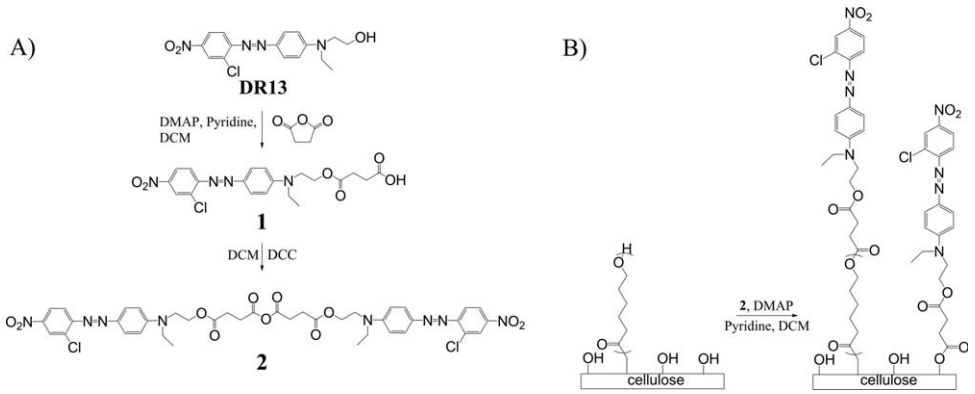
A solution of $Sn(Oct)_2$ (10 wt % of the pulp fibers) and toluene (2 mL) was added to unmodified kraft pulp fibers (0.65 g), vigorously shaken, and dried under reduced pressure at 50°C for 72 h. A separate pulp-fiber sample was prepared in the same way, but without addition of $Sn(Oct)_2$. Both pulp samples were analyzed with TGA as references for the effect of $Sn(Oct)_2$ on thermal degradation of kraft-pulp fibers.

Attachment of Disperse Red (DR13) onto PCL-Grafted Cellulose Fibers

The preparation of anhydride from the dye, DR13, and its subsequent attachment to cellulose were adopted from a similar procedure described by Montañez *et al.*[38] illustrated in Scheme 2.

Synthesis of Acid. To a round-bottomed flask, DR13 (1.0 g, 2.9 mmol), DMAP (70 mg, 0.58 mmol), and pyridine (0.70 mL, 8.6 mmol) were added in a small amount of DCM and the flask was cooled to 0°C. SA (0.43 g, 4.3 mmol) was dissolved separately in DCM, added drop-wise to the flask, and the reaction was left to stir overnight at room temperature. The reaction was quenched with H_2O, THF, and small amounts of DMAP and extracted with 10% aq. $NaHSO_4$ (5 × 10 mL). The organic phase was dried with $MgSO_4$, filtered off, concentrated under reduced pressure, and dried under reduced pressure overnight. The product was denoted *DR13 acid* (***1***). Yield: 1.07 g, 83%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.35 (1H, Ar), 8.10 (1H, Ar), 7.92 (2H, Ar), 7.75 (1H, Ar), 6.78 (2H, Ar), 4.29 (2H, —NCH_2CH_2—), 3.67 (2H, —NCH_2CH_2—), 3.52 (2H, —CH_2CH_3), 2.64 (4H, —$OC(O)CH_2CH_2(O)COH$—), 1.26 (3H, —CH_2CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 177.9, 172.3, 153.2, 151.8, 147.4, 144.6, 134.2, 126.2, 122.8, 118.2, 111.7, 68.1, 61.8, 48.9, 46.0, 28.9, 25.8, 12.5.

Synthesis of Anhydride. In a round-bottomed flask, DR13 acid (1.07 g, 2.4 mmol) was dissolved in a small amount of DCM



Scheme 2. (A) Preparation of anhydride (**2**) from disperse red 13 (**DR13**), and (B) immobilization of the anhydride of DR13 (**2**) onto modified fibers to give dye-labeled kraft pulp (F*g*S*g*DR13).

and the flask was cooled to 0°C. DCC (246 mg, 1.2 mmol) was dissolved in DCM and added drop-wise to the flask. The reaction was left to proceed at room temperature overnight and then filtered. The product was denoted *DR13 anhydride* (***2***). Yield: (880 mg, 98%). FTIR spectrum (Supporting Information Figure S1): 1820 and 1785 cm^{-1} corresponds to symmetric and asymmetric stretching of the carbonyls in the anhydride, respectively.[40] ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.35 (2H, Ar), 8.10 (2H, Ar), 7.92 (4H, Ar), 7.75 (2H, Ar), 6.78 (4H, Ar), 4.29 (4H, —NCH_2CH_2—), 3.67 (4H, —NCH_2CH_2—), 3.52 (4H, —CH_2CH_3), 2.79 (4H, —$CH_2C(O)OC(O)$ —), 2.64 (4H, —$CO(O)CH_2$—), 1.26 (6H, —CH_2CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 172.3, 167.9, 153.2, 151.8, 147.4, 144.6, 134.2, 126.2, 122.8, 118.2, 111.7, 61.8, 55.6, 48.9, 46.0, 35.9, 28.9, 25.8, 12.5.

Labeling of Fibers with DR13. Polymer-grafted fibers (F*g*S, 3.4 g) were dried under reduced pressure at 50°C for 5 h prior to the reaction. The fibers were dispersed in DCM (75 mL), followed by addition and subsequent dissolution of DMAP (0.90 mg, 76 µmol) and pyridine (92 µL, 0.11 mmol). DR13 anhydride (50 mg, 57 µmol) was dissolved in DCM (10 mL) and subsequently added to the fiber dispersion and left stirring overnight at room temperature. The fibers were then purified through Soxhlet extraction with DCM overnight followed by drying at reduced pressure at 50°C and denoted *fiber-g-short-g-DR13* (F*g*S*g*DR13).

Paper-Sheet Biocomposite Preparation

Modified (dry, denoted F*g*S/*M*/*L*) and unmodified kraft pulp fibers (denoted *F*, 30 wt % dry content) were mixed in different weight ratios (10 : 90, 50 : 50, 90 : 10 based on dry weight) with 400 mL of water and stirred overnight. The suspensions were beaten in a PFI beater at 6000 rpm prior to forming of a paper-sheet biocomposite. Sheets with a grammage of about 120 g/m^2 were prepared using a Rapid-Köthen sheet former (PTI, Vorchdorf, Austria). The paper-sheet biocomposites were then dried under restrained conditions at 93°C at a pressure of 95 kPa below the atmospheric pressure for 10 min and denoted F*g*(S/M/L)/F (10 : 90, 50 : 50, or 90 : 10), respectively. The formed paper-sheet biocomposites were evaluated with DSC, contact angle measurements, FTIR microscopy, peel test, and tensile test. In addition, according to the same procedure paper sheets containing kraft pulp fibers dyed with DR13 were prepared in two ratios of modified (dry) and unmodified (30 wt % dry content) fibers and denoted F*g*S*g*DR13/F (10 : 90 and 90 : 10). Table II summarizes the ratios of modified-to-unmodified fibers in the manufactured paper-sheet composites and their respective denotation.

Furthermore, in an attempt to prepare the paper-sheet biocomposite simply by blending unmodified kraft pulp fibers and free PCL, PCL powder was dispersed in water. However, as expected this approach proved to be impossible due to the poor miscibility between PCL powder and water (Supporting Information Figure S2).

RESULTS AND DISCUSSION

Covalent grafting was used in the "grafting-from" approach to grow a polymer, PCL, from, never-dried kraft pulp (cellulose fibers) in three different lengths (DP target): 120, 240, and 480 denoted F*g*S, F*g*M, and F*g*L, respectively. The kraft pulp was

Table II. Paper-Sheet Biocomposites Produced

Sample name	Sample composition (wt %)			
	PCL-grafted kraft-pulp fibers			Unmodified kraft-pulp fibers
	F*g*S	F*g*M	F*g*L	F
F*g*S/F (10 : 90)	10			90
F*g*S/F (50 : 50)	50			50
F*g*S/F (90 : 10)	90			10
F*g*M/F (10 : 90)		10		90
F*g*M/F (50 : 50)		50		50
F*g*M/F (90 : 10)		90		10
F*g*L/F (10 : 90)			10	90
F*g*L/F (50 : 50)			50	50
F*g*L/F (90 : 10)			90	10
F*g*S*g*DR13/F (10 : 90)	10[a]			90
F*g*S*g*DR13/F (90 : 10)	90[a]			10

[a] DR13 dyed PCL-grafted fibers.

Table III. Molecular Weight and Molar-Mass Dispersity ($Đ_M$) of Free PCL Formed During ROP from Kraft Pulp

Sample	Theoretical M_w (g/mol)[a]	M_w by NMR$^{end\text{-}group}$ (g/mol)[b]	M_w by NMR$^{initiating\text{-}group}$ (g/mol)[c]	M_n from SEC (g/mol)	$Đ_M$
PCL (short)	13,800	4600	6400	11,000	1.40
PCL (medium)	27,500	8400	18,800	20,000	1.56
PCL (long)	54,900	6800	24,200	21,800	1.75

[a] Based on 80% conversion of targeted DPs.
[b] Molecular weights from NMR calculated by end-group analysis (hydroxyl).
[c] Molecular weights from NMR calculated by initiating-group analysis (benzylic protons).

solvent-exchanged from water, to acetone, to toluene, to avoid hornification. The grafted fibers were then combined with unmodified kraft pulp to prepare paper-sheet biocomposites, a type of composite that has a high cellulose fiber-to-matrix ratio, appearance of regular paper sheets and paper-feel. Finally, the paper-sheet biocomposites were hot-pressed into laminates.

Grafting of PCL from Kraft Pulp *via* SI-ROP

The targeted DP's of the polymerizations were controlled by the addition of a sacrificial initiator, benzyl alcohol. Determination of molecular weight of the PCL grafts is known to be challenging. Acid hydrolysis after grafting to degrade the cellulose fibers, for the purpose of liberating the PCL chains to enable molecular-weight analysis, would degrade the PCL chains as well. Furthermore, accessibility of enzymes for specific degradation of cellulose fibers has shown to be severely restricted by grafting of PCL.[36] If a cleavable initiator would be used, it would, as well as benzyl alcohol, most likely have a different reactivity than native hydroxyl groups present on the fiber surface.[13,41] Hence, the assumption that addition of a sacrificial initiator to surface-initiated graft polymerizations is suitable to control molecular weight of the grafted chains, has been used in studies prior to the present investigation.[21,42] The polymerizations could have been conducted in the absence of sacrificial initiator, but without it there would be no control of the molecular weight of the grafted PCL.[43] In Table III, molecular weight and $Đ_M$ of the free PCL formed from the sacrificial initiator, as obtained from NMR spectroscopy and SEC, are presented. Molecular weights from NMR are estimated by the integrated ratio of the methylene units in the polymer backbone to either the methylene group adjacent to the terminal hydroxyl chain-end (end-group analysis) or to the benzylic protons (initiating-group analysis) emanating from benzyl alcohol. In theory, these two values should be the same, but in fact they are not. This discrepancy is hypothesized to be mainly an effect of initiation of ROP of ε-CL from remaining water, in parallel with initiation from hydroxyl groups in benzyl alcohol and cellulose. The yield of the grafting reaction was difficult to estimate as a slight decrease in mass of the fibers, after grafting, was observed due to loss of fibers. This indicates that the amount of PCL grafted was low.

As observed by FTIR spectra [Figure 1(A)], the intensity in the carbonyl region (1760–1700 cm^{-1}) is increasing with increasing targeted DP of the polymer grafts, suggesting that the grafting was successful in accordance with previous findings.[44] Therefore, when aiming for a higher DP of PCL, a larger amount of polymer was grafted from the surface.

The thermal degradation of unmodified kraft pulp, free PCL (PCL(s)), FgS, FgM, and FgL was studied with TGA [Figure 1(B)]. From the thermograms it can be corroborated that the grafting was successful despite the fact that kraft pulp and non-

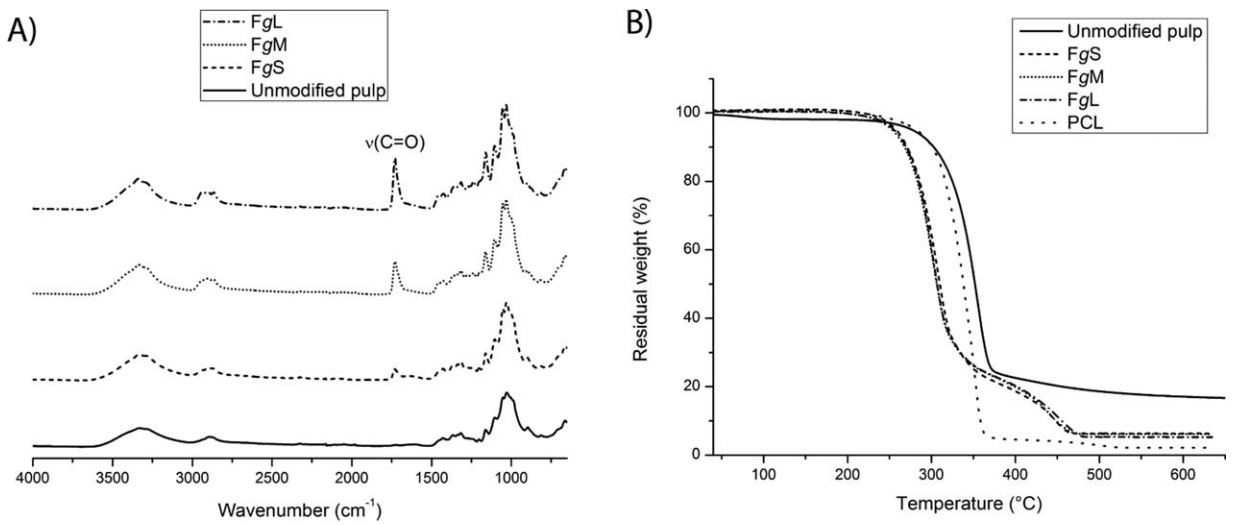


Figure 1. (A) FTIR spectra of unmodified pulp, and PCL-grafted pulp fibers (FgS, FgM, and FgL) and (B) TGA thermograms of unmodified pulp, free PCL, and FgS, FgM, and FgL.

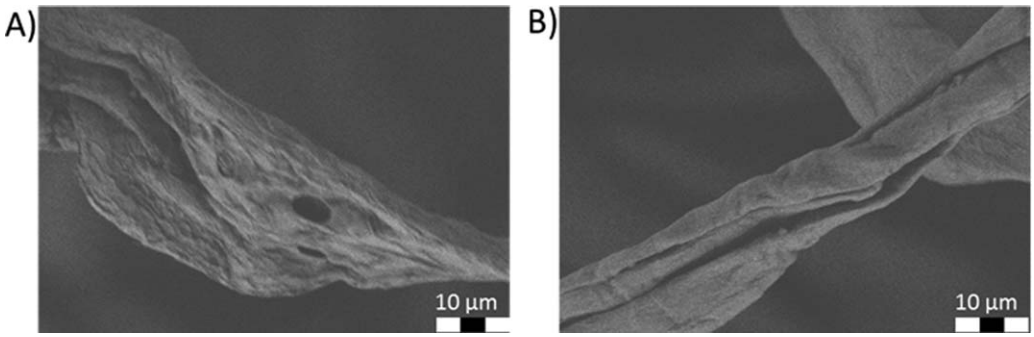


Figure 2. SEM micrographs of (A) unmodified kraft pulp fiber and (B) F*g*S.

dried monomer were used. Both unmodified pulp and neat PCL have slightly different degradation temperatures compared with the grafted fibers. There could potentially be two reasons; first, due to the grafting of PCL the number of intermolecular secondary interactions within the fibers, which help to thermally stabilize unmodified pulp, decrease. Therefore, the degradation of the grafted fibers starts at a lower temperature. Second, $Sn(Oct)_2$ may coordinate to the fiber surface, and upon extensive heating catalyze degradation of the fibers (Supporting Information Figure S2). Most likely, it is a combination of both. The grafted amounts from TGA are difficult to estimate; however, the grafted amounts are lower than previously reported for CNF prepared in a similar manner (around 20 wt %),[41] which is probably an effect of the larger surface area of CNF as compared with that of kraft-pulp fibers.

The microstructure of the unmodified and modified kraft pulp fibers was investigated by SEM. After grafting, the surface of the fibers has a smoother appearance, as shown in Figure 2, which suggests that the surface has been covered with polymer, as the rough fiber structure is no longer visible, indicating successful grafting.[36]

Preparation of Paper-Sheet Biocomposites

Paper-sheet biocomposites were prepared by mixing three different weight ratios, based on dry weight, of modified-to-unmodified fibers: 10 : 90, 50 : 50, and 90 : 10, Table II. Reference sheets were also prepared from unmodified kraft-pulp fibers. Both in terms of appearance and tactility all paper-sheet biocomposites were similar to the reference paper sheet.

Contact-angle measurements were performed to investigate both hydrophobic character and oleophilic character, which could corroborate whether the goal to obtain both appearance and paper-feel of ordinary paper-sheets had been achieved. This was performed through measurements with MilliQ water and rapeseed oil, respectively. None of the paper-sheet biocomposites displayed an increase in either hydrophobic nor oleophilic character compared with the reference paper sheets. Thus, despite that the paper-sheet biocomposites contain PCL, they can indeed be perceived as ordinary papers.

Two methods were used to investigate the compatibility between grafted and neat pulp fibers within the paper-sheet biocomposite. First, FTIR microscopy of the paper-sheet biocomposites (Figure 3) and, second, labeling of the modified fibers with a dye, DR13, prior to making the paper sheets (Figure 4). FTIR microscopy was conducted on paper-sheet biocomposites composed of 90 wt % polymer grafted pulp fibers. Compatibility at high loadings of modified fibers with varied amounts of the grafted polymer, in combination with the distribution of polymer along the individual fibers, was investigated. In Figure 3, the FTIR images from representative areas for all samples and one reference sheet made from unmodified kraft pulp are shown. Note that a different scale bar is used to visualize the fiber structure for the reference material (unmodified pulp), and that the papers are non-dense materials, which results in air being present between the fibers. Hence, low-absorbance regions are observed (purple regions for modified fiber-containing papers). There is a higher absorbance in the carbonyl region (1760–1700 cm^{-1}) in F*g*L/F (90 : 10) than in F*g*S/F (90 : 10) and F*g*M/L (90 : 10), which suggests that there is more polymer present, and possibly longer chains, grafted on the fibers in that material. However, irrespective of the length of the grafted PCL on the modified fibers, the modified fibers are

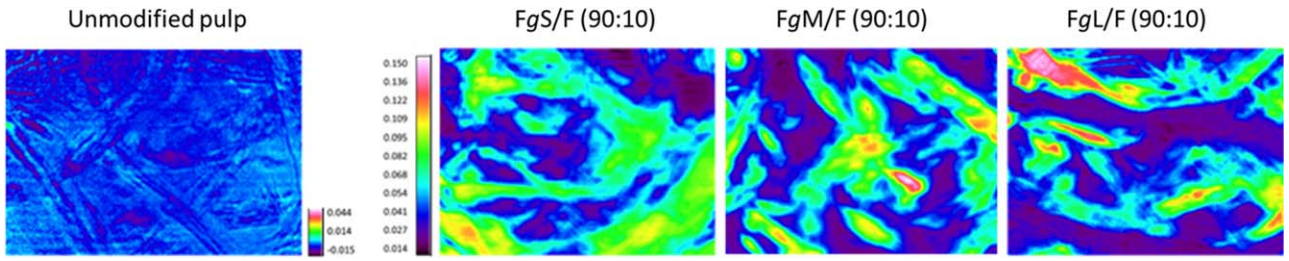


Figure 3. FTIR microscopy images (400 × 300 μm^2) of total absorbance over the carbonyl region (1760–1700 cm^{-1}) of paper-sheet biocomposites consisting of unmodified and PCL-grafted kraft pulp fibers. The reference sheet is prepared solely from unmodified kraft pulp. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

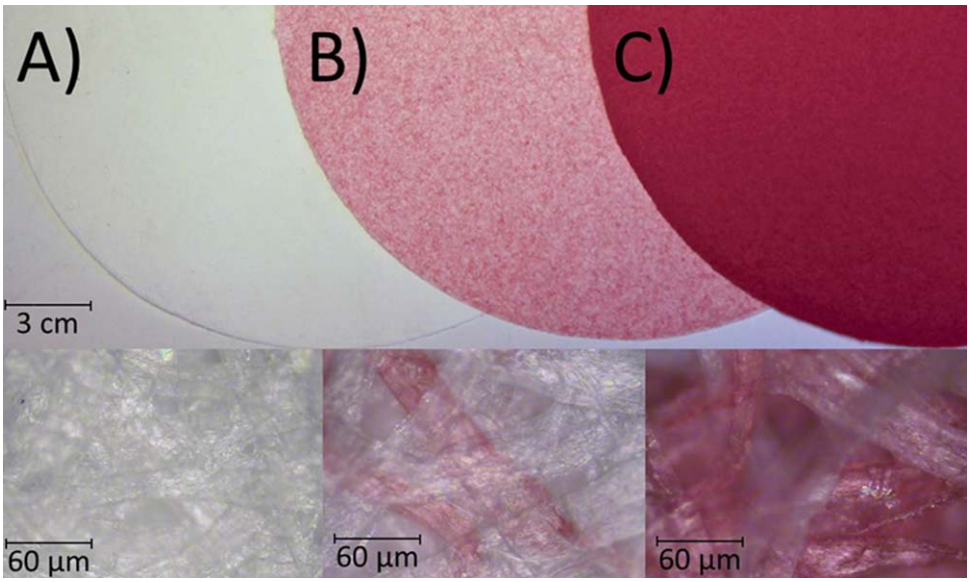


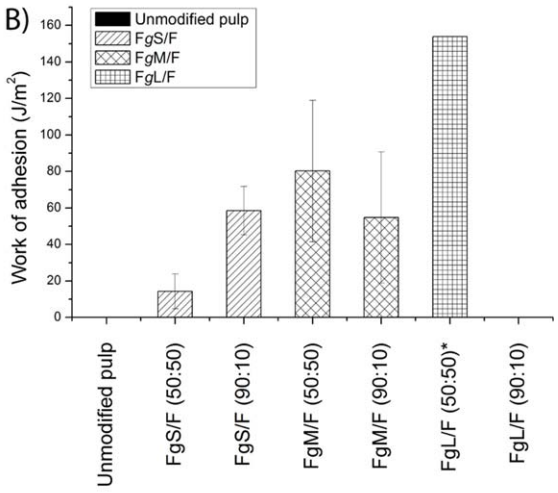
Figure 4. Photographs (top) and optical microscopy images (bottom) of a (A) reference sheet from unmodified pulp, (B) Fg*S*g*DR13*/F (10 : 90), and (C) Fg*S*g*DR13*/F (90 : 10). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

well-dispersed, suggesting that the paper-sheet biocomposites are overall homogeneous, even though the dispersion of PCL-grafted fibers was slightly inferior for Fg*L* in Fg*L*/F (90 : 10).

To further investigate the homogeneity of the papers, DR13 was covalently attached to the Fg*S*-sample, to give dye-labeled polymer-grafted fibers, Fg*S*g*DR13* (Scheme 2). Paper-sheet biocomposites were then prepared by mixing Fg*S*g*DR13*-fibers with unmodified fibers in two ratios: 10 : 90 and 90 : 10, yielding Fg*S*g*DR13*/F (10 : 90 and 90 : 10, respectively), according to the sheet-forming procedure. In Figure 4, paper-sheet biocomposites produced from labeled fibers and neat pulp are presented both as photographs and optical microscopy images, showing that the modified fibers are homogeneously dispersed within the biocomposites, independently of modified fiber content.

A)

B)



C)

	ΔH_m (J/g)
FgS/F 10:90	-
FgS/F 50:50	0.25
FgS/F 90:10	-
FgM/F 10:90	-
FgM/F 50:50	-
FgM/F 90:10	0.12
FgL/F 10:90	-
FgL/F 50:50	1.4
FgL/F 90:10	1.8
Paper sheets from unmodified pulp	-

Figure 5. (A) Laminated paper-sheet biocomposites (left) and paper sheets from unmodified pulp (right) subjected to hot pressing; (B) interfacial work of adhesion from peel test of laminated paper-sheet biocomposites. *Only one specimen was possible to peel, the rest broke within one of the layers, through cohesive failure, and (C) melt enthalpy of all paper sheets from DSC measurements. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

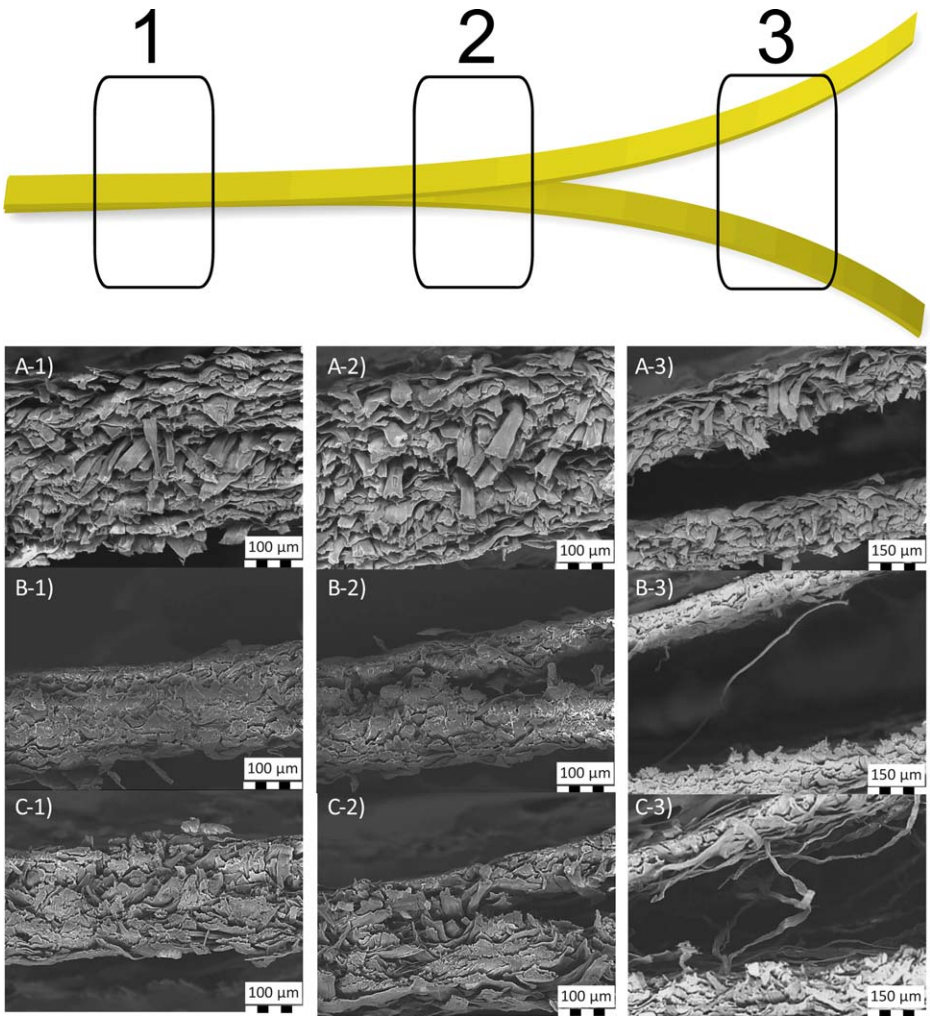


Figure 6. Laminated paper-sheet biocomposites of (A) FgS/F (50 : 50), (B) FgL/F (50 : 50), and (C) FgL/F (90 : 10) showing three regions from the side: (1) non-peeled region, (2) beginning of peeling, and (3) peeled region schematically illustrated on top. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

An attempt to disperse free PCL in water (Supporting Information Figure S3) to allow preparation of a paper-sheet biocomposite by addition and dispersion of PCL to pulp fibers was performed. As expected, contrary to pulp fibers, the PCL powder was not possible to disperse in water. Therefore, it is suggested that if a paper-sheet would be produced from this mixture it would be, as the mixture, inhomogeneous and with patches of PCL. Furthermore, as an effect of free polymer and inhomogeneous material, the paper-feel would not be obtained. In addition, after grafting of PCL from pulp fibers, those fibers should be possible to introduce in a paper machine, as demonstrated with the Rapid-Köthen equipment. A mixture of pulp fibers and free PCL (either added or residual from the polymerization), conversely, could cause problems as free PCL is not compatible with existing processes.

Laminated Paper-Sheet Biocomposites

Interestingly, it was found that paper-sheet biocomposites composed of 50 or 90 wt % modified fibers could be hot-pressed into laminates [Figure 5(A)] without the need for any matrix polymer.

Our interpretation of this is that PCL grafts on fibers from adjacent sheets may come close enough to interact, possibly entangle, or even co-crystallize, when hot-pressed above the melting temperature of PCL (approx. 60°C).[45] This is in accordance with previous results obtained from colloidal probe experiments.[46] The effect of temperature during hot pressing was evaluated and it was found that when the composition was 90 : 10, the biocomposite sheets adhere together already at 50°C, whereas for samples with a lower content of polymer-grafted fibers (50 : 50) a significantly higher temperature, 120°C, was needed. To assess how well the sheets adhered, a peel test was performed. In Figure 5(B) the interfacial work of adhesion, estimated for the compositions 50 : 50 and 90 : 10, is presented. Composition 10 : 90 could not be evaluated as it did not form a laminate with any mechanical integrity. This result was in line with the results from the melt-enthalpy analyses of the different paper sheets from DSC measurements [Figure 5(C)], as none of the paper sheets of composition 10 : 90 crystallized. As a reference material, two paper sheets based on kraft pulp fibers were hot pressed. For

this reference material, the hot pressing did, as expected, not result in any adhesion between the sheets.

The strongest adhesion was found for samples containing F*g*L, which was so strong that at the highest loading of FgL a cohesive failure was observed in the paper sheet, instead of an adhesive failure. The results from the peel test also confirm that longer grafts are indeed formed when higher degrees of polymerization are targeted, despite the fact that the free polymers formed in parallel do not seem to increase substantially, Table III. To obtain further understanding on the hot-pressed laminates, the peeled samples were analyzed by SEM, Figure 6. SEM images were obtained from the side of three different regions in the peel-tested laminated paper-sheet biocomposites F*g*S/F (50 : 50) (A), F*g*L/F (50 : 50) (B), and F*g*L/F (90 : 10) (C): (1) non-peeled region, (2) beginning of peel, and (3) peeled region (as schematically illustrated in Figure 6). When short and medium length grafts were used (F*g*S/F [50 : 50 or 90 : 10] and F*g*M/F [50 : 50 or 90 : 10]) adhesive failures occurred when peeled, and the fracture surface showed no fiber tear [Figure 6(A-3)]. Conversely, when F*g*L was used in the biocomposites, the adhesion increased, and for F*g*L/F (50 : 50) only one specimen could be peeled. In the peeled specimen, a small amount of fiber tear can be detected [Figure 6(B-3)]. This indicates that the combination of amount of modified fibers and the length of PCL grafted is on the limit where adhesive failure turns into cohesive failure for this system. Furthermore, for F*g*L/F (90 : 10) no specimens could be peeled, all samples failed through cohesive failures, illustrated in Figure 6(C-3) where extensive fiber tear is observed. Hence, no interfacial work of adhesion could be estimated, but most likely it is higher than for the other samples as the adhesive joint was shown to be stronger than the paper itself. The strong adhesion between paper sheets can be correlated to the inherent ability of crystallization of the different sheets; for both 50 : 50 and 90 : 10 compositions of F*g*L/F papers the melt enthalpy is higher than for all other papers (Figure 5C).

Furthermore, for the bilayer laminates that could be peeled, the interfacial work of adhesion (Figure 5B) between the paper-sheets was estimated to range from approximately 10 to 160 J/m^2 depending on the amount of grafted fibers used and the length of the PCL chains grafted from them. In a comparable study by Lönnberg *et al.*[27] where CNF films grafted with PCL of DP150, 300, and 600, were laminated with PCL films and peeled off. The interfacial work of adhesion was estimated to be ranging from 15 to 65 J/m^2 depending on the graft length. Hence, even though the amount of PCL grafted from kraft pulp in this study is substantially lower, as demonstrated by TGA and contact-angle measurements, than was obtained on CNF in the above-referred study, a significant effect can be achieved with respect to lamination and adhesion.

To elucidate the effect of the polymer grafting on the mechanical properties of the paper-sheet biocomposites, tensile testing was performed. It was shown that the mechanical properties weakened. Both tensile index—that is, the ultimate force per sample width normalized to sample weight, a unit used due to the porosity of a paper-based material—and strain at break were reduced (Supporting Information Figures S4 and S5). Tensile index was reduced from 35 to 5 Nm/g and strain at break from 4 to 1%, when comparing unmodified pulp sheets with 90 : 10 sheets, independent of the PCL DP. An expected result as the polymer grafts probably obstruct and decrease the formation of secondary interactions between fibers; less intermolecular forces can be formed and a weaker network is thus created.

CONCLUSIONS

In this work, homogenous paper-sheet biocomposites from PCL-grafted kraft pulp fibers and neat kraft pulp fibers were prepared. These biocomposites could be hot pressed together into a laminate structure without the need for any matrix polymer. In addition, in some cases the joint produced in the laminate was even stronger than the paper-sheet biocomposites themselves. All the biocomposites possessed both the appearance and paper-feel of ordinary paper sheets, which is important in packaging applications, for example. This was achieved through grafting of three different lengths of PCL (F*g*S, F*g*M, and F*g*L) *via* ring-opening polymerization, followed by preparation of the paper sheets in three different ratios of modified-to-unmodified fibers (10 : 90, 50 : 50, and 90 : 10) in a Rapid-Köthen sheet former. FTIR microscopy and attachment of a dye, disperse red 13, revealed good compatibility between modified and unmodified fibers independent of the length of the grafted PCL chains and modified fiber content. The lamination of the ordinary paper sheets through hot pressing is not possible, therefore these paper-sheet biocomposites could have the potential to be used in the packaging industry, with further development, where the grafted PCL chains would act as an adhesive free joint.

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