The impact of thermomechanical pulp fiber modifications on thermoplastic lignin composites

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ABSTRACT

Cellulose and lignin are abundant renewable biopolymers that can be used for the manufacture of new, environmentally friendly materials. The objective of this study was to produce composites of kraft lignin, which were reinforced with cellulosic thermomechanical pulp (TMP) fibers. Furthermore, the fibers were chemically modified resulting in cross-linking or increased hydrophobicity. Ideally, these modifications improve interaction between the components in the composite. The effects of the modifications on the tensile strength and thermal properties of the composites were investigated, and the interactions between components were examined by infrared spectroscopy and scanning electron microscopy. When the fibers were cross-linked with polyethylene glycol diglycidyl ether (PEGDE), the tensile strength properties of the composite were significantly improved. Depending on the amount of PEGDE added, tensile strength was increased by 16–34%, and Young's Modulus by 6–18%, but at the same time the strain at break remained the same. Similarly, by using PEGDE, the amount of free plasticizer (PEG) could be reduced, which also improved the water-resistance of the composite. According to scanning electron microscopy, all chemical treatments improved the compatibility of the fibers with the lignin matrix. However, the increase in compatibility was highest when the fibers were cross-linked with a combination of glyoxal and neopentyl glycol (GL/NPG) or by increasing hydrophobicity through acetylation (AC), although the tensile strength properties were the best in case of cross-linking with PEGDE.

1. Introduction

Significant amounts of kraft lignin are produced as a by-product of the pulp and paper industry, and during recent decades there has been increasing interest to utilize lignin more efficiently and developing lignin-based materials and products [1,2]. Lignin has good mechanical properties, although the major carbohydrate of natural fibers, cellulose, is better in terms of strength properties [3,4]. Moreover, lignin has many interesting material properties, such as thermal stability, adhesive, antioxidative, and antimicrobial properties [5]. The material properties as well as the thermal properties are associated with the chemical structure of lignin, consisting of an aromatic backbone and hydroxyl groups involved in hydrogen bonding [6]. Therefore, lignin can act both

as a thermoplastic and thermosetting matrix material [7,8]. The glass-transition temperature (T_g) of various lignin preparations may vary from 93 °C to 174 °C, while the T_g of softwood kraft lignin is at the higher end of the scale (124–174 °C) [7-10]. The T_g of lignin is dependent on the source and on the method of isolation, which affect the molecular weight and chemical structure of lignin. For easier processing of lignin as a thermoplastic, lignin can be blended with synthetic polymers that plasticize and decrease the T_g of lignin [11-13]. One effect of these plasticizers, including water, is their demonstrated ability to form hydrogen bonds with lignin. Therefore, plasticizers can improve the flow properties of lignin, which has a structural tendency to form aggregates in different solvents and blending compositions [14]. Another strategy for improving the processing properties of lignin is chemical

Table 1

Amounts of reagents in the reaction solution. In all other tables and text the batches are abbreviated: glyoxal/neopentyl glycol(concentration of glyoxal/concentration of neopentyl glycol) = GL/NPG [c(GL)/c(NPG)].

Entry	1	2	3	4	5	6	7	8	9	10
Glyoxal (mol l^{-1})	0.05	0.1	0.1	0.1	0.2	0.2	0.2	0.3	0.6	0.6
Neopentyl glycol (mol l^{-1})	0.05	0.025	0.05	0.1	0.05	0.1	0.2	0.3	0.0	0.3

derivatization by different reagents, such as polyethylene glycol (PEG) derivatives [5,14,15].

Recently, another subject of interest has been the reinforcement of composites with natural fibers, which have been already applied before development of the now commonly used plastic materials [4,16-19]. Previously, the research was more focused on fiber-reinforced synthetic plastics, but more recently biopolymers used as a matrix have increased in popularity, with the aim of producing environmentally friendly, biodegradable composites consisting of renewable raw materials. In terms of mechanical and physical properties, natural fibers have relatively high strength and stiffness, and low density and price, which can decrease the weight of materials [3,4,16,20,21]. For example, in the automotive sector reduction in weight is directly related to the fuel consumption of the vehicle, which affects the CO_2 emissions [21]. However, the properties of the fibers are always influenced by their growth conditions [4]. The use of natural fibers in composites is also restricted by their degradation temperature ($\sim$200 °C), which limits the choice of the available matrices for those softening below this temperature [16]. One of the undesired properties of natural fibers is their hydrophilicity, which affects the properties and processing of composites [3,4,16,19-21]. Hydrophilicity increases the moisture absorption of composites and makes the surfaces of fibers incompatible with hydrophobic polymer matrices, such as polypropene (PP), leading to decreased mechanical properties. As a result of hydrophilicity and internal hydrogen bonding, natural fibers also tend to form aggregates that may cause difficulties in processing [20]. However, different chemical treatments can be used to increase the hydrophobicity of fibers, and further to improve the compatibility between hydrophobic matrices and fibers [4,20,21].

The removal of lignin from lignocellulosic fibers is not cost-effective or beneficial prior to preparation of composite materials, because higher lignin-contents might improve compatibility with hydrophobic or other matrices [3,22]. Lignin is an amphiphilic polymer composed of phenylpropane units, where the aromatic ring provides hydrophobic, and hydroxyl groups hydrophilic nature to the molecule. Furthermore, TMP fibers are cheaper compared to bleached cellulosic fibers, such as those from kraft pulping [23]. In thermomechanical pulping, moist wood chips are steamed and refined at temperatures of 100 °C or higher, producing separated fibers with lignin enriched on the surface [24-26]. When combined with glass fiber, TMP fibers showed positive effects on the strength properties of composites when PP was used as the matrix [27]. In another case, TMP fibers improved the strength properties when polylactic acid (PLA) was used as the matrix, whereas with PP, the properties were very similar between TMP and bleached kraft pulp fibers [28]. Similarly to TMP fibers, wood flour also contains lignin. However, because of the higher aspect ratio (ratio of length to diameter), separated fibers are able to mechanically reinforce the composites, whereas wood flour has been considered to act more as a filler component [23,27-29].

Studies conducted on lignin composites have shown that the effect of lignin on the mechanical performance of composites is dependent on the proportion of lignin used, the type of matrix, and the possible use of reinforcing fibers. Composites composed of lignin as the matrix (30–60%) and natural fibers as reinforcement (10–60%) with promising mechanical performance have been prepared by injection molding [30]. Similar to the lignocellulosic fibers containing lignin explained above, addition of lignin (up to 20%) in PP composites reinforced with natural fibers did not improve the tensile strength properties, but did enhance interfacial compatibility [31]. Higher proportions of lignin in PP-lignin composites decreased tensile and impact strengths, but increased stiffness (Young's modulus) [32]. The reason for the decreased strength values can be attributed to the brittle nature of lignin as a material. Decrease in tensile strength with unchanged Young's modulus has also been observed with lower amounts of lignin (6%) for vinyl ester reinforced with hemp [33]. On the other hand, tensile strength and Young's modulus of polybutylene succinate (PBS) increased with fairly high proportions of lignin (up to 65%) [34,35]. However, the impact strength also decreased in PBS-lignin composites. In addition to improved processing, chemical modification of lignin can also improve compatibility of lignin with certain matrices [14].

The aim here was to produce and analyze composite material in which the lignin matrix, plasticized with PEG, was reinforced with thermomechanical pulp (TMP) fibers. We assumed that the presence of lignin on the surface of TMP fibers would improve compatibility with the matrix lignin. After optimization of the composition, the tensile strength properties and morphology of this reference composite was evaluated. In order to improve the results, the TMP fibers were chemically modified to induce cross-linking or hydrophobicity, and the effects of these modifications were analyzed. In contrast with many other studies, the chemical modifications were designed to retain the lignin in fibers. The success of the chemical treatments were first evaluated with different methods. Furthermore, the tensile strength properties and morphology of the composites from modified fibers were evaluated and compared with the reference composite from unmodified TMP fibers.

2. Experimental

2.1. Materials

The TMP (UPM Paper Mills, Lappeenranta, Finland) and LignoBoost lignin from industrial processes (separated by acidic precipitation from kraft black liquor [36], provided by Valmet AB, Gothenburg, Sweden) were dried in an air-circulating oven at 60–80 °C for 2–3 h before use in reactions and preparation of composites.

The chemicals used in the chemical modifications were: glyoxal (GL) (40 wt.% solution in water, Sigma-Aldrich; now MilliporeSigma, St. Louis, MO, USA), neopentyl glycol (NPG) (2,2-dimethyl-1,3-propanediol, Honeywell Fluka, Charlotte, NC, USA), acetic anhydride (AC) (Fluka), pyridine (Honeywell Riedel-de Haën, AG, Seelze, Germany), and polyethylene glycol diglycidyl ether (PEGDE, M_w(pEO) 200, Polysciences, Inc., Warrington, PA, USA).

2.2. Chemical modification of fibers (Scheme 1)

Modification of fibers by glyoxal or glyoxal / neopentyl glycol. The procedure was modified from Xu et al. [37]. A buffer (25 mM Na-citrate, 0.4 mM MgCl$_2$, pH 3.7, 250 ml) containing appropriate amounts of reagents was mixed with TMP. The amounts of reagents, GL and NPG, for the eight different batches are shown in Table 1. The moist pulp was dried, using suction filtration, to a moisture content of 60–70%.

The cross-linking reaction was performed by heating the mixture in an oil bath at 140 °C for 10 min. After the reaction, the product was washed twice by pouring the mixture into water for 15 min. The product was then suction-filtered and dried.

Partial acetylation of hydroxyl groups. AC (40 ml, 290 mmol) and pyridine (10 ml, 120 mmol) in toluene (150 ml) were added to a flask

Table 2

Weight percentage gains (WPG%) of the modified TMP fibers. The naming for the GL/NPG modifications is explained in Table 1. The value in parentheses is the wt.% of PEG in the PEGDE-modified fiber.

Entry	Fiber modification	Amount of TMP before reaction (g)	Yield of modified TMP (g)	WPG %
1	GL/NPG(0.05/0.05)	50.1	50.5	0.8
2	GL/NPG(0.1/0.025)	50.0	49.5	0.0
3	GL/NPG(0.1/0.05)	50.0	49.7	0.0
4	GL/NPG(0.1/0.1)	50.1	50.4	0.6
5	GL/NPG(0.2/0.05)	50.1	49.4	0.0
6	GL/NPG(0.2/0.1)	50.0	50.2	0.4
7	GL/NPG(0.2/0.2)	50.1	50.6	1.0
8	GL/NPG(0.3/0.3)	50.1	50.8	1.4
9	GL/NPG(0.6/0.0)	50.0	50.1	0.2
10	GL/NPG(0.6/0.3)	48.3	50.0	3.5
11	AC	48.6	56.3	15.8
12	PEGDE (PEG 6%)	48.3	51.2	6.0
13	PEGDE (PEG 12%)	48.2	54.9	13.9
14	PEGDE (PEG 17%)	48.2	58.1	20.5
15	PEGDE-NaOH (PEG 18%)	48.4	58.8	21.5

Table 3

Compositions of different batches in compounding experiments. The naming for the GL/NPG modifications is explained in Table 1. The value in parentheses is the wt.% of PEG in the PEGDE-modified fiber.

Entry	Fiber	Fiber (wt. %)	LignoBoost lignin (wt.%)	Free PEG (wt.%)
Ref1	Untreated TMP	20	56	24
1	GL/NPG (0.05/0.05)	20	56	24
2	GL/NPG (0.1/0.025)	20	56	24
3	GL/NPG (0.1/0.05)	20	56	24
4	GL/NPG (0.1/0.1)	20	56	24
5	GL/NPG (0.2/0.05)	20	56	24
6	GL/NPG (0.2/0.1)	20	56	24
7	GL/NPG (0.2/0.2)	20	56	24
8	GL/NPG (0.3/0.3)	20	56	24
Ref2	Untreated TMP	20	56	24
11	AC	23	56	21
12	PEGDE (PEG 6%)	21	56	23
13	PEGDE (PEG 12%)	23	56	21
14	PEGDE (PEG 17%)	25	56	19
15	PEGDE-NaOH (PEG 18%)	24	56	20

containing TMP. The mixture was refluxed at 80 °C for 4 h. After the reaction, the solvent and reagents were evaporated under reduced pressure. The product was washed with water several times, and the final wash was performed by stirring the product in water overnight. After washing, the product was suction-filtered and dried.

Modification of fibers by PEGDE. Typically, the appropriate amount of PEGDE (5.0 g, 15.0 g or 25.0 g) was dissolved in toluene (200 ml). The solution was added to a flask containing TMP, and the mixture was refluxed at 80 °C for 2 h. The solvent was evaporated and the pulp washed with water. The pulp was suction-filtered and dried.

Modification of NaOH-pretreated fibers with PEGDE. TMP was allowed to absorb an aqueous solution of sodium hydroxide (NaOH) (1 M, 250 ml). After drying the pulp, PEGDE (10.0 g) in 200 ml toluene was added, and the reagent was allowed to react at ambient temperature for 3.5 h. The mixture was acidified with aqueous hydrochloric acid (HCl), filtered, washed with water, and dried.

2.3. Analysis of modified fibers

Weight percentage gain (WPG%). The amount of the unmodified and modified TMP of each batch is reported in Table 2.

The WPG% of each batch was calculated according to:

$$\text{WPG\%} = \frac{m(\text{modified TMP}) - m(\text{unmodified TMP})}{m(\text{unmodified TMP})} \times 100\%$$

Fourier-transform infrared (FT-IR) spectroscopy. The IR spectra were recorded with a Bruker Alpha attenuated total reflectance (ATR)-FT-IR spectrometer (Bruker Corp., Billerica, MA, USA).

Elemental analysis was performed for the starting material, for partially acetylated fiber, for one PEGDE-cross-linked sample (content of PEG 12 wt.%), and for one GL/NPG cross-linked sample [Batch 3, GL/NPG (0.1/0.05)], using an Elementar Vario MICRO Cube (Elementar Analysensysteme GmbH, Langenselbold, Germany). Prior to analysis, the samples were frozen in liquid nitrogen, and ball-milled for 15 min at 350 rpm, using Fritsch pulverisette 6 (Fritsch GmbH, Idar-Oberstein, Germany) and a tungsten carbide grinding set.

^{13}C *CPMAS NMR* was acquired for unmodified TMP and one GL/NPG-sample [Batch 10, GL/NPG (0.6/0.3)]. Solid-state cross-polarization magic-angle spinning (CPMAS) ^{13}C nuclear magnetic resonance (NMR) experiments were carried out using a Bruker Avance III spectrometer operating at 500 MHz for protons and equipped with a 4-mm

CPMAS probehead. Samples packed into the ZrO_2 rotors were spun at 10 kHz, and spectra (2000 scans) obtained with a 4-s delay between scans and a 2-ms contact time for cross-polarization.

2.4. Preparation, testing and characterization of the composites

Preparation of tensile test specimens. The mixture of fiber, lignin, and external plasticizer (PEG) were compounded, using a Brabender Plasticorder batch mixer (Brabender GmbH & Co. KG, Duisburg, Germany) with a sample size of 44 g followed by injection molding by MiniJet (ThermoHaake) (ThermoFisher Scientific, Waltham, MA, USA). The compounding temperature and time were 180 °C and 5 min. The roller mixer (Walzen) was used with the speed of 100 r min⁻¹. The temperature in the injection molding was 180 °C and injection pressure 800 bar. The compounds were injection molded into tensile test specimens according to the ISO-527–2 standard. The compositions of the various batches are shown in Table 3.

Tensile testing of composites. Tensile tests were performed on an Instron 4505 Universal Tensile Tester machine (Instron Corp., Norwood, MA, USA) and operated at a cross-head speed of 2 mm min⁻¹. Cross-sectional dimensions were determined for each tensile specimen with a slide gauge. The values of Young's modulus and tensile strength at maximum load were determined from the average of five stress-strain curves.

Testing the water resistance of the composites. The test specimens were dried and weighed before soaking in water at room temperature for 24 h. After soaking, the test specimens were dried at 60 °C and weighed again.

TGA. Thermal decomposition was analyzed by thermogravimetric analysis (TGA), using a Mettler Toledo TGA/SDTA 851e (Mettler-Toledo International Inc., Columbus, OH, USA). The samples (5–10 mg) were analyzed in alumina crucibles with pinhole lids. The heating rate used was 10 °C min⁻¹ and N_2 flow rate 50 ml min⁻¹.

DSC. Differential-scanning calorimetry (DSC) measurements were performed with a DSC Q200 (TA Instruments, Somerset, NJ, (now New Castle, DE), USA). The samples (5–10 mg) were analyzed in aluminum pans with lids. A heat-cool-heat cycle was used with a heating rate of 10 °C min⁻¹ and a cooling rate of 5 °C min⁻¹, and the measurements were performed under N_2. The maximum temperature used was below the degradation temperature of the material to be analyzed. The second heating stage was used to analyze the data.

SEM. The morphology of the composites was evaluated, using a field-emission scanning electron microscope (FESEM, Hitachi S-4800; Hitachi Ltd., Tokyo, Japan). All the mechanically tested composites were too
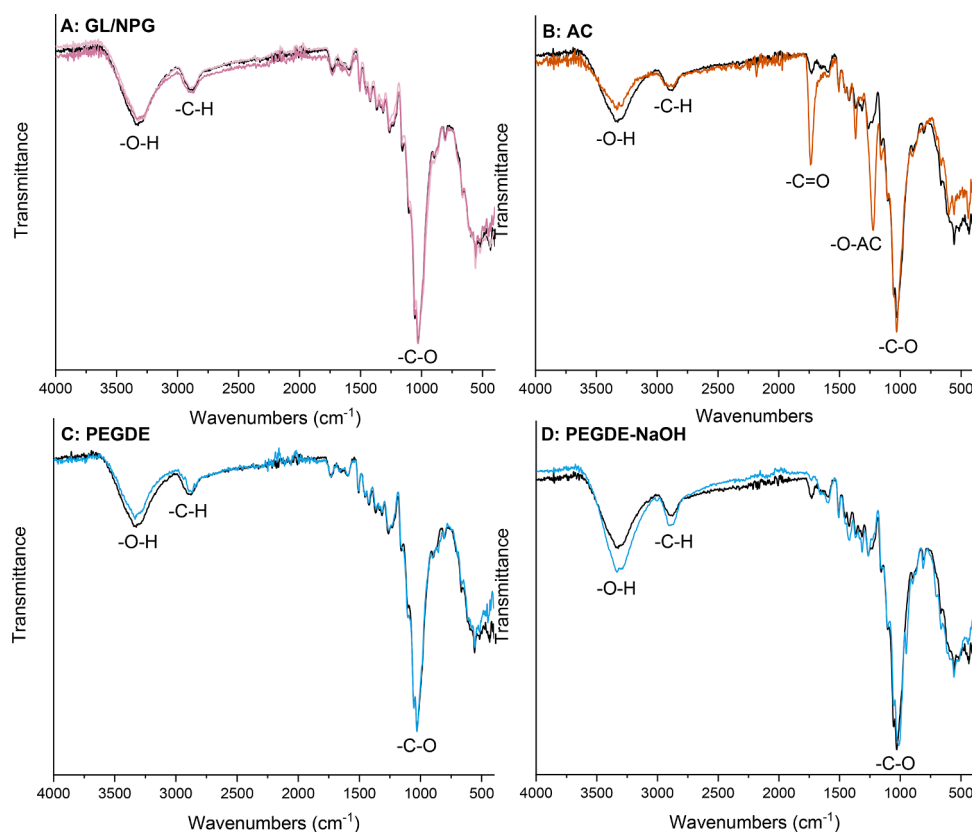
Fig. 1. Infrared (IR) spectra of modified compared with unmodified fiber. The C—O bands (1050 cm^{-1}), as a signal of the cellulose backbone, were normalized to compare other changes. The IR of unmodified TMP is presented as a black line in all spectra, the treatments are shown in colors. A: GL/NPG (0.6/0.0) light purple, GL/NPG (0.6/0.3) purple, B: AC brown, C: PEGDE (PEG 12%) light blue, and D: PEGDE-NaOH (PEG 18%) light blue.

brittle for cutting samples probably due to the high proportion of lignin. Thus, the SEM samples were obtained by manually bending the composite after freezing by immersion in liquid nitrogen. The samples were coated prior to imaging with Au/Pd (4 nm) using a Cressington 208HR High-Resolution Sputter Coater (Cressington Scientific Instruments, Oxhey, Watford, UK).

3. Results and discussion

Composite material was prepared from kraft lignin, TMP, and PEG. The proportions of the components were first optimized by determining the tensile strength properties (tensile strength and Young's modulus). To further improve these strength properties, the TMP fibers were modified by three different chemical treatments: reaction with glyoxal/ neopentyl glycol (GL/NPG), polyethylene glycol diglycidyl ether (PEGDE) or acetic anhydride (AC). The GL/NPG and PEGDE treatments were expected to cross-link the fibers by covalent bonding. NPG was used in a combination with GL in order to increase the flexibility of the resulting structure (**Scheme 1, i**). The AC was used to partially acetylate the hydroxyl groups in the fibers, leading to increased hydrophobicity. After analyzing the chemical changes in the modified fibers, these were used in place of unmodified fibers, and the effect on the tensile strength properties of the composites was determined. To explain the changes observed, the chemical, thermal, and morphological properties of the composites were assessed.

3.1. Preparation and performance of the reference tensile test specimens composed of lignin, unmodified TMP, and PEG

To prepare the tensile test specimens, the kraft lignin (abbreviated to lignin in the following text) and TMP were first compounded with the

external plasticizer (PEG), using an extrusion technique. Previously, FT-IR has been used to show that PEG forms miscible blends with lignin, in which hydrogen bonds are formed between the hydroxyl groups of lignin and the etheric oxygen of PEG [11,12,38,39]. The temperature in the compounding used (180 °C) was above the T_g of the lignin used (150 °C), but at the same time lower than the degradation temperature of the fibers (200–220 °C) [16,20]. After compounding, the composite was injection-molded to produce tensile test specimens. The compositions of the composites were optimized to be able to use the highest possible proportion of lignin while achieving the highest possible performance at the same time. During the optimization, the changes in tensile strength and stiffness (Young's modulus) were taken into account.

For the reference composite, for which unmodified TMP was used, the tensile strengths were 20–23 MPa, stiffness 5–6 GPa, and strain at break 0.5–0.7%. The strength values determined for all the composites, from unmodified and modified TMP, are shown in the Supporting information (**Table S1**).

During the optimization to produce reference composites from unmodified TMP, increasing the proportion of lignin clearly decreased the tensile strength of the composites. Thus, the TMP fibers were chemically modified, and the modified fibers were tested to gain a better understanding of how the mechanical performance of the composites could be improved.

3.2. Chemical modification of TMP fibers

The TMP fibers were modified with GL and NPG, acetylated (AC), or modified with PEGDE. The aim of the GL/NPG and PEGDE modifications was to produce covalent cross-linkages in the fiber, which could provide additional strength to the final composite product. On the other hand,

Table 4

Elemental analysis of unmodified and modified fibers. One sample has been selected for each modification.

Entry	Sample	N%	C%	H%	O%	H/C	O/C
Ref	Untreated TMP	0.04	49.08	6.329	44.56	1.54	0.68
3	GL/NPG (0.1/0.05)	0.03	48.60	6.281	45.09	1.54	0.70
11	AC	0.03	50.48	5.992	43.50	1.14	0.65
13	PEGDE (PEG 12%)	0.03	49.83	6.385	43.76	1.53	0.66
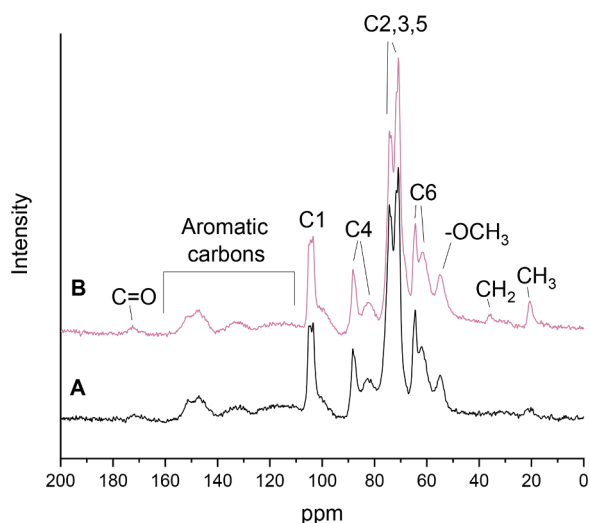
Fig. 2. ^{13}C CPMAS NMR spectra of unmodified TMP fiber (A) and GL/NPG (0.6/0.3, B). The assignments C1–C6 refer to the carbons of β-D-glucose unit of cellulose.

the AC modification was used to evaluate the effect of increased hydrophobicity of the fiber on the strength properties of the composite.

The result of each modification was evaluated by WPG%, (**Table 2**), FT-IR (**Fig. 1**), and elemental analysis (**Table 4**). ^{13}C CPMAS NMR was used to verify the expected outcome of the modification reaction with GL/NPG (**Fig. 2**).

WPG% was clearly increased by modification with GL/NPG only with the highest amounts of the reagents used. The numbers in parentheses in the following text are the concentrations of reagents in the reaction solutions. In the FT-IR spectra (**Fig. 1**, **GL/NPG**) the intensity of

the –OH band (~3300 cm^{-1}) in comparison to the C—O band (~1030 cm^{-1}) was slightly decreased for the modified fibers GL/NPG (0.6/0.0) and GL/NPG (0.6/0.3), indicating formation of low amounts of acetal/hemiacetal functionalities. The changes in the FT-IR spectra were not apparent, possibly because mainly hemiacetals were formed in the reaction. The unmodified TMP and the GL/NPG (0.6/0.3) were further analyzed with ^{13}C CPMAS NMR (**Fig. 2**), and the changes, increased intensities at ~20 ppm (methyl) and ~35 ppm (methylene) indicated that aliphatic hydrocarbons were indeed attached to the fibers.

The chemical composition of the fibers modified with low amounts of GL and NPG could not be confirmed because there were no apparent changes in the WPG% or the FT-IR of these samples. Elemental analysis (**Table 4**) of sample GL/NPG (0.1/0.05) showed that the ratio O/C was increased, which could indicate, for example, that the citric acid used as the catalyst was retained in the fiber. However, no $C = O$ bands (1700–1740 cm^{-1}) were detected in the FT-IR spectra. We further attempted to analyze the amount of hydroxyl groups with ^{31}P NMR, but the sample could not be dissolved in an ionic liquid, 1-allyl-3-methyl-imidazolium chloride ([A*mim*]Cl), without extensive ball-milling [40, 41], which on the other hand is not tolerated by hemiacetal and acetal functionalities. This insolubility indirectly points to the desired cross-linking as the non-modified fibers dissolve readily under these conditions. Thus, we assumed that the reaction performed with lower amounts of reagent would give products similar to those obtained with higher amounts.

In the case of acetylation, the reaction was evident according to WPG % (**Table 2**), FT-IR, and elemental analysis, as could be expected. In the FT-IR spectrum of the acetylated TMP fibers (**Fig. 1**, **AC**), the intensity of the $C = O$ band (~1740 cm^{-1}) clearly increased, while the intensity of the –OH band (~3300 cm^{-1}) decreased slightly. Similarly, the elemental analysis (**Table 4**) indicated acetylation through the decreased ratios H/C and O/C. The degree of substitution could not be exactly determined for the heterogeneous TMP, containing both cellulose and lignin. As a rough estimation, using a literature value of 13.3 mmol/g for the amount of hydroxyl groups in spruce TMP [41] showed that the degree of substitution of the acetylated fiber was 29%.

The PEGDE modifications were performed in neutral pH and in the presence of the base NaOH. The WPG% values showed that PEGDE was attached to the fibers. The decreased ratio O/C also indicated the attachment of the glycol backbone, O—C-C, to the fibers. In the FT-IR spectra (**Fig. 1 PEGDE and PEGDE-NaOH**), the addition of PEGDE was indicated by the changes in the –OH (~3300 cm^{-1}) and –CH (~2870 cm^{-1}) areas. When the reaction was performed at neutral pH,
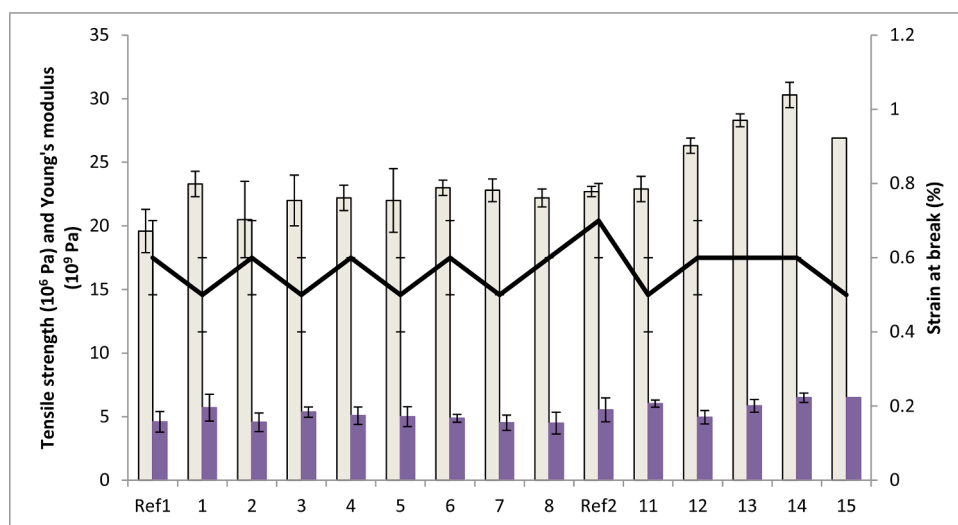

Fig. 3. Tensile strength properties of the composites. Tensile strength: light grey, Young's modulus: purple, and strain at break: black. The compositions for the references and entries 1–15 are in **Table 3** and the numerical values in the supporting information, **Table S1**.

Table 5

Relative changes in tensile strength properties for composites prepared from modified fibers.

Entry	Fiber treatment	Tensile strength (%)	Young's modulus (%)	Strain at break (%)
1	GL/NPG (0.05/0.05)	18.9	24.4[a]	−16.7
2	GL/NPG (0.1/0.025)	4.6	−0.7	0.0
3	GL/NPG (0.1/0.05)	12.2	16.8	−16.7
4	GL/NPG (0.1/0.1)	13.3	10.7	0.0
5	GL/NPG (0.2/0.05)	12.2	8.9	−16.7
6	GL/NPG (0.2/0.1)	17.3	6.1	0.0
7	GL/NPG (0.2/0.2)	16.3	−1.5	−16.7
8	GL/NPG (0.3/0.3)	13.3	2.2	0.0
11	AC	0.9	8.9	−28.6
12	PEGDE (PEG 6%)	15.9	−10.3	−14.3
13	PEGDE (PEG 12%)[b]	24.7	5.8	−14.3
14	PEGDE (PEG 17%)	33.5	17.4	−14.3
15	PEGDE-NaOH (PEG 18%)	18.5	17.5	−28.6

[a] Modulus, the Youngs's modulus could not be determined.
[b] Faster rotation rate of the screw during compounding.

the intensity of the –OH area was slightly decreased (**Fig. 1, PEGDE**), whereas in the presence of NaOH, the intensity was increased (**Fig. 1, PEGDE-NaOH**). The changes in the –CH area in case of neutral treatment were not so clear because new C—O bonds, which were used for normalization of the spectra, were created at the same time with addition of methylene groups. These intensity changes in the –OH area indicated that both diepoxides of the difunctional PEGDE reacted with fibers at neutral pH, indicating cross-linking of the fibers. On the other hand, in the presence NaOH, the other diepoxide functionality of PEGDE seemed to be hydrolyzing, indicating that PEGDE was attached to fibers mainly only from the other end without causing efficient cross-linking.

3.3. Tensile strength properties of the composites from modified TMP

For more comparable results, the amount of external plasticizer (PEG) was reduced to prepare composites from PEGDE-modified or acetylated fibers (the compositions of the various composites are shown in **Table 3**). The amount of PEG was the same for composites prepared from unmodified or GL/NPG fibers. On the other hand, acetylation causes plasticization of both cellulosic fibers and softwood kraft lignin [10,11,42].

The determined tensile strength properties of the composites prepared on a laboratory scale are presented in **Fig. 3**. For a more relevant comparison, the increase or decrease in strength, compared with the reference composite, without chemical modification, are presented in **Table 5**. The GL/NPG-modified fibers (Entries 1–8) were compared with Ref1 (from unmodified fibers), while AC- (Entry 11) and PEGDE-

modified fibers (Entries 12–15) with Ref2 (from unmodified fibers). The strength results for the second reference (Ref2) were slightly better compared with Ref1. One difference between Ref1 and Ref2 was that the lignin was not from the same batch. Thus, the possible variability in the compositions or some other differences of lignins from different batches may be an additional factor affecting the results. However, as the analyses performed with these different batches gave precisely similar results, e.g. FT-IR and DSC, this explanation is uncertain.

The tensile strengths of the GL/NPG composites were improved by 5–19% compared with Ref1. The tensile strength of the AC composite (Entry 11) was very similar to that of Ref2. Apparently, the best improvement in tensile strength (16–34%) was obtained with PEGDE-modified fibers, especially with the cross-linked fibers, which were prepared at neutral pH.

The effect of modifications on Young's moduli was dependent on the amount of reagents used in the modification of fibers. In the case of the GL/NPG modifications, the highest increase in Young's modulus was achieved (Entry 1, 24%) with small amounts of reagents. With further increase in the amounts of reagents, Young's moduli decreased, and the values approached those of Ref1. In contrast to the GL/NPG modifications, the Young's moduli for PEGDE composites were decreased with lower amounts of reagents (Entry 12, PEGDE 6%, 10% decrease in Young's modulus compared with Ref2), and increased with increasing amounts of PEGDE (Entries 13–15, PEGDE 12–18%, increase in Young's modulus 6–18%). Young's modulus for the AC composite was increased by 9% compared with Ref2.

The strain at break either remained the same or was slightly decreased in all modifications. The decrease seemed to be more evident for the AC and PEGDE-NaOH modifications (Entries 11 and 15), which could have resulted from internal plasticization of the fibers. In case of PEDGE-modifications it is noteworthy that although the tensile strength clearly increased, the strain at break was not affected in the same direction. For all other samples, the strain at break was within the standard deviation of the references.

The main aim in using modified fibers was to increase the tensile strength, which was clearly affected by use of fairly high proportion of lignin in the composites. Apparently, increased hydrophobicity of partially acetylated fibers (AC) did not increase the tensile strength. On the other hand, the cross-linking treatments seemed to positively affect this mechanical property. The type of cross-linking was also a factor affecting the improvement in tensile strength: the increase in GL/NPG composites was clear, but modest compared to PEGDE composites. In addition, the strain properties of the PEGDE composites did not deteriorate, although the amount of free PEG was reduced.

3.4. Thermal properties of the composites

The T_g of lignin and the composites were determined by differential-scanning calorimetry (DSC, **Table 6**, the rightmost column). The T_g determined for the kraft lignin used was 150 °C, which was in the range reported previously for lignins (~120–174 °C) [7,8]. The T_g values of all

Table 6

Results of thermogravimetric analysis for composites and components of reference composite. The m%$_x$ is the residual m% at temperature x °C (m% of water evaporated at 100 °C was subtracted from the results). Glass-transition temperatures (T_g) of lignin and composites, determined by differential scanning calorimetry are presented in the rightmost column.

Entry	Sample	T_{onset} (°C)	T_{endset} (°C)	m%$_{300}$	m%$_{400}$	m%$_{500}$	m%$_{800}$	T_g (°C)
–	Untreated TMP	310.68	381.23	71.26	16.86	11.74	ND	ND
–	Lignin	329.69	459.41	88.94	65.24	49.41	39.60	149.62
–	PEG 35,000	369.90	417.91	88.97	35.26	0.00	0.00	ND
–	Ref calculated[a]	335.54	433.81	85.41	48.37	30.02	–	–
Ref1	Ref measured	352.97	426.17	85.05	47.25	30.74	22.89	45.21
3	GL/NPG(0.1/0.05)	354.82	425.82	88.40	53.91	34.59	25.00	47.43
11	AC	346.83	425.05	87.46	48.35	33.38	26.60	59.64
14	PEGDE (PEG 17%)	357.40	427.82	89.80	52.36	34.57	27.74	44.99

[a] Value was calculated, using the measured values of each component and weight fractions used in the preparation of the composite (**Table 3**).
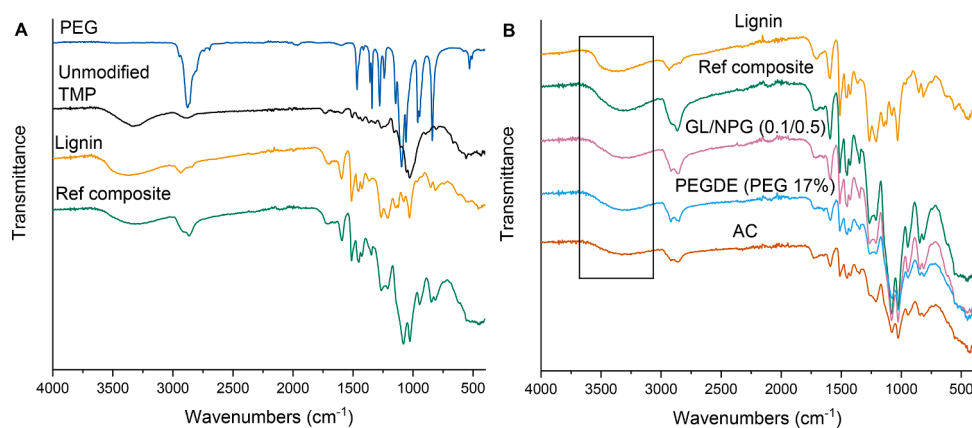
Fig. 4. A: IR-spectra of components and the composite (reference from unmodified pulp). B: Infrared (IR) spectra of lignin and composites: reference composite and composites from chemically modified fibers. The –OH area is marked with a rectangle.

the composites were significantly lower (46–60 °C) than that of lignin, which can be expected when PEG is used as an external plasticizer. The plasticizer PEG (also known as PEO) forms miscible blends with lignin, which is also reflected by the existence of one T_g for the composite of PEG and lignin [38,39] and the T_g of the blends decreases with increasing proportion of PEG in the composite. PEG and lignin interact through hydrogen bonding in the blend: the phenolic hydroxyl groups of lignin form stronger hydrogen bonds with etheric oxygen of PEG than with the aliphatic hydroxyl groups, as shown previously by FT-IR [39].

The modification of fibers had some effect on the T_g values of the composites. The composite from GL/NPG-modified fibers showed a slightly higher T_g than did the reference. Increased T_g values, due to restricted segmental motion, have also been reported for composites of microfibrillated cellulose and polyvinyl alcohol that were cross-linked with GL [43]. On the other hand, cross-linking of fibers with a significant amounts of PEGDE did not have the same increasing effect on T_g, which could indicate that longer PEGDE molecules form more flexible structures with fibers than do the shorter GL molecules. The NPG used in the reaction with GL did not apparently improve the flexibility of the structure. Replacing part of the free PEG (by weight) with acetyl groups led to clearly increased T_g, which indicates that PEG is a more effective plasticizer in the type of composites prepared.

The thermal stability of the composites was evaluated by TGA (Table 6). The fairly high proportion of lignin affected the thermal stability of the composites, which was also expected, since lignin has better thermal stability than natural fibers alone [16,20,44]. The measured onset temperature of the reference composite was 17 °C higher than the one calculated, based on the values of each component, which indicates that the components possibly interact through hydrogen bonding in the composite. Composites made of GL/NPG- and PEGDE-cross-linked fibers showed slightly higher thermal stability and residue left at 800 °C, in comparison to the reference.

Analogously to the results above, cross-linking with GL increases the thermal stability of composites from microfibrillated cellulose and polyvinyl alcohol [43]. The composite produced from acetylated fibers showed clearly lower thermal stability, while the amount of residue at 800 °C was slightly higher than that of the reference. In contrast, acetylation has been reported to increase the thermal stability of fibers, resulting in a lower amount of residue than in untreated fiber [45,46].

3.5. Chemical characterization of the composites by FT-IR

The IR spectra of all the components, PEG, unmodified fiber and lignin, and the composite from the unmodified fiber are compared in **Fig. 4**A. The composite exhibits all the characteristic IR bands of its components. It is worth noting that the –OH area (~3300 cm^{-1}) of the fiber and the lignin were both at higher wavenumbers than was the –OH

Table 7
FT-IR absorption peaks of the hydroxyl group areas for the composites, fibers and lignin.

Entry	Composite		Fiber		Lignin
	Modification	Waveno. (cm^{-1})	Modification	Waveno. (cm^{-1}) (Δ composite)	Waveno. (cm^{-1}) (Δ composite)
Ref1	Ref	3284	Ref	3330 (46)	3358 (74)
	GL/NPG	3326	GL/NPG	3326 (0)	3358 (32)
	AC	3328	AC	3331 (3)	3358 (30)
	PEGDE	3328	PEGDE	3334 (6)	3358 (30)

area of the composite. This suggests that the fibers and lignin in the composite are partially hydrogen-bonded with each other, which may explain the positive effect on the strength of the composite. Apparently, the oxygen in the ether bond of PEG also take part in this hydrogen-bonding, although the shift in the C–O signal of PEG is overlapped by the C–O signal of the cellulose backbone in the IR spectrum.

The IR spectra of lignin and all composites are compared in **Fig. 4**B. The –OH wavenumbers for composites, fibers, and lignin are presented in **Table 7**. The wavenumbers in the –OH area of the composites are clearly decreased compared with lignin, although the shift is more significant for the reference composite. In the case of the reference composite, the –OH area of the fiber was also shifted. Similarly, significant shifting was not detected for the modified fibers, which does not necessarily indicate that modified fibers are not hydrogen bonded; ATR-IR measures the surface of surface- modified fibers, which can affect the results observed. This means that hydrogen bonds, which are most probably also taking part in formation of the composites, are existing below the surface of the material.

3.6. Examination of the fracture surfaces by SEM

SEM images of the composites were acquired to visualize the compatibility of the components. SEM images of the fracture surfaces, obtained by manual bending after immersing the sample in liquid nitrogen (**Fig. 5**) show some, but no extensive fiber pull-outs. Fibers are mainly covered by the matrix, indicating fairly good interfacial adhesion (compatibility) for composites of both unmodified and modified fibers. Furthermore, in the magnified images of the interfaces between matrix and fiber (**Fig. 6**), there is no detectable gap between the matrix and the GL/NPG- or AC-modified fibers. The gap is smaller for PEGDE-modified fiber than for unmodified fiber, indicating that all modifications enhanced compatibility of lignin with the fibers. Lignin is amphiphilic in nature, since it contains, in addition to amphiphilic phenols, also hydrophobic aromatic rings and hydrophilic hydroxyl groups in the side
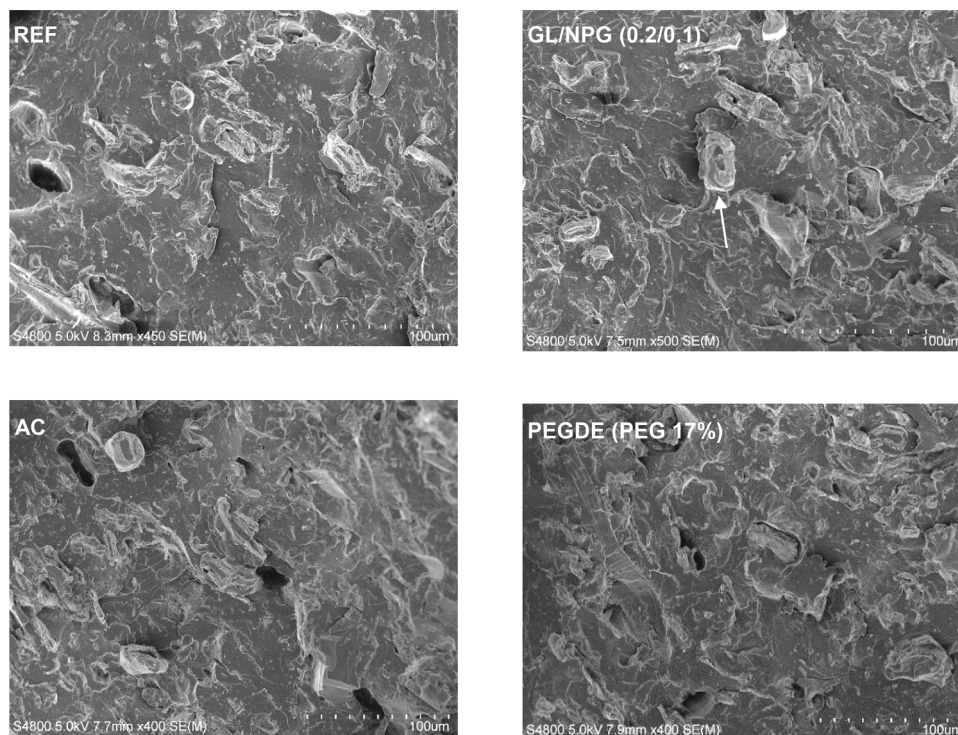
Fig. 5. Scanning electron microscope (SEM) images of fracture surfaces for composites. The arrow is pointing out a fiber as an example.
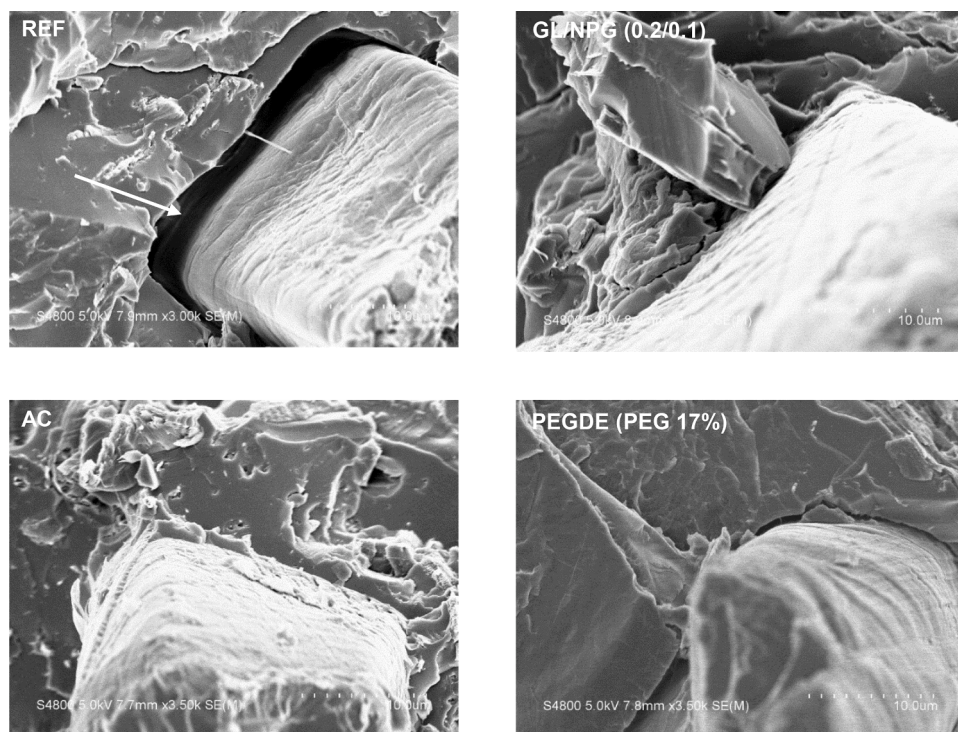

Fig. 6. Scanning electron microscope (SEM) images of interface between matrix and fiber for composites. The arrow is pointing out a gap between the fiber and matrix. The total length of the scale bar is 10 μm in all images.

chains. The hydrophobic interaction between acetylated fiber and lignin seemed to improve adhesion but it did not improve tensile strength. Adhesion was also improved for GL/NPG-fiber, which has more hydrophilic surface than the acetylated fiber. The GL in the fibers may react further with the matrix during processing, resulting in covalent bonding between the fibers and the matrix. In the case of the PEGDE-modified

fibers, the improved adhesion in comparison to the reference may have been due to cross-linking, resulting in increased hydrophobicity, and/or different types of hydrogen bonding caused by the PEG in the fiber. In Fig. 6 the gap for PEGDE-modified fiber is bigger compared to GL/NPG and AC treatments but, on the other hand the tensile strength was clearly improved. Our hypothesis is that the more flexible structure

Table 8

Mass loss (in wt.% and relative to the total amount of PEG) of reference, PEGDE (PEG 12%), and PEGDE-NaOH (PEG 18%) composites soaked in water for 24 h.

Entry	Composite	Mass loss (%)	Mass loss/Total amount of PEG (%)
Ref1	Reference	4.9	20.4
13	PEGDE (PEG 12%)	3.1	12.9
15	PEGDE-NaOH (PEG 18%)	5.4	20.4

provided by longer chains in the reacting chemicals may provide flexibility for the fiber, which improves the results for some reason.

The separation and dispersion of fibers was evident for all samples and no bundles of fibers could be observed. Cellulosic fibers tend to form aggregates, although dispersion can often be improved using intensive mixing [16], e.g. by the utilization of a twin-screw batch mixer used in this study. The dispersion was not apparently affected by the cross-linking (GL/NPG and PEDGE), since the aggregation could have been even more enhanced, if covalent cross-linking were occurring between the fibers. However, dispersion seemed to be poorer for the cross-linked fiber containing 12% PEGDE, and thus a higher mixing rate during compounding had to be used.

3.7. Water-resistance of the pegde cross-linked fibers

PEG is able to plasticize lignin well, but it is also soluble in water. Indeed, we found that part of the composite was dissolved after soaking the test specimen in water. The mass losses after soaking reference, PEGDE (PEG 12%), and PEGDE-NaOH (PEG 17%) composites in water for 24 h are in Table 8. The PEGDE-NaOH composite, in which the PEGDE was attached to fibers only from one end, suffered from similar or more pronounced mass loss than did the reference composite with only free PEG. However, the mass loss was lower for the composite, in which the PEGDE was cross-linked. Thus, in addition to gaining improvements in the tensile strength properties, cross-linking with PEGDE gives additional beneficial properties for composites reinforced with this modified fiber.

4. Conclusions

Composite material with favorable mechanical properties was produced from lignin and TMP, considering the brittle nature of lignin. The composite produced contained high share of renewable materials, lignin, and TMP fibers (76%). IR-analysis indicated hydrogen bonding between lignin and fiber, which should improve compatibility of the component. After chemical modifications of the TMP fibers, the compatibility with lignin was further improved. Improvements in the mechanical properties could be obtained with some of the chemical treatments tested for the fibers. Cross-linking of fibers improved the mechanical properties, whereas acetylation (AC) seemed to have no effect. However, the type of cross-linkage was also significant in view of the mechanical results and better results were obtained with PEGDE compared to GL/NPG. The high share of lignin in the composites improved their thermal stability, which was further improved by both of the cross-linking treatments. According to SEM images, the compatibility of components was better with GL/NPG compared to PEGDE, which leads to a hypothesis that the more flexible structure of PEGDE aids in improving the strength properties. As an additional advantage, treatment with PEGDE improved also the water-resistance of the composite.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jcomc.2021.100170.

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