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**Title:** Castor oil-based biopolyurethane reinforced with wood microfibers derived from mechanical pulp

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**Abstract**

Wood fibers with high lignin content have prospect to function in numerous applications with advantageous properties if the fiber features are appropriately capitalized. The present study introduces a new approach to disintegrate and disperse wood fibers from groundwood pulp (GWP) directly to polyol without additional solvent exchanges or chemical modifications. In comparison bleached chemical pulp with low lignin content was ground in the polyol but only low consistency (1wt%) operation was possible whereas up to 5wt% consistency with GWP was carried out with ease. The micron sized fibers in polyol were reacted with polymeric diphenylmethane diisocyanate to produce fiber reinforced biopolyurethane (bioPU) composites. The mechanical properties of the composites improved compared to reference bioPU showing 14.6% increase in Young’s modulus, 54.5% in tensile strength and 26.1% in strain at break. The tan δ peaks shifted to higher temperature from 5.5 to 10.4 ºC when fibers up to 5.1wt% were incorporated to bioPU. Overall the bulk microfibers from GWP with low degree of processing were cost-effective reinforcements for bioPUs, which improved the qualities of the fabricated composites and showed good compatibility with polyurethane.
Introduction

Polyurethane (PU), which can be synthesized from an isocyanate reaction with polyol, has widely been applied in numerous applications in coatings (Somani et al. 2004), adhesives (Ferreira et al. 2007), foams (Zhou et al. 2016a), automotive parts (Faruk et al. 2013) composites (Özgür Seydibeyoğlu and Oksman 2008) and thermal insulations (Tibério Cardoso et al. 2012). Both the components and possible other additives such as catalysts may cause environmental stress as they are mainly derived from non-renewable petroleum resources (Meier et al. 2007) and the synthesized product is poorly biodegradable (Barioni et al. 2015). Currently there is a strong desire to discover sustainable routes to produce PU with greener, isocyanate-free (Lee and Deng 2015) approaches by replacing the current ingredients partly or fully with naturally occurring components. In PU fabrication reinforcing fillers with varying functionalities could be capitalized by harvesting the potential from various biomass fractions, mineral particles (Xu et al. 2009) or process waste streams (Silva and Silva 2005).

Vegetable oils, which are universally available, abundant, renewable, inexpensive and have prospect for further polymerization with chemical modifications can function as nature derived polyols in bioPUs (Kunduru et al. 2015). The mechanical and thermophysical properties of bioPU have been reported to alter when different vegetable oils were tested (Zhang et al. 2013). Among the numerous vegetable oils castor oil is the only one containing hydroxyl groups in its natural form, which enables its direct use in bioPU-manufacture. Hydroxyl groups can also be introduced to vegetable oils with different functionalization routes (Petrović et al. 2008; Mohammed et al. 2013; Chaudhari et al. 2013) to improve bioPU crosslinking density, glass transition temperature and mechanical properties (Petrović et al. 2005). Embedding of fillers (Zhang et al. 2015) or fibers can further improve chemical resistance and both mechanical and thermal properties of bioPUs. Thus far, reinforcing of bioPUs with renewable fibers have been conducted in few studies with cotton
powder (Oprea et al. 2016), natural fibers (Maafi et al. 2010), microcrystalline cellulose (MCC) (Głowińska and Datta 2015), cellulose nanofibers (CNF) (Benhamou et al. 2015) or cellulose nanocrystals (CNC) (Wik et al. 2011).

Cellulosic fibers can be obtained from numerous renewable sources from biomasses and various waste materials, the properties of which are governed by their chemical composition, fiber structure and bonding between the components. The lignin content of wood fibers deviates greatly depending on the species and cellulose processing (pulping) conditions (Spence et al. 2010; Iakovlev and Heiningen 2012; Rojo et al. 2015). Wood fibers closer to their native state, without any delignification, can be obtained from thermomechanical pulping (TMP) or pressure groundwood (PGW) processes. Wood fibers with high lignin content could be beneficial in the processing of bioPU-based composites as the surfaces of the fibers are more hydrophobic than that of chemical pulp (delignified) fibers. Thus, a better dispersion with hydrophobic polyols is plausible. The reinforcement potential of fibers can potentially further be enhanced by size reduction to result in micro- or nanofibers (Zhou et al. 2016b) with high aspect ratio and specific surface area.

In this article a new method for straightforward micronization and dispersion of GWP wood fibers directly to castor oil at consistencies up to 5% is presented. The GWP was mixed and ground in the polyol at elevated temperature without any water present. BioPU composites were fabricated from the ground fiber in polyol dispersions by reacting solely with polymeric diphenylmethane diisocyanate without applying any additional processing steps like solvent exchanges of aqueous cellulose fiber suspension. The impact of the fiber loading on mechanical and thermal properties of bioPU was investigated with tensile testing, dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA). The morphology of ground fibers, and cross-sectional structure and fiber dispersion in composites were analyzed with field emission electron microscopy (FE-SEM). The chemical structure was analyzed with attenuated total reflection infrared (ATR-IR)
spectroscopy. The properties of the GWP reinforced composites were compared to reference bioPU and to composite reinforced with bleached chemical pulp cellulose fibers.

2. Experimental

2.1. Materials

Castor oil with a hydroxyl value of $\geq 160$ mg KOH/g, acid value $\leq 1.5$ mg KOH/g and water content $\leq 0.3\%$ was purchased from Carl Roth (Germany). Polymeric diphenylmethane diisocyanate (pMDI) prepolymer (VIBRATHANE® 8000) with NCO/OH-ratio of 1.03/1 was obtained from Chemtura (Italy). Unbleached spruce groundwood pulp (GWP) in never-dried form and a bleached sulfate spruce pulp (BP) in the form of dried pulp sheets were acquired from Stora Enso, Veitsiluoto pulp mill (Finland). Track etched Nuclepore membranes (pore size 0.20 $\mu$m) used for the preparation of FE-SEM samples were acquired from Millipore (France).

2.2. Methods

2.2.1. Fiber content

Standard methods were used to analyze the fiber content of GWP and BP. The lignin content of fibers was analyzed with TAPPI T 222 om-02 (GWP 27.4wt%, BP 0.2wt%), the acetone soluble extractives were determined by TAPPI T 280 pm-99 (GWP 2.2wt%, BP 0.1wt%) and the hemicellulose and degraded cellulose portion were analyzed according to TAPPI T 212 om-02 (GWP 13.0wt%, BP 3.9wt%).

2.2.2. Disintegration of cellulosic fibers to polyol

Instead of water, castor oil was utilized for the first time as a less polar medium to disintegrate GWP fibers with high lignin content. The never dried GWP was mixed with the polyol in three different consistencies to produce suspensions with 1, 3 and 5wt% fiber content. Similar 1wt% fiber-polyol suspension was prepared from BP. The pretreatment of each suspensions consisted of
the following steps: First the fiber in polyol suspension was heated to 100 °C under continuous mixing with a Teflon blade to remove majority of the residual water. At this stage also Ultraturrax mixer (IKA T25, Germany) was equipped to break the remaining pulp flocks, ease the release of trapped water and to achieve better mixture of the components. When boiling of the suspension ceased, the temperature was raised to 150 °C and cooking was proceed for additional two hours to make sure all residual water had evaporated. Same procedure was conducted with the BP fibers.

The fibers were directly disintegrated with a 10-inch Masuko Super MassColloider (MKCA6-2J CE, Masuko Sangyo Co, Japan) at 1500 rpm after cooking. The GWP suspensions were all passed once through 0, -50 µm and 15 times through -100 µm disc clearance, respectively. The samples were collected on a pot, which was placed on top of a hot plate set to maintain temperature of the suspension around 100 °C throughout the grinding process. The reference BP sample, was much more difficult to process as it required two passes through +30 µm, three passes through 0 µm, and one pass through -30, -50, -60, and -70 µm disc clearance, prior reaching the targeted -100 µm gap for circulation of 15 times. Samples were collected from each of the ground suspensions after 5, 10 and 15 passes through the -100 µm clearance.

2.2.3. Increase in solid content of fiber in polyol dispersion

Centrifugation was used to increase the solids content of the 5wt% GWP fiber in polyol dispersion. 500 ml of the fiber in polyol dispersion was centrifuged (Beckham Coulter, Avanti J26-XPI, USA) for 1 hour at 8000 rpm at 40 °C. After centrifugation the fibers were clearly separated from the polyol and the required amount of polyol was removed to prepare dispersions with a consistency of 7 and 9wt%. The dispersions were treated with an Ultraturrax mixer at 13 000 rpm for 5 min to mix back the polyol and fibers to ensure homogenous dispersion of the components.

2.2.4. Preparation of composites
From the prepared fiber in polyol dispersions composites were fabricated by mixing with pMDI. First, the pMDI and fiber in polyol dispersion were preheated in an oven at 100 °C. Excess of pMDI was used in the fabrication to achieve sufficient reaction with the hydroxyl groups of the fibers and polyol. 30 g of preheated pMDI was mixed with 40 g of fiber in polyol dispersion with a hot plate magnetic stirrer adjusted to 100 °C. The reference bioPU was fabricated with the same pMDI (30 g) polyol (40 g) ratio. The mixing was continued for around 5 minutes until the viscosity of the mixture notably increased. The sample preparation was finished with defoaming and mixing for two minutes with a Thinky mixer (ARE-250, Japan). Finally the sample was poured in a Teflon mold (10x10x0.4 cm), which was transferred in an oven for overnight curing at 100 °C. Smaller Teflon mold (11x5x0.4 cm) was utilized for the sample with the highest degree of fibers due to increased viscosity, which made the casting more difficult as air bubbles occurred when using mold with larger surface area. Reference bioPU was prepared from pure castor oil without any added fibers and named as Ref. The samples were labeled according to the total fiber content of the composites. Composites prepared from the ground GWP fiber dispersion of 1, 3, 5, 7 and 9 wt% were named as L0.6%, L1.7%, L2.9%, L4% and L5.1%, respectively. The composite from BP fiber in polyol dispersion of 1 wt% was labeled as B0.6%.

2.3. Characterization

2.3.1. Fiber morphology

Morphological imaging of the original GWP, BP and the fibers ground in polyol was performed with a FE-SEM (Sigma HD VP, Germany) at an accelerating voltage of 3kV. For the imaging of ground fibers small drop from each of the fiber in polyol dispersion was placed in a beaker and diluted to 100 ml of acetone/water mixture. The dilutions were dispersed with Ultraturrax mixer at 10000 rpm for 3 min. From the dilutions 5 ml of the dispersed sample was taken and filtered slowly with low pressure on top of membrane (pore size 0.2 µm). The original GWP and BP were disintegrated and diluted to water. Similar filtering was applied as stated above. The filtered
samples together with the membrane were dipped into liquid nitrogen to freeze the fibers and the specimens were immediately transferred to a freezer. The frozen samples were freeze-dried (ScanVac, Coolsafe 55-15 Pro, Denmark) overnight. After freeze-drying specimens were fixed to sample holders and the surfaces were sputter-coated with platinum (Pt).

2.3.2. Tensile testing

Dog bone shaped standard specimens (Fig. 3) were cut from the casted bioPUs with an Instron hollow die punch (Pneumatic P/N 6054.000, Italy). Mechanical properties were tested according to a standard method (ISO 527) using a Zwick/Roell universal testing machine (Z010, Germany) fixed with extensometer and a 200 N load cell. The distance of the grips was 45 mm, the sample width 3.9 mm and thickness 4-5 mm. In total 5 specimens from each sample were measured to investigate the mechanical properties. In the beginning the measurement 1 mm/min strain rate was applied to calculate Young’s modulus followed by increase to constant 50 mm/min strain rate until breakage of the sample from which maximum stress and strain at break were determined. Standard deviations were calculated accordingly.

2.3.3. Composites morphology

The cross-sectional structure of composites was studied by imaging the fractured surfaces with FE-SEM (Zeiss ULTRA plus, Germany) at an accelerating voltage of 5kV. Prior to imaging the specimen were sputter coated with Pt. The fractured samples were obtained from the broken specimen after tensile testing.

2.3.4. Dynamic mechanical analysis

DMA of the reference bioPU and composites was conducted with TA instruments (DMA Q800, Delaware, USA) equipped with a liquid nitrogen cooling apparatus, in the single cantilever clamp mode. The samples were cooled down and held isothermally for 2 min at −100 °C and then heated to 150 °C with a constant heating rate of 5 °C/min. The DMA measurements were performed at a
fixed frequency of 1Hz and a fixed oscillation displacement of 0.02 mm. Rectangular samples had length, width and thickness of 15 mm, 3.9 mm and 4-5 mm, respectively.

2.3.5. FTIR

Chemical characterization of the composites and the reference bioPU was performed with ATR-IR spectroscopy. Spectra were collected with a Bruker Tensor II FT-IR Spectrometer (Hyperion 3000 FT-IR Microscope, USA) from dried samples. Spectra were obtained in the 100–3500 cm\(^{-1}\) range, and 40 scans were taken at a resolution of 4 cm\(^{-1}\) from each sample.

2.3.6. Thermogravimetric analysis

TGA of BP and GWP fibers, reference bioPU and composites was performed with Netsch (STA 409 PC, Germany) under nitrogen atmosphere with a flow speed of 60 ml/min. The specimens were placed on a sample carrier and were heated from room temperature to 700 ºC at a heating speed of 10 ºC/min.

3. Results & discussion

3.1. Characterization of ground fibers in polyol

All the fibers in polyol dispersions from GWP in consistencies up to 5wt% were successfully passed through the Masuko grinder. In the beginning the GWP consisted of its characteristic larger fiber particles and clusters, which made the suspension more chunky and viscous with the first circulations through the grinder. However, the viscosity started to reduce and good uniformity of fibers was achieved already before the fifth bypass through the -100 µm clearance. After this all of the prepared dispersions were flowing with ease through the grinding discs.

The BP with 1wt% was far more difficult to process as it required more pretreating passes through the larger disc clearance prior reaching the targeted -100 µm. With the first five passes through -100 µm clearance the discs had to be released at the end of each circulation due to high consistency of
the residual pulp left between discs. The hot polyol tended to separate from the hydrophilic BP and flowed faster through the discs separating a chunky portion of pulp at the end of each circulation. After the release of the discs sufficient mixing was required to disperse the fibers homogenously with the polyol. The later bypasses were performed with continuous operation as the suspension started to reach more homogenous liquid flowing form. The poor dispersion between the BP and polyol resulted in processing difficulties and higher consistencies were not practical or feasible to employ. The better compatibility with GWP is related to the high lignin content, which makes the fiber surface hydrophobic and improves the fiber dispersion to polyol. In this study we were able to fabricate ground GWP fiber in polyol dispersions up to 5wt% but we believe up to 8wt% consistency would still be possible to process. Also the use of elevated temperature is advantageous for the processing because of the viscosity decrease and possible thermal softening of both lignin (Goring 1963) and wood (Blechschmidt et al. 1986). Standard water-based systems are limited in their low maximum operation consistency (Hu et al. 2015), which restricts their capacity.

The stability of the ground fibers in polyol dispersions was investigated by letting the samples settle for 7 weeks (Fig. 1). The specimen with the least amount of GWP show most rapid sedimentation compared to the dispersions with higher consistencies (3wt% and 5wt%), which all remained almost as a single phase system even after 7 weeks. In the top part of the samples (3wt% and 5wt%) a small separated polyol layer can be seen. A higher viscosity of the samples constrained the fiber settling and increased the dispersion stability. The 1wt% BP and GWP showed most clear and rapid settling of fibers depending on the processing degree i.e. the samples with the least amount of bypasses (5) settled faster and formed more compact layers to polyol, which is best seen with the BP samples after 7 weeks. The centrifugation of 5wt% fiber in polyol dispersion led to clear separation of transparent polyol in the top and compacted fibers in the bottom of the decanter indicating the settling can be forced by subjecting the dispersion to external gravitational force.
**Figure 1.** Settling of ground fibers in polyol dispersions as a function of storage time. From left to right: Pure castor oil, BP 1wt%, GWP 1wt%, GWP 3wt% and GWP 5wt%. Fibers in polyol dispersions are in the sets of three after 5, 10 and 15 bypasses through -100µm Masuko disc clearance.

The morphology of the original pulps and the Masuko ground pulps was investigated by FE-SEM. It was observed that the original BP prior to grinding (Fig. 2 (1)) occurred in its characteristic long and flexible fibers without defects whereas the GWP had both large fibers and smaller disintegrated fibrils with small filaments produced by the initial mechanical processing of wood. The Masuko grinding caused random cutting and tearing of the fibers, which resulted in micron sized fibers with a broad size distribution with all of the prepared samples (Fig. 2 (3-6)). Compared to traditional
aqueous fibrillation of fibers, opening of the fibrillar fiber structure was hardly observed on the surface of the fibers neither with GWP nor with BP. Favorable internal fibrillation of fibers does most likely not occur as the hydrophobic polyol does not penetrate inside the fiber cell wall causing swelling like water does (Iwamoto et al. 2007). The Masuko grinding of BP in water (instead of polyol) using the applied parameters would ultimately lead to a formation of CNF (Abe et al. 2007). Here, it was shown that lignin is not alone the prohibitive factor for the fibrillation of fibers as the morphology of ground BP was similar with the GWP specimens. Also the polyol was working as a lubricant and its low viscosity induced by heating reduced the fiber friction and thus total combined shear and tear forces impacting the fibers were lower compared to water-based system. The GWP is challenging to fibrillate even in water due to the cross-linked barrier of lignin binding the fibers together. In previous studies intensive mechanical grinding has also been subjected to wood fibers with high lignin content but the liberation of fibrils below micron size has not been successful (Spence et al. 2010; Hoeger et al. 2013) without newly applied pulping strategies (Rojo et al. 2015). In respect to the current study, microfibers with increased surface area were directly obtained in fiber in polyol dispersions from the low-cost GWP fibers for reinforcements in bioPU composites.
Figure 2. Morphology of the original BP (1) and GWP (2) prior to grinding and ground fiber specimens after 15 passes through the grinder BP 1wt% (3), GWP 1wt% (4), GWP 3wt% (5) and GWP 5wt% (6).

3.2. Characterization of composites
Composites were fabricated from the ground and centrifuged fibers in polyol dispersions by reacting with the pMDI (Fig. 3). The proposed manufacture route can be regarded as a step towards greener approach in PU development as no harmful tertiary amine catalyst (Shirke et al. 2015), chemical modification of the components, petroleum-based polyols, solvents for the functionalization of polyol or embedding fiber fillers were used. Especially the direct preparation of fiber in polyol dispersion pose several advantages as the fibers are readily dispersed to polyol in their micron size after grinding and no time-consuming solvent exchange and evaporation or dispersing of dried fibers were required. Though we used never dried GWP fibers, we hypothesize dried GWP would disintegrate in a similar manner. The utilization of cost-effective renewable GWP as reinforcement in the bioPUs allows the production of composites in which the abundant hydroxyl groups of cellulose react favorably with pMDI leading to a cross-linked fiber reinforced structure with good interfacial adhesion.

**Figure 3.** Reference bioPU, its composites and corresponding dog bone specimen (top row from left to right: Ref, B0.6%, L0.6%, L1.7%, L2.9%, bottom row from left to right: fibers separated from supernatant after centrifugation of 5wt% fiber in polyol dispersion, composites of L4.0%, L5.1% (smaller mold was applied to L5.1% to ease casting of viscous dispersion).
3.2.1. Chemical structure

The FTIR spectra (Fig. 4) for the analysis of reference bioPU and composites chemical structure had a characteristic absorption band for N-H stretching at 3340 cm\(^{-1}\) and sharp peak at 1526 cm\(^{-1}\) associated to N-H bending. C-H stretching linked to the vibrations of formed urethane bonds were seen in two distinctive peaks at 2925 and 2854 cm\(^{-1}\). Free C=O stretching occurred at 1730 cm\(^{-1}\), bonded C=O stretching at 1596 cm\(^{-1}\) and C=O stretching took place at 1218 cm\(^{-1}\). The centered band at 1730 cm\(^{-1}\) without clear splitting of the band to additional peaks indicate majority of diisocyanate groups reacted in the polymerization reaction and urethane linkages and amide groups were formed (Narine et al. 2006). No –NCO absorption band was observed around 2270 cm\(^{-1}\) confirming the consumption of isocyanate groups during the polymerization reaction.

**Figure 4.** FTIR spectra for the reference bioPU and its composites.
3.2.2. Mechanical properties

Stress-strain curves for reference bioPU and composites plotted from tensile test results are shown in Figure 5 and their corresponding numeric values are presented in Table 1. Incorporation of evenly dispersed micron-sized GWP to bioPU had a positive impact on the mechanical properties where maximum increase in modulus 14.6% (L5.1%), stress 54.5% (L5.1%), and strain 26.1% (L2.9%) were obtained compared to bioPU reference. Even with the lowest fiber loading (L0.6%) both the strength and strain improved. The stiffness of the composites started to decidedly increase only with the highest fiber content (L5.1%) while the strain decreased simultaneously. Interestingly with all of the studied specimen no sacrifice in contrast to reference bioPU was noted in any property, which has usually been the case in previous studies when natural fibers (Maafi et al. 2010), MCC (Głowińska and Datta 2015), CNF (Benhamou et al. 2015) or CNCs (Wik et al. 2011) have been added to bioPU. Generally the cellulosic fibers with fluctuating dimensions have improved stiffness of the bioPU composites but decreased ductility. In this study however, both toughness and ductility were improved in addition to moderate build-up of stiffness, which bespoke of good interfacial adhesion between the bioPU matrix and fibers (Wu et al. 2007). The use of reinforcing microfibers from BP also improved the properties of composites and features similar with L1.7% were obtained even with small addition of fibers (B0.6%). The cellulose rich microfibers have similar reinforcing tendency in respect to GWP and their hydroxyl group rich surface improves the compatibility in bioPU fabrication. Overall, the microfibers reinforced the bioPU and withstood higher loads as additional fiber pulling or breakage was required prior fracture of the composites. It is believed the mechanical features could yet be improved if the fiber loading could be increased and all the trapped air within the casted composites could be removed, which created some issues with the highest fiber contents and was seen in larger deviations between the measured specimens.
Table 1. Mechanical properties and location of tan δ peaks from DMA of composites and reference bioPU.

<table>
<thead>
<tr>
<th>Sample:</th>
<th>Young’s modulus [MPa]</th>
<th>Maximum tensile strength [MPa]</th>
<th>Strain at break [%]</th>
<th>DMA tan δ peak [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref</td>
<td>3.7 ± 0.1</td>
<td>2.1 ± 0.1</td>
<td>101.5 ± 3.7</td>
<td>5.5</td>
</tr>
<tr>
<td>B0.6%</td>
<td>3.8 ± 0.1</td>
<td>2.7 ± 0.2</td>
<td>117.2 ± 5.7</td>
<td>7.7</td>
</tr>
<tr>
<td>L0.6%</td>
<td>3.6 ± 0.1</td>
<td>2.5 ± 0.1</td>
<td>116.7 ± 7.6</td>
<td>5.9</td>
</tr>
<tr>
<td>L1.7%</td>
<td>3.8 ± 0.1</td>
<td>2.8 ± 0.2</td>
<td>117.0 ± 5.3</td>
<td>7.7</td>
</tr>
<tr>
<td>L2.9%</td>
<td>3.8 ± 0.1</td>
<td>2.7 ± 0.1</td>
<td>127.9 ± 5.2</td>
<td>8.3</td>
</tr>
<tr>
<td>L4.0%</td>
<td>3.8 ± 0.1</td>
<td>2.9 ± 0.3</td>
<td>121.0 ± 6.5</td>
<td>10.4</td>
</tr>
<tr>
<td>L5.1%</td>
<td>4.2 ± 0.2</td>
<td>3.4 ± 0.3</td>
<td>112.5 ± 12.0</td>
<td>9.9</td>
</tr>
</tbody>
</table>

Figure 5. Stress-strain curves of reference bioPU and composites with different fiber loadings.

3.2.3. Composites surface morphology
The fractured surfaces from tensile tested materials were investigated with FE-SEM. From the images a partly lamellar (Maafi et al. 2010) but rather smooth surface with little porosity was observed (Fig 6). Fibers that were completely pulled out or partially sticking out from the surface can be seen as small cavities and projecting filaments, respectively. In some of the samples larger symmetrically shaped round cavities were observed indicating the presence of residual trapped air within the composite. The reinforcing microfibers occur in random ordering without orientation but were evenly dispersed without any visible aggregated zones with their surfaces covered with PU. These findings indicate a successful reaction between pMDI and good interaction between the fibers and matrix.

Figure 6. Cross-sectional fractured surfaces of the composites showing the occurrence of both individual micro-sized fibers and empty cavities remaining after the fracture of the structures.
B0.6% (1), L1.7% (2), L4.0% (3) and close-up image of fibers from L4.0% sticking out of the fractured surface (4).

3.2.4. Viscoelastic properties

Dynamic mechanical properties presented as storage modulus and tan δ as a function of temperature for reference bioPU and its composites are shown in Figure 7. All the samples had two tan δ peaks, the first relaxation is seen at low temperature (around -35 °C) and a more elevated distinct peak at higher temperature. The first low peak likely originates from the mobility of the pMDI pre-polymer segments (Hassan et al. 2006) as the total amount of pMDI was constant with all of the samples and the curves in this region were close to identical with each other. Incorporation of reinforcing fibers to bioPU was noticed as a moderate shift of the higher tan δ peaks towards elevated temperature range where maximum peak transition (Table 1) compared to the reference sample was 4.9 °C. Small reduction of the tan δ peaks was observed when the fiber loading of composites increased as less polymer was participating in the relaxation. The transition with the steepest drop in storage moduli occurs close to the second tan δ peak (-15 °C to 5) before reaching the plateau. In the temperature region from -14 °C to 15 °C increase in storage modulus was observed with all of the composites (excluding L0.6%) compared to reference bioPU (Ref). With the composites increased storage modulus in the higher temperature region also shows more cross-linked structure indicating possible covalent bonds between the fibers and pMDI.
Figure 7. Storage modulus and tan δ of bioPUs and reference as a function of temperature.

3.2.5. Thermal properties

The reference bioPU and the composites with the least amount of embedded fibers shared identical TGA curves in nitrogen atmosphere (Fig. 8 a) indicating the low addition of fibers does not affect the thermal properties of composites. The composites with increasing fiber loading exhibited higher final mass yields compared to bioPU. The GWP with high lignin content showed lower onset temperature and highest char content. The fibers had a high lignin content, which is difficult to decompose (Gani and Naruse 2007) in addition to other wood components, which were not present in BP. BP had a high cellulose content with only small traces of residual components, which explains the differences between GWP in the results. From the curves gradual decomposition was noted to occur at 230 °C and more drastic drop appeared after reaching 310 °C where 50% weight loss ($T_{50}$) was observed between 415-408 °C, for reference bioPU and composites, respectively. The
TGA curves confirm the successful compatibility with PU and reinforcing fibers as the decomposition of fibers in composites was restricted and occurred together with PU at higher temperature compared to neat fibers. The reference bioPU and composites started to degrade in three stages based on the derivative TGA curves (Fig. 8 b), which are associated to the weight loss steps of specimen. In the early stages (150-200 °C) urethane bonds start to degrade and are irreversibly decomposed after reaching temperatures higher than 200 °C (Javni et al. 2000). Castor oil is known to undergo complex degradation steps and its decomposition has been reported to occur around 420 °C (Choi et al. 2015). In the final stage the remaining PUs ultimately decomposes and no further reactions occur in nitrogen at temperatures above 500 °C.

![TGA thermograms](image)

**Figure 8.** TGA thermograms in nitrogen atmosphere (a) and derivative TGA curves (b) for fibers, reference bioPU and composites.

### 4. Conclusions

Based on the results the presented methodology introduces a new way to produce fiber reinforced bioPU composites by utilizing low-cost fibers with minor processing degree directly for fabrication. The first time demonstrated route indicated good compatibility between polyol and GWP with high
lignin content as grinding of the fibers to their micron size in consistencies up to 5wt% was possible whereas BP separated to its own phase already at low consistency (1wt%). Here, the presence of lignin was hypothesized to act as an advantageous component making the fibers more hydrophobic and thus improving the dispersion to hydrophobic polyol. The use of GWP has several advantages as no harmful bleaching or other chemical treatment were required to process the fibers and fabrication of the composites was possible without the use of harmful solvents or catalysts. The fabricated composites retained the characteristics of reference bioPU as the fiber embedding did not sacrifice any of the original mechanical properties as improvements in all of the investigated aspects in terms of modulus, stress and strain were reported. The DMA results showed the reinforcing impact of fibers in the composites where the effect was more pronounced in the rubbery regions. When incorporated to bioPUs the micron-sized GWP and BP fibers shifted the tan δ peaks to higher temperature region indicating restricted molecular motion of the PU main segments. Good compatibility between the reinforcing fibers and PU was shown with improved mechanical properties, restricted decomposition of fibers in composites at elevated temperatures and the formation of more cross-linked structure with increasing fiber loading.

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