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

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15 **Abstract**

16 Wood fibers with high lignin content have prospect to function in numerous applications with
17 advantageous properties if the fiber features are appropriately capitalized. The present study
18 introduces a new approach to disintegrate and disperse wood fibers from groundwood pulp (GWP)
19 directly to polyol without additional solvent exchanges or chemical modifications. In comparison
20 bleached chemical pulp with low lignin content was ground in the polyol but only low consistency
21 (1wt%) operation was possible whereas up to 5wt% consistency with GWP was carried out with
22 ease. The micron sized fibers in polyol were reacted with polymeric diphenylmethane diisocyanate
23 to produce fiber reinforced biopolyurethane (bioPU) composites. The mechanical properties of the
24 composites improved compared to reference bioPU showing 14.6% increase in Young's modulus,
25 54.5% in tensile strength and 26.1% in strain at break. The $\tan \delta$ peaks shifted to higher temperature
26 from 5.5 to 10.4 °C when fibers up to 5.1wt% were incorporated to bioPU. Overall the bulk
27 microfibers from GWP with low degree of processing were cost-effective reinforcements for
28 bioPUs, which improved the qualities of the fabricated composites and showed good compatibility
29 with polyurethane.

30 Keywords: Biopolyurethane; lignin; cellulose; biocomposite; polyol

31 **1. Introduction**

32 Polyurethane (PU), which can be synthesized from an isocyanate reaction with polyol, has widely
33 been applied in numerous applications in coatings (Somani et al. 2004), adhesives (Ferreira et al.
34 2007), foams (Zhou et al. 2016a), automotive parts (Faruk et al. 2013) composites (Özgür
35 Seydibeyoğlu and Oksman 2008) and thermal insulations (Tibério Cardoso et al. 2012). Both the
36 components and possible other additives such as catalysts may cause environmental stress as they
37 are mainly derived from non-renewable petroleum resources (Meier et al. 2007) and the synthesized
38 product is poorly biodegradable (Barrioni et al. 2015). Currently there is a strong desire to discover
39 sustainable routes to produce PU with greener, isocyanate-free (Lee and Deng 2015) approaches by
40 replacing the current ingredients partly or fully with naturally occurring components. In PU
41 fabrication reinforcing fillers with varying functionalities could be capitalized by harvesting the
42 potential from various biomass fractions, mineral particles (Xu et al. 2009) or process waste streams
43 (Silva and Silva 2005).

44 Vegetable oils, which are universally available, abundant, renewable, inexpensive and have
45 prospect for further polymerization with chemical modifications can function as nature derived
46 polyols in bioPUs (Kunduru et al. 2015). The mechanical and thermophysical properties of bioPU
47 have been reported to alter when different vegetable oils were tested (Zhang et al. 2013). Among
48 the numerous vegetable oils castor oil is the only one containing hydroxyl groups in its natural
49 form, which enables its direct use in bioPU-manufacture. Hydroxyl groups can also be introduced to
50 vegetable oils with different functionalization routes (Petrović et al. 2008; Mohammed et al. 2013;
51 Chaudhari et al. 2013) to improve bioPU crosslinking density, glass transition temperature and
52 mechanical properties (Petrović et al. 2005). Embedding of fillers (Zhang et al. 2015) or fibers can
53 further improve chemical resistance and both mechanical and thermal properties of bioPUs. Thus
54 far, reinforcing of bioPUs with renewable fibers have been conducted in few studies with cotton

55 powder (Oprea et al. 2016), natural fibers (Maafi et al. 2010), microcrystalline cellulose (MCC)
56 (Głowińska and Datta 2015), cellulose nanofibers (CNF) (Benhamou et al. 2015) or cellulose
57 nanocrystals (CNC) (Wik et al. 2011).

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

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

79 spectroscopy. The properties of the GWP reinforced composites were compared to reference bioPU
80 and to composite reinforced with bleached chemical pulp cellulose fibers.

81 **2. Experimental**

82 2.1. Materials

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

90 2.2. Methods

91 2.2.1. Fiber content

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

97 2.2.2. Disintegration of cellulosic fibers to polyol

98 Instead of water, castor oil was utilized for the first time as a less polar medium to disintegrate
99 GWP fibers with high lignin content. The never dried GWP was mixed with the polyol in three
100 different consistencies to produce suspensions with 1, 3 and 5wt% fiber content. Similar 1wt%
101 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

125 From the prepared fiber in polyol dispersions composites were fabricated by mixing with pMDI.
126 First, the pMDI and fiber in polyol dispersion were preheated in an oven at 100 °C. Excess of pMDI
127 was used in the fabrication to achieve sufficient reaction with the hydroxyl groups of the fibers and
128 polyol. 30 g of preheated pMDI was mixed with 40 g of fiber in polyol dispersion with a hot plate
129 magnetic stirrer adjusted to 100 °C. The reference bioPU was fabricated with the same pMDI (30 g)
130 polyol (40 g) ratio. The mixing was continued for around 5 minutes until the viscosity of the
131 mixture notably increased. The sample preparation was finished with defoaming and mixing for two
132 minutes with a Thinky mixer (ARE-250, Japan). Finally the sample was poured in a Teflon mold
133 (10x10x0.4 cm), which was transferred in an oven for overnight curing at 100 °C. Smaller Teflon
134 mold (11x5x0.4 cm) was utilized for the sample with the highest degree of fibers due to increased
135 viscosity, which made the casting more difficult as air bubbles occurred when using mold with
136 larger surface area. Reference bioPU was prepared from pure castor oil without any added fibers
137 and named as Ref. The samples were labeled according to the total fiber content of the composites.
138 Composites prepared from the ground GWP fiber dispersion of 1, 3, 5, 7 and 9wt% were named as
139 L0.6%, L1.7%, L2.9%, L4% and L5.1%, respectively. The composite from BP fiber in polyol
140 dispersion of 1wt% was labeled as B0.6%.

141 2.3. Characterization

142 2.3.1. Fiber morphology

143 Morphological imaging of the original GWP, BP and the fibers ground in polyol was performed
144 with a FE-SEM (Sigma HD VP, Germany) at an accelerating voltage of 3kV. For the imaging of
145 ground fibers small drop from each of the fiber in polyol dispersion was placed in a beaker and
146 diluted to 100 ml of acetone/water mixture. The dilutions were dispersed with Ultraturrax mixer at
147 10000 rpm for 3 min. From the dilutions 5 ml of the dispersed sample was taken and filtered slowly
148 with low pressure on top of membrane (pore size 0.2 µm). The original GWP and BP were
149 disintegrated and diluted to water. Similar filtering was applied as stated above. The filtered

150 samples together with the membrane were dipped into liquid nitrogen to freeze the fibers and the
151 specimens were immediately transferred to a freezer. The frozen samples were freeze-dried
152 (ScanVac, Coolsafe 55-15 Pro, Denmark) overnight. After freeze-drying specimens were fixed to
153 sample holders and the surfaces were sputter-coated with platinum (Pt).

154 2.3.2. Tensile testing

155 Dog bone shaped standard specimens (Fig. 3) were cut from the casted bioPUs with an Instron
156 hollow die punch (Pneumatic P/N 6054.000, Italy). Mechanical properties were tested according to
157 a standard method (ISO 527) using a Zwick/Roell universal testing machine (Z010, Germany) fixed
158 with extensometer and a 200 N load cell. The distance of the grips was 45 mm, the sample width
159 3.9 mm and thickness 4-5 mm. In total 5 specimens from each sample were measured to investigate
160 the mechanical properties. In the beginning the measurement 1 mm/min strain rate was applied to
161 calculate Young's modulus followed by increase to constant 50 mm/min strain rate until breakage
162 of the sample from which maximum stress and strain at break were determined. Standard deviations
163 were calculated accordingly.

164 2.3.3. Composites morphology

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

169 2.3.4. Dynamic mechanical analysis

170 DMA of the reference bioPU and composites was conducted with TA instruments (DMA Q800,
171 Delaware, USA) equipped with a liquid nitrogen cooling apparatus, in the single cantilever clamp
172 mode. The samples were cooled down and held isothermally for 2 min at $-100\text{ }^{\circ}\text{C}$ and then heated
173 to $150\text{ }^{\circ}\text{C}$ with a constant heating rate of $5\text{ }^{\circ}\text{C}/\text{min}$. 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 °C at a heating speed of 10 °C/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

197 the residual pulp left between discs. The hot polyol tended to separate from the hydrophilic BP and
198 flowed faster through the discs separating a chunky portion of pulp at the end of each circulation.
199 After the release of the discs sufficient mixing was required to disperse the fibers homogenously
200 with the polyol. The later bypasses were performed with continuous operation as the suspension
201 started to reach more homogenous liquid flowing form. The poor dispersion between the BP and
202 polyol resulted in processing difficulties and higher consistencies were not practical or feasible to
203 employ. The better compatibility with GWP is related to the high lignin content, which makes the
204 fiber surface hydrophobic and improves the fiber dispersion to polyol. In this study we were able to
205 fabricate ground GWP fiber in polyol dispersions up to 5wt% but we believe up to 8wt%
206 consistency would still be possible to process. Also the use of elevated temperature is advantageous
207 for the processing because of the viscosity decrease and possible thermal softening of both lignin
208 (Goring 1963) and wood (Blechsmidt et al. 1986). Standard water-based systems are limited in
209 their low maximum operation consistency (Hu et al. 2015), which restricts their capacity.

210 The stability of the ground fibers in polyol dispersions was investigated by letting the samples settle
211 for 7 weeks (Fig. 1). The specimen with the least amount of GWP show most rapid sedimentation
212 compared to the dispersions with higher consistencies (3wt% and 5wt%), which all remained almost
213 as a single phase system even after 7 weeks. In the top part of the samples (3wt% and 5wt%) a
214 small separated polyol layer can be seen. A higher viscosity of the samples constrained the fiber
215 settling and increased the dispersion stability. The 1wt% BP and GWP showed most clear and rapid
216 settling of fibers depending on the processing degree i.e. the samples with the least amount of
217 bypasses (5) settled faster and formed more compact layers to polyol, which is best seen with the
218 BP samples after 7 weeks. The centrifugation of 5wt% fiber in polyol dispersion led to clear
219 separation of transparent polyol in the top and compacted fibers in the bottom of the decanter
220 indicating the settling can be forced by subjecting the dispersion to external gravitational force.

221

222 **Figure 1.** Settling of ground fibers in polyol dispersions as a function of storage time. From left to
 223 right: Pure castor oil, BP 1wt%, GWP 1wt%, GWP 3wt% and GWP 5wt%. Fibers in polyol
 224 dispersions are in the sets of three after 5, 10 and 15 bypasses through -100µm Masuko disc
 225 clearance.

226 The morphology of the original pulps and the Masuko ground pulps was investigated by FE-SEM.
 227 It was observed that the original BP prior to grinding (Fig. 2 (1)) occurred in its characteristic long
 228 and flexible fibers without defects whereas the GWP had both large fibers and smaller disintegrated
 229 fibrils with small filaments produced by the initial mechanical processing of wood. The Masuko
 230 grinding caused random cutting and tearing of the fibers, which resulted in micron sized fibers with
 231 a broad size distribution with all of the prepared samples (Fig. 2 (3-6)). Compared to traditional

232 aqueous fibrillation of fibers, opening of the fibrillar fiber structure was hardly observed on the
233 surface of the fibers neither with GWP nor with BP. Favorable internal fibrillation of fibers does
234 most likely not occur as the hydrophobic polyol does not penetrate inside the fiber cell wall causing
235 swelling like water does (Iwamoto et al. 2007). The Masuko grinding of BP in water (instead of
236 polyol) using the applied parameters would ultimately lead to a formation of CNF (Abe et al. 2007).
237 Here, it was shown that lignin is not alone the prohibitive factor for the fibrillation of fibers as the
238 morphology of ground BP was similar with the GWP specimens. Also the polyol was working as a
239 lubricant and its low viscosity induced by heating reduced the fiber friction and thus total combined
240 shear and tear forces impacting the fibers were lower compared to water-based system. The GWP is
241 challenging to fibrillate even in water due to the cross-linked barrier of lignin binding the fibers
242 together. In previous studies intensive mechanical grinding has also been subjected to wood fibers
243 with high lignin content but the liberation of fibrils below micron size has not been successful
244 (Spence et al. 2010; Hoeger et al. 2013) without newly applied pulping strategies (Rojo et al. 2015).
245 In respect to the current study, microfibers with increased surface area were directly obtained in
246 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

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

264
265 **Figure 3.** Reference bioPU, its composites and corresponding dog bone specimen (top row from
266 left to right: Ref, B0.6%, L0.6%, L1.7%, L2.9%, bottom row from left to right: fibers separated
267 from supernatant after centrifugation of 5wt% fiber in polyol dispersion, composites of L4.0%,
268 L5.1% (smaller mold was applied to L5.1% to ease casting of viscous dispersion).

269 3.2.1. Chemical structure

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

279
 280 **Figure 4.** FTIR spectra for the reference bioPU and its composites.

281 3.2.2. Mechanical properties

282 Stress-strain curves for reference bioPU and composites plotted from tensile test results are shown
283 in Figure 5 and their corresponding numeric values are presented in Table 1. Incorporation of
284 evenly dispersed micron-sized GWP to bioPU had a positive impact on the mechanical properties
285 where maximum increase in modulus 14.6% (L5.1%), stress 54.5% (L5.1%), and strain 26.1%
286 (L2.9%) were obtained compared to bioPU reference. Even with the lowest fiber loading (L0.6%)
287 both the strength and strain improved. The stiffness of the composites started to decidedly increase
288 only with the highest fiber content (L5.1%) while the strain decreased simultaneously. Interestingly
289 with all of the studied specimen no sacrifice in contrast to reference bioPU was noted in any
290 property, which has usually been the case in previous studies when natural fibers (Maafi et al.
291 2010), MCC (Głowińska and Datta 2015), CNF (Benhamou et al. 2015) or CNCs (Wik et al. 2011)
292 have been added to bioPU. Generally the cellulosic fibers with fluctuating dimensions have
293 improved stiffness of the bioPU composites but decreased ductility. In this study however, both
294 toughness and ductility were improved in addition to moderate build-up of stiffness, which bespoke
295 of good interfacial adhesion between the bioPU matrix and fibers (Wu et al. 2007). The use of
296 reinforcing microfibers from BP also improved the properties of composites and features similar
297 with L1.7% were obtained even with small addition of fibers (B0.6%). The cellulose rich
298 microfibers have similar reinforcing tendency in respect to GWP and their hydroxyl group rich
299 surface improves the compatibility in bioPU fabrication. Overall, the microfibers reinforced the
300 bioPU and withstood higher loads as additional fiber pulling or breakage was required prior fracture
301 of the composites. It is believed the mechanical features could yet be improved if the fiber loading
302 could be increased and all the trapped air within the casted composites could be removed, which
303 created some issues with the highest fiber contents and was seen in larger deviations between the
304 measured specimens.

Table 1. Mechanical properties and location of $\tan \delta$ peaks from DMA of composites and reference bioPU.

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

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

3.2.3. Composites surface morphology

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

321 **Figure 6.** Cross-sectional fractured surfaces of the composites showing the occurrence of both
322 individual micro-sized fibers and empty cavities remaining after the fracture of the structures.

323 B0.6% (1), L1.7% (2), L4.0% (3) and close-up image of fibers from L4.0% sticking out of the
324 fractured surface (4).

325

326 3.2.4. Viscoelastic properties

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

342

343 **Figure 7.** Storage modulus and $\tan \delta$ of bioPUs and reference as a function of temperature.

344 3.2.5. Thermal properties

345 The reference bioPU and the composites with the least amount of embedded fibers shared identical
 346 TGA curves in nitrogen atmosphere (Fig. 8 a) indicating the low addition of fibers does not affect
 347 the thermal properties of composites. The composites with increasing fiber loading exhibited higher
 348 final mass yields compared to bioPU. The GWP with high lignin content showed lower onset
 349 temperature and highest char content. The fibers had a high lignin content, which is difficult to
 350 decompose (Gani and Naruse 2007) in addition to other wood components, which were not present
 351 in BP. BP had a high cellulose content with only small traces of residual components, which
 352 explains the differences between GWP in the results. From the curves gradual decomposition was
 353 noted to occur at 230 °C and more drastic drop appeared after reaching 310 °C where 50% weight
 354 loss (T_{50}) was observed between 415-408 °C, for reference bioPU and composites, respectively. The

355 TGA curves confirm the successful compatibility with PU and reinforcing fibers as the
 356 decomposition of fibers in composites was restricted and occurred together with PU at higher
 357 temperature compared to neat fibers. The reference bioPU and composites started to degrade in
 358 three stages based on the derivative TGA curves (Fig. 8 b), which are associated to the weight loss
 359 steps of specimen. In the early stages (150-200 °C) urethane bonds start to degrade and are
 360 irreversibly decomposed after reaching temperatures higher than 200 °C (Javni et al. 2000). Castor
 361 oil is known to undergo complex degradation steps and its decomposition has been reported to
 362 occur around 420 °C (Choi et al. 2015). In the final stage the remaining PUs ultimately decomposes
 363 and no further reactions occur in nitrogen at temperatures above 500 °C.

364
 365 **Figure 8.** TGA thermograms in nitrogen atmosphere (a) and derivative TGA curves (b) for fibers,
 366 reference bioPU and composites.

368 4. Conclusions

369 Based on the results the presented methodology introduces a new way to produce fiber reinforced
 370 bioPU composites by utilizing low-cost fibers with minor processing degree directly for fabrication.
 371 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 $\tan \delta$ 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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References

- Abe K, Iwamoto S, Yano H (2007) Obtaining Cellulose Nanofibers with a Uniform Width of 15 nm from Wood. *Biomacromolecules* 8:3276–3278. doi: 10.1021/bm700624p
- Barrioni BR, de Carvalho SM, Oréfice RL, et al (2015) Synthesis and characterization of biodegradable polyurethane films based on HDI with hydrolyzable crosslinked bonds and a homogeneous structure for biomedical applications. *Mater Sci Eng C* 52:22–30. doi: 10.1016/j.msec.2015.03.027

- 398 Benhamou K, Kaddami H, Magnin A, et al (2015) Bio-based polyurethane reinforced with cellulose
399 nanofibers: A comprehensive investigation on the effect of interface. *Carbohydr Polym*
400 122:202–211. doi: 10.1016/j.carbpol.2014.12.081
- 401 Blechschmidt J, Engert P, Stephan M (1986) The glass transition of wood from the viewpoint of
402 mechanical pulping. *Wood Sci Technol* 20:263–272. doi: 10.1007/BF00350984
- 403 Chaudhari AB, Tatiya PD, Hedao RK, et al (2013) Polyurethane Prepared from Neem Oil
404 Polyesteramides for Self-Healing Anticorrosive Coatings. *Ind Eng Chem Res* 52:10189–
405 10197. doi: 10.1021/ie401237s
- 406 Choi KK, Park SH, Oh KW, Kim SH (2015) Effect of castor oil/polycaprolactone hybrid polyols on
407 the properties of biopolyurethane. *Macromol Res* 23:333–340. doi: 10.1007/s13233-015-
408 3052-y
- 409 Faruk O, Sain M, Farnood R, et al (2013) Development of Lignin and Nanocellulose Enhanced Bio
410 PU Foams for Automotive Parts. *J Polym Environ* 22:279–288. doi: 10.1007/s10924-013-
411 0631-x
- 412 Ferreira P, Pereira R, Coelho JFJ, et al (2007) Modification of the biopolymer castor oil with free
413 isocyanate groups to be applied as bioadhesive. *Int J Biol Macromol* 40:144–152. doi:
414 10.1016/j.ijbiomac.2006.06.023
- 415 Gani A, Naruse I (2007) Effect of cellulose and lignin content on pyrolysis and combustion
416 characteristics for several types of biomass. *Renew Energy* 32:649–661. doi:
417 10.1016/j.renene.2006.02.017
- 418 Głowińska E, Datta J (2015) Bio polyetherurethane composites with high content of natural
419 ingredients: hydroxylated soybean oil based polyol, bio glycol and microcrystalline
420 cellulose. *Cellulose* 23:581–592. doi: 10.1007/s10570-015-0825-6
- 421 Goring D (1963) Thermal softening of lignin, hemicellulose and cellulose. *Pulp Pap Mag Can*
422 64:517–527.
- 423 Hassan MK, Mauritz KA, Storey RF, Wiggins JS (2006) Biodegradable aliphatic thermoplastic
424 polyurethane based on poly(ϵ -caprolactone) and L-lysine diisocyanate. *J Polym Sci Part*
425 *Polym Chem* 44:2990–3000. doi: 10.1002/pola.21373
- 426 Hoeger IC, Nair SS, Ragauskas AJ, et al (2013) Mechanical deconstruction of lignocellulose cell
427 walls and their enzymatic saccharification. *Cellulose* 20:807–818. doi: 10.1007/s10570-013-
428 9867-9
- 429 Hu C, Zhao Y, Li K, et al (2015) Optimizing cellulose fibrillation for the production of cellulose
430 nanofibrils by a disk grinder. *Holzforschung* 69:993–1000. doi: 10.1515/hf-2014-0219
- 431 Iakovlev M, Heiningen A van (2012) Kinetics of fractionation by SO₂–ethanol–water (SEW)
432 treatment: understanding the deconstruction of spruce wood chips. *RSC Adv* 2:3057–3068.
433 doi: 10.1039/C2RA00957A
- 434 Iwamoto S, Nakagaito AN, Yano H (2007) Nano-fibrillation of pulp fibers for the processing of
435 transparent nanocomposites. *Appl Phys A* 89:461–466. doi: 10.1007/s00339-007-4175-6

436 Javni I, Petrović ZS, Guo A, Fuller R (2000) Thermal stability of polyurethanes based on vegetable
 437 oils. *J Appl Polym Sci* 77:1723–1734. doi: 10.1002/1097-4628(20000822)77:8<1723::AID-
 438 APP9>3.0.CO;2-K

439 Kunduru KR, Basu A, Haim Zada M, Domb AJ (2015) Castor Oil-Based Biodegradable Polyesters.
 440 *Biomacromolecules* 16:2572–2587. doi: 10.1021/acs.biomac.5b00923

441 Lee A, Deng Y (2015) Green polyurethane from lignin and soybean oil through non-isocyanate
 442 reactions. *Eur Polym J* 63:67–73. doi: 10.1016/j.eurpolymj.2014.11.023

443 Maafi EM, Tighzert L, Malek F (2010) Elaboration and characterization of composites of castor oil-
 444 based polyurethane and fibers from alfa stems. *J Appl Polym Sci* 118:902–909. doi:
 445 10.1002/app.32464

446 Meier MAR, Metzger JO, Schubert US (2007) Plant oil renewable resources as green alternatives in
 447 polymer science. *Chem Soc Rev* 36:1788–1802.

448 Mohammed IA, Al-Mulla EAJ, Kadar NKA, Ibrahim M (2013) Structure-Property Studies of
 449 Thermoplastic and Thermosetting Polyurethanes Using Palm and Soya Oils-Based Polyols.
 450 *J Oleo Sci* 62:1059–1072. doi: 10.5650/jos.62.1059

451 Narine SS, Kong X, Bouzidi L, Sporns P (2006) Physical Properties of Polyurethanes Produced
 452 from Polyols from Seed Oils: I. Elastomers. *J Am Oil Chem Soc* 84:55–63. doi:
 453 10.1007/s11746-006-1006-4

454 Oprea S, Potolinca VO, Gradinariu P, et al (2016) Synthesis, properties, and fungal degradation of
 455 castor-oil-based polyurethane composites with different cellulose contents. *Cellulose* 1–12.
 456 doi: 10.1007/s10570-016-0972-4

457 Özgür Seydibeyoğlu M, Oksman K (2008) Novel nanocomposites based on polyurethane and micro
 458 fibrillated cellulose. *Compos Sci Technol* 68:908–914. doi:
 459 10.1016/j.compscitech.2007.08.008

460 Petrović ZS, Guo A, Javni I, et al (2008) Polyurethane networks from polyols obtained by
 461 hydroformylation of soybean oil. *Polym Int* 57:275–281. doi: 10.1002/pi.2340

462 Petrović ZS, Zhang W, Javni I (2005) Structure and Properties of Polyurethanes Prepared from
 463 Triglyceride Polyols by Ozonolysis. *Biomacromolecules* 6:713–719. doi:
 464 10.1021/bm049451s

465 Rojo E, Peresin MS, Sampson WW, et al (2015) Comprehensive elucidation of the effect of residual
 466 lignin on the physical, barrier, mechanical and surface properties of nanocellulose films.
 467 *Green Chem* 17:1853–1866. doi: 10.1039/C4GC02398F

468 Shirke A, Dholakiya B, Kuperkar K (2015) Novel applications of castor oil based polyurethanes: a
 469 short review. *Polym Sci Ser B* 57:292–297. doi: 10.1134/S1560090415040132

470 Silva MC, Silva GG (2005) A new composite from cellulose industrial waste and elastomeric
 471 polyurethane. *J Appl Polym Sci* 98:336–340. doi: 10.1002/app.22043

472 Somani K, Kansara S, Parmar R, Patel N (2004) High Solids Polyurethane Coatings from Castor--
 473 Oil--Based Polyester--Polyols. *Int J Polym Mater* 53:283–293. doi:
 474 10.1080/00914030490267618

475 Spence KL, Venditti RA, Rojas OJ, et al (2010) The effect of chemical composition on
 476 microfibrillar cellulose films from wood pulps: water interactions and physical properties
 477 for packaging applications. *Cellulose* 17:835–848. doi: 10.1007/s10570-010-9424-8

478 Tibério Cardoso G, Claro Neto S, Vecchia F (2012) Rigid foam polyurethane (PU) derived from
 479 castor oil (*Ricinus communis*) for thermal insulation in roof systems. *Front Archit Res*
 480 1:348–356. doi: 10.1016/j.foar.2012.09.005

481 Wik V m., Aranguren M i., Mosiewicki M a. (2011) Castor oil-based polyurethanes containing
 482 cellulose nanocrystals. *Polym Eng Sci* 51:1389–1396. doi: 10.1002/pen.21939

483 Wu Q, Henriksson M, Liu X, Berglund LA (2007) A High Strength Nanocomposite Based on
 484 Microcrystalline Cellulose and Polyurethane. *Biomacromolecules* 8:3687–3692. doi:
 485 10.1021/bm701061t

486 Xu B, Huang WM, Pei YT, et al (2009) Mechanical properties of attapulgite clay reinforced
 487 polyurethane shape-memory nanocomposites. *Eur Polym J* 45:1904–1911. doi:
 488 10.1016/j.eurpolymj.2009.04.004

489 Zhang C, Wu H, Kessler MR (2015) High bio-content polyurethane composites with urethane
 490 modified lignin as filler. *Polymer* 69:52–57. doi: 10.1016/j.polymer.2015.05.046

491 Zhang C, Xia Y, Chen R, et al (2013) Soy-castor oil based polyols prepared using a solvent-free and
 492 catalyst-free method and polyurethanes therefrom. *Green Chem* 15:1477–1484. doi:
 493 10.1039/C3GC40531A

494 Zhou X, Sain MM, Oksman K (2016a) Semi-rigid biopolyurethane foams based on palm-oil polyol
 495 and reinforced with cellulose nanocrystals. *Compos Part Appl Sci Manuf* 83:56–62. doi:
 496 10.1016/j.compositesa.2015.06.008

497 Zhou X, Sethi J, Geng S, et al (2016b) Dispersion and reinforcing effect of carrot nanofibers on
 498 biopolyurethane foams. *Mater Des* 110:526–531. doi: 10.1016/j.matdes.2016.08.033

499