

Sphagnum moss as a functional reinforcement agent in castor oil-based biopolyurethane composites

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SUMMARY

- (1) Sphagnum mosses are an abundant source of structural molecules, similar to lignocelluloses in rooted plants, having properties advantageous in biopolyurethane composites: their hydrophobicity when dry facilitates dispersion into biopolyols; hydroxyl groups provide cross-linking with the polyurethane (PU) matrix; and easy grindability enables small particle size, down to 10 μm with low energy consumption and a large interface for isocyanate to react with.
- (2) The present study introduces a novel use of Sphagnum moss as a reinforcement filler incorporated into castor oil. Two moss grades, a slightly and a moderately humified moss (having hydroxyl, equivalent to KOH, of 255 and 359 mg g^{-1} , respectively), were pulverised and dispersed into castor oil (KOH equivalent 160 mg g^{-1}) in mass proportions of 0–28 %. Mixtures were reacted with polymeric diphenylmethane diisocyanate to produce reinforced biopolyurethane (bioPU) composites.
- (3) The mechanical properties tested according to ISO 527 improved similarly with both fillers. With increasing filler content, tensile strength increased monotonically up to 450 % and Young's modulus up to 350 % while the strain at break point (at around 90 %) remained almost unchanged over the whole range of filler contents. The shift of the 'tan delta' peak' (energy damping coefficient during deformation) toward higher temperatures with increasing filler content indicated strong cross-linking between the filler and the PU matrix, while the width of the peaks was narrow and remained virtually unchanged showing the filler to be homogeneously dispersed within the matrix.
- (4) Overall, Sphagnum filler may provide a straightforward and cost-effective reinforcement for (bio)polyurethanes.

KEY WORDS: biocomposite, biofiller, peat, polyurethane, vegetable oil

INTRODUCTION

Renewability, abundance, and low cost are motivators for the use of biobased raw materials in a sustainable economy. For polyurethane (PU) products, potential candidates to replace polyols originating from petroleum byproducts are vegetable oils and lignocelluloses or their components (Petrović 2008, Laurichesse & Avérous 2014, Arshanitsa *et al.* 2016, Mahmood *et al.* 2016). Another way to increase the content of renewable resources in a product is to use biomass filler. Biopolyurethane (bioPU) may be included in products like foams, elastomers, and adhesives (Narine *et al.* 2007, Zhou *et al.* 2016, Santan *et al.* 2018).

Biopolyurethane is synthesised via the reaction of isocyanate and biobased polyol. Various vegetable oils such as sunflower, canola (rapeseed), soybean, corn, and linseed oils, have been studied as a renewable source of biopolyols in PU production

(Zlatanovic *et al.* 2004). In addition to these, castor oil is a widely studied biopolyol because it contains natural hydroxyl groups. This enables its direct use in bioPU manufacture while other vegetable oils need chemical modification to introduce hydroxyl groups (Petrović 2008, Chaudhari *et al.* 2013, Mohammed *et al.* 2013). By altering the amount of hydroxyl groups of any biopolyol, the cross-linking density, glass transition temperature, and mechanical properties of bioPU can be adjusted (Petrović *et al.* 2008).

Lignocelluloses are also a prominent raw material for polyurethanes because there are many reactive hydroxyl groups in their main constituents: cellulose, hemicellulose, and lignin. The use of lignocellulose materials together with polyols in biopolyurethane synthesis has been studied in several publications. Lignocelluloses have often been used in liquefied form in order to ensure good mixing of reagents (Demirbas 2008, Shao *et al.* 2012, Wang *et al.* 2013, Lee & Lee 2016). Lignocelluloses have also been

used in their particulate or fibrous form as reinforcement filler (Silva & Silva 2005, Casado *et al.* 2009, Rácz *et al.* 2009, Maafi *et al.* 2010, Shao *et al.* 2012, Tavares *et al.* 2016, Visanko *et al.* 2017) and these materials could be called polyurethane biocomposites or biopolyurethane composites. It has been suggested that biofiller incorporated into biopolyol increases the susceptibility of polyurethanes to fungal attack and therefore increases their biodegradability (Oprea *et al.* 2016) which may be a desirable or undesirable feature depending on usage.

Sphagnum moss may not be lignocellulose in the strict sense but its structural molecules are similar to those in rooted plants. It is an abundant and productive moss that grows in bogs and other wetlands, especially in the boreal region. Globally, peatlands cover about 3 % (4 Mm²) of the land area (Charman 2002). Sphagnum growth is indeterminate; its upper part continues growing upwards while the previously upper but now buried part decomposes and is slowly transformed to peat (Gobat *et al.* 2004). Annual biomass production can be 2.5–4.5 metric tons per hectare (Silvan 2010) but even higher rates, of up to 6.9 t ha⁻¹, have been reported (Gaudig *et al.* 2014). Sphagnum peat is nowadays harvested from drained natural bogs and wetlands but for the sake of sustainability paludiculture is now emerging, i.e., Sphagnum farming is expected to take place by rewetting cut-away peatlands (Pouliot *et al.* 2015).

Sphagnum has the interesting property of being hydrophobic when dried (Koivuranta *et al.* 2017), which makes it easily dispersible into hydrophobic polyols. During humification, the hydrophobicity of moss increases, which is attributed to a decreasing proportion of easily degraded polysaccharides and an increasing share of phenolic compounds, waxes, and extractives. Due to its hydrophobicity and good dispersibility into oils, Sphagnum is an interesting biomass for biopolyurethanes. The urethane linkage in polyurethane is a result of reaction between diisocyanate's isocyanate group (NCO) and a polyol's hydroxyl group (OH). Sphagnum contains abundant hydroxyl groups, which makes it reactive during synthesis and a strong interfacial adhesion between matrix and filler during PU synthesis is expected. An additional advantage of Sphagnum is its easy grindability: grinding energy consumption for a given particle size being only of the order of 10 % of that for other biomasses such as wood, straw, and cellulose (Ämmälä *et al.* 2018). Utilisation of Sphagnum filler in polyurethanes would be a straightforward, economically viable process and could easily be adopted in practice. There is no need for thermochemical pre-processing, use of organic

solvent, or other chemicals: drying, grinding, and mixing with a polyol is enough.

Because of its advantageous properties described above, Sphagnum can be expected to be an outstanding choice as a low-cost reinforcement biofiller for use in biopolyurethane composites. We know of no earlier publications on using *Sphagnum* in this kind of application. We now report the first such attempt.

METHODS

Two Sphagnum peat grades, slightly-humified and moderately-humified, were chosen for this study. We refer to them as 'Sphagnum' rather than 'peat' because it is the properties of the moss that are important: samples of peat without Sphagnum would not produce the effects that interest us. The aim was to evaluate the processability of the biofillers and their reinforcement effects on the mechanical properties of biopolyurethane composites.

Raw materials

Castor oil was purchased from Carl Roth (Germany). Hydroxyl value, as KOH equivalent, and acid value of castor oil was ≥ 160 mg g⁻¹ and ≤ 1.5 mg g⁻¹, respectively. Polymeric diphenylmethane diisocyanate (pMDI) prepolymer (VIBRATHANE® 8000, NCO = 16.5 %) was obtained from Chemtura (Italy).

The two Sphagnum samples were obtained from Vapo (Finland), differing from each other in their degree of humification. According to the von Post classification (H1–H10), one was slightly humified (H2) and the other was moderately humified (H6). The samples having a moisture content of 20–30 % were homogenised by pre-grinding using a Rapid 40 knife mill (Rapid Granulator, Sweden) with a perforated screen of 4 mm. After that the samples were dried at 65 °C for at least 48 h. Size reduction was finalised by grinding the dry mosses (moisture content 2–3 %), in a 50 ZPS high-speed rotary impact mill (Hosokawa Alpine, Germany) integrated in a closed grinding circuit with a 50 ATP air classifier (Hosokawa Alpine, Germany) - a machine which separates materials using their size, shape, and density, by streaming the material into a chamber which contains a column of rising air. A mill rotor frequency of 20,000 rpm and a classifier frequency of 10,000 rpm were used. The visual appearance of the resulting powders is shown in Figure 1.

The characterisation of the two von Post humification grades is presented in Table 1. The chemical composition of the homogenised samples was analysed using standard methods for acetone

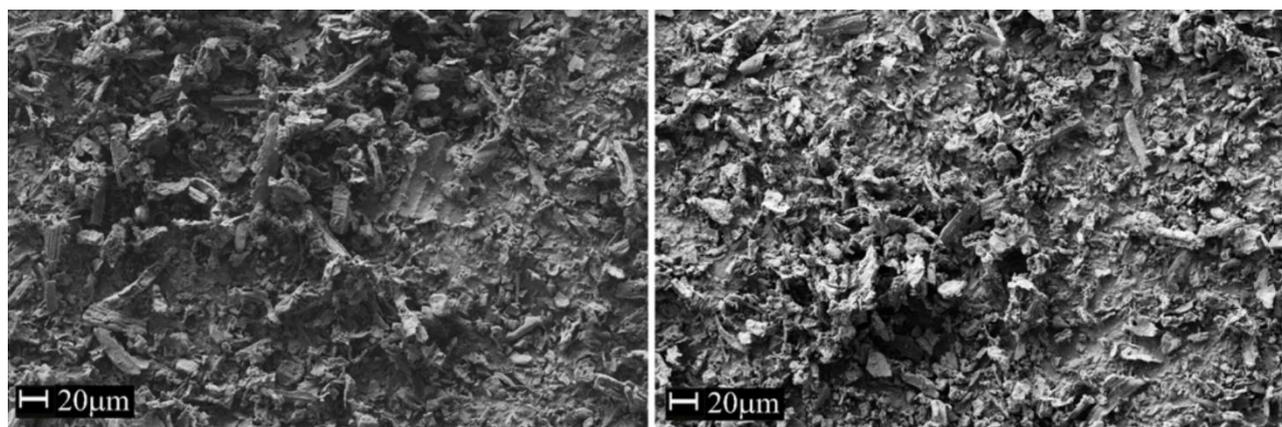


Figure 1. Enlarged particle morphology of the samples: H2 (left) and H6 (right).

Table 1. Composition of Sphagnum moss grades, mean and range ($n = 2$).

Grade (von Post humification)	H2	H6
Acetone extractives (%)	4.3 ± 0.1	7.6 ± 0.1
Cellulosic (%)	19.6 ± 0.7	12.0 ± 0.2
Weak acid hydrolysed substances (%)	55.1 ± 1.1	36.9 ± 0.4
Klason lignin (%)	20.9 ± 0.1	43.8 ± 0.3
Ash 525 °C (%)	1.3 ± 0.1	3.1 ± 0.8
Particle median size (μm)	10.7	17.3
Aspect ratio (as quotient)	3.7	4.8
Water contact angle ($^{\circ}$)	107 ± 2	110 ± 2
Hydroxyl value (KOH equiv, mg g^{-1})	255 ± 5	359 ± 3

soluble extractives (TAPPI T280), acid insoluble lignin, i.e., Klason lignin (TAPPI T222), and ash content at 525 °C (ISO 1762) and 900 °C (ISO 2144). Easily hydrolysed substances, including hemicellulose, pectin, and proteins, were leached from extractant-free samples by acid hydrolysis with boiling 2 % hydrochloric acid for five hours (Smith *et al.* 1958). ‘Cellulose’ was measured by the Kürchner-Hoffner method (Reid & Lynch 1937). Hydroxyl groups were analysed using acetic anhydride acetylation in accordance with ASTM E222-10.

The volumetric particle size distribution was measured with an LS 13320 laser diffraction-based particle size analyser (Beckmann Coulter, USA). A one-dimensional particle size (diameter) is related to

the size of an equivalent sphere.

The aspect ratios (quotients; length divided by width) of the particles were determined from optical images of a CCD camera with a Metso IMG image analyser. Analysis was based on more than 100,000 particles. For the analysis, samples were diluted with deionised water into a suspension of 0.3 % and fractionated in a tube flow fractionator (Valmet, Finland), similarly to the method presented by Karinkanta & Laitinen (2017).

The water contact angles of the dry powder samples compressed by hydraulic press were measured by a static sessile-drop contact angle measurement method. Milli-Q water was used as a probe liquid at room temperature with a Krüss DSA100 system (Germany).

Preparation of biopolyurethane (bioPU) samples

The pMDI and polyol dispersion (castor oil and Sphagnum filler) were heated in an oven at 100 °C. The mass proportion of the filler in the polyol was adjusted as an experimental variable from 0 % to 28 %. To achieve sufficient reaction with the hydroxyl groups of the filler and polyol, stoichiometric excess of diisocyanate (NCO:OH ratio 1.03:1) was used in the curing reaction, in which 30 g of pMDI was added to 40 g of polyol dispersion while mixing with a hot plate magnetic stirrer at 100 °C. The viscosity of the mixture was monitored visually. After around 5 min the viscosity of the mixture started to increase rapidly. The mixture was defoamed and mixed for 2 min with a planetary centrifugal mixer (Thinky Mixer ARE-250, Japan) at 2000 rpm before moulding. The sample was poured into a Teflon mould (100 × 100 × 4 mm), which was further heated in an oven overnight at 100 °C in order to ensure complete curing. Besides neat castor oil, eight polyurethane samples with differing filler content were made with each (H2, H6) Sphagnum filler. The samples were named according to the total filler mass proportion of the biocomposites. Thus, the prepared biocomposites had a filler mass proportion of 0, 2, 4, ...16 %.

Characterisation of bioPU composites

Viscosity

Viscosities of the polyol/biofiller mixtures were measured as a function of three temperatures (21, 60, 105 °C) on a Discovery HR-1 rheometer (TA Instruments) using cone-plate geometry (cone diameter of 40 mm and cone-plate angle of 2°). All measurements were conducted at a constant shear rate of 100 s⁻¹.

Field-emission scanning electron microscopy (FESEM)

FESEM (Zeiss Ultra Plus, Germany) was employed to study the particle morphology of the samples and fracture surfaces from the broken specimens after tensile testing. Prior to FESEM imaging, the samples were conditioned overnight in a desiccator to remove moisture, and were then coated with carbon using the SEM sputter coater to improve the electric conductivity of the samples. The accelerating voltage during imaging was 5 kV.

Dynamic mechanical analysis (DMA)

In general, DMA is used to measure stiffness and the damping property of materials. These are reported as 'modulus' and 'tan delta'. In the analysis, sinusoidal force is applied to a sample of the material and the

response recorded. The modulus can be expressed as an in-phase component (the storage modulus), and an out-of-phase component (the loss modulus). The storage modulus expresses elasticity, and the loss modulus the viscous behaviour of the material. The quotient of loss/storage is the 'tan delta', which can also be called the damping factor. It is a measure of the energy dissipation, and it increases when approaching the transition temperatures of the material (see Figure 4 for examples).

DMA of the bioPU composites was conducted using a DMA Q800 (TA Instruments, 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 at a constant heating rate of 5 °C per minute. The DMA measurements were performed at a fixed frequency of 1 Hz and a fixed oscillation displacement of 0.02 mm. The rectangular samples had a length, width, and thickness of 15, 4, and 4 mm, respectively.

Tensile testing

An Instron hollow die punch (Pneumatic P/N 6054.000, Italy) was used to cut dog-bone shaped test specimens from the cast bioPUs. The specimens were 4 mm wide, 4 mm thick, and 75 mm long. Tensile properties of the samples were tested according to a standard method (ISO 527) using a Z010 universal testing machine (Zwick/Roell, Germany) equipped with a 200 N load cell and a MultiXtens extensometer. The initial distance between the grips was 45 mm and results are the means of measurements on 5–7 separate specimens from each sample. Young's modulus was measured at the beginning of the tensile test using a 1 mm per minute strain rate followed by a constant 50 mm per minute strain rate in tensile strength determination.

RESULTS

Figure 2 shows the visual appearance of the cast biopolyurethane samples. Neat biopolyurethane without filler was translucent and light in colour. Although the Sphagnum particles were brownish - H6 darker than H2 - even the smallest amount of Sphagnum filler (2 %) coloured the biopolyurethane samples black, which predicts enhanced UV stability.

Viscosity

Viscosity increased with increasing biofiller proportion in the polyol and decreasing temperature, as shown in Figure 3. From a practical point of view, with higher proportions the viscosity of the dispersion



Figure 2. Biopolyurethane samples. Mass proportions (%) of Sphagnum moss (from top to bottom): 16, 10, 4, and 0 %.

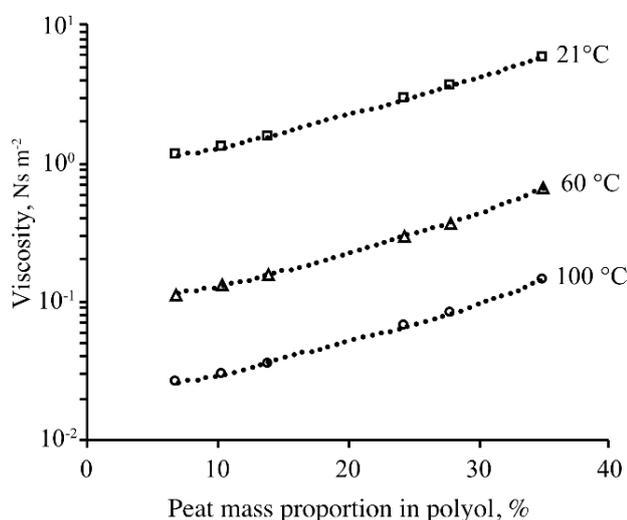


Figure 3. Viscosity of the mixture of H6 filler and castor oil at three temperatures.

may become too high at room temperature, which may cause inferior mixing with isocyanate during the polymerisation phase. Increasing the processing temperature, however, will reduce viscosity to a value similar to that of many commercial polyols.

Dynamic mechanical analysis (DMA)

The storage modulus and 'tan delta' (energy damping coefficient during deformation) as a function of temperature are shown in Figure 4 for H2 composites and in Figure 5 for H6 composites. Characteristic values of the DMA are listed in Table 2. In the glassy area at the lower temperature region, the proportional

differences between samples in storage modulus were insignificant (the y-axis is log scaled). In the rubbery area at the higher temperature region, the storage modulus increased proportionally with increasing biofiller content, which is a result of a structure more cross-linked by covalent bonds between the filler and isocyanate as well as a particulate reinforcement effect. Between the glassy and rubbery areas was a transition area that appears as a large decrease in the storage modulus, roughly in the temperature range from 0 to 50 °C (Figures 4 and 5).

The 'tan delta', whose clearly distinguishable peak is linked to the glass-to-rubber transition temperature, moved consistently toward higher temperatures with an increasing amount of biofiller (Table 2, Figures 4 and 5). The increasing trend shows that the filler and the polyurethane matrix interact strongly.

Fracture surfaces (FESEM)

The influence of the H2 filler loading proportion can be observed from the tensile fracture surface shown in Figure 6. Similar fracture surfaces were found with H6 filler. The micrograph at a low Sphagnum filler proportion (4 %) exhibited a smooth surface, and no particle pullouts are visible. At a high filler proportion (16 %), the surface is much rougher indicating suppression of crack propagation during specimen breakage. Additionally, the filler exhibited excellent dispersion across the fracture surfaces regardless of their mass proportions and no filler agglomerates are visible. The particles are covered with a polymer layer and there are no voids around the particles, indicating good wetting of the filler by the polymer matrix.

Tensile properties

The mechanical properties - tensile strength (Figure 7) and stiffness (Young's Modulus, Figure 8) - of the biopolyurethane composites was increased significantly by Sphagnum filler. Increasing the replacement of unmodified castor oil with finely ground Sphagnum increased tensile strength and tensile modulus monotonically up to filler proportions of 28 %, which corresponds to 16 % of the total proportion of mass of biopolyurethane (Figures 7 and 8). Although the chemical compositions and hydroxyl values differed from each other, the tensile properties developed in a similar manner with both the Sphagnum grades used, H2 and H6; these results were not surprising on the basis of the DMA results. The increase in tensile strength was about 450 % and in tensile modulus 350 %, without

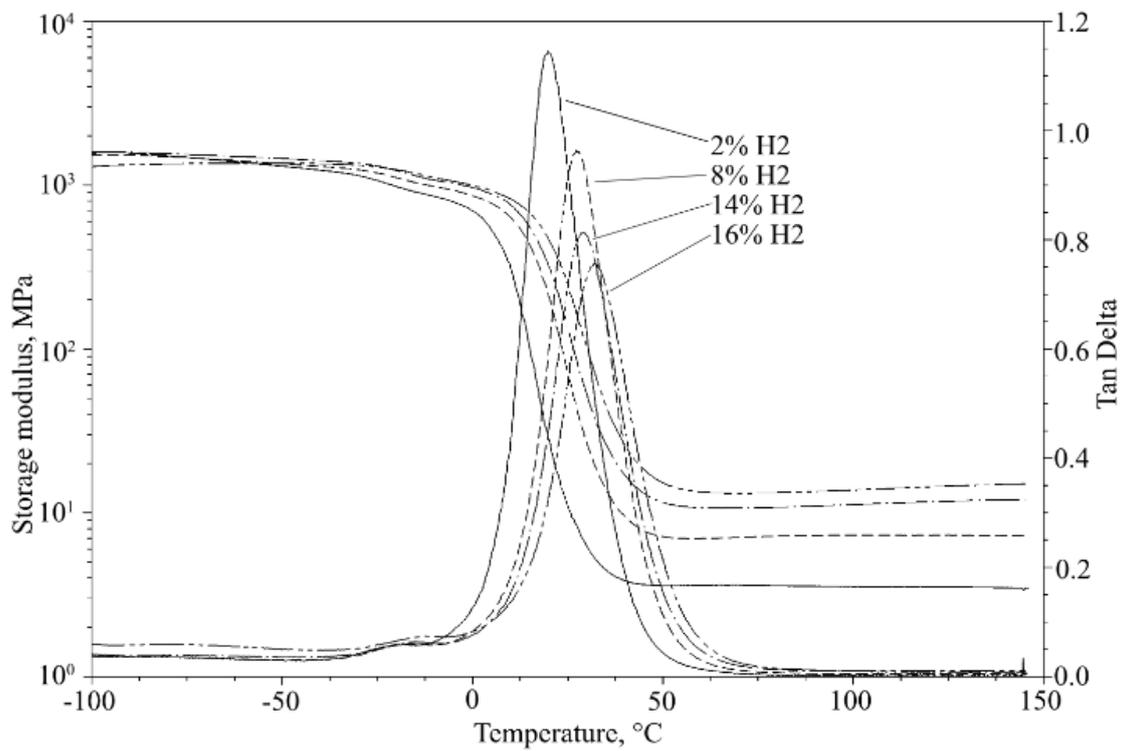


Figure 4. Storage modulus (left axis, rounded step curves) and 'tan delta' (right axis, peaked curves) of H2 composites. The upper plateau of the storage modulus curves is the 'glassy' region; the lower plateau (at higher temperatures) is the 'rubbery' region. The peak in 'tan delta' is the glass transition (T_g).

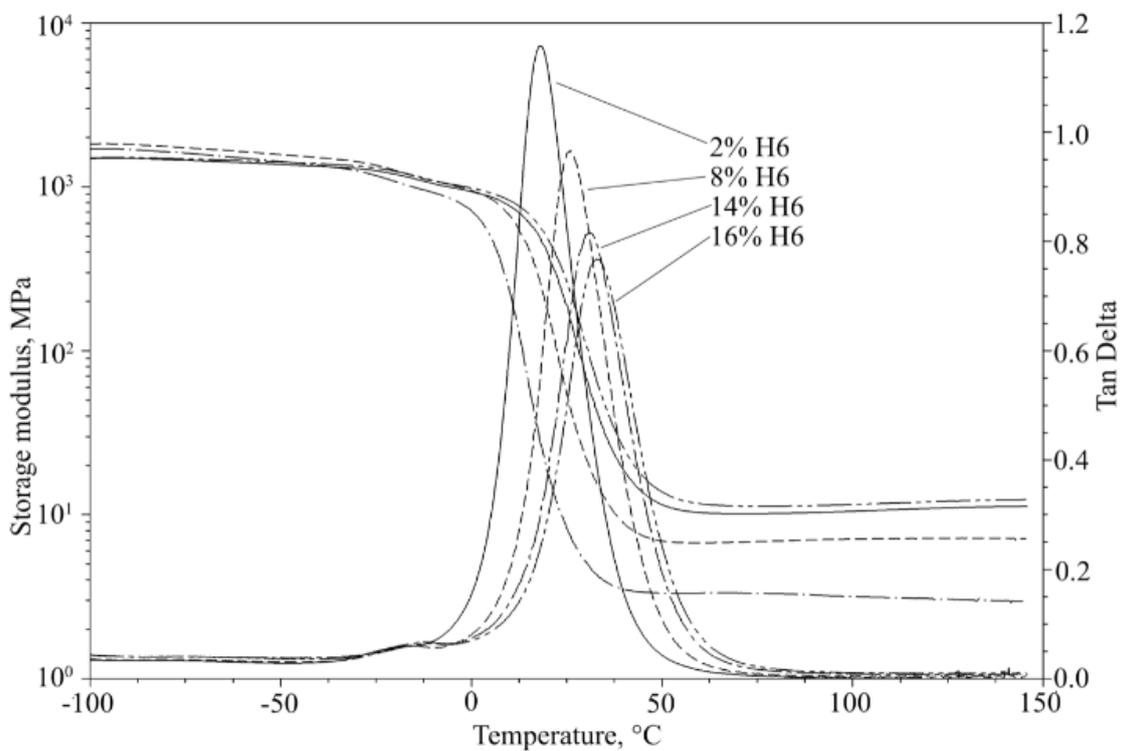


Figure 5. Storage modulus (left axis, rounded step curves) and 'tan delta' (right axis, peaked curves) of H6 composites. See Figure 4 caption for other details.

Table 2. Summary of DMA results.

Filler mass proportion	Glass transition temperature (°C)		'tan delta' peak (°C)		'tan delta' width at half peak height (°C)	
	H2	H6	H2	H6	H2	H6
0 %	2.8	2.8	6.3	6.3	20.4	20.4
2 %	10.2	7.2	19.8	18.2	19.5	19.7
8 %	15.7	14.7	27.3	26.5	19.8	21.6
14 %	17.6	20.4	29.4	31.8	21.6	22.7
16 %	20.0	20.9	32.0	32.8	22.7	23.3

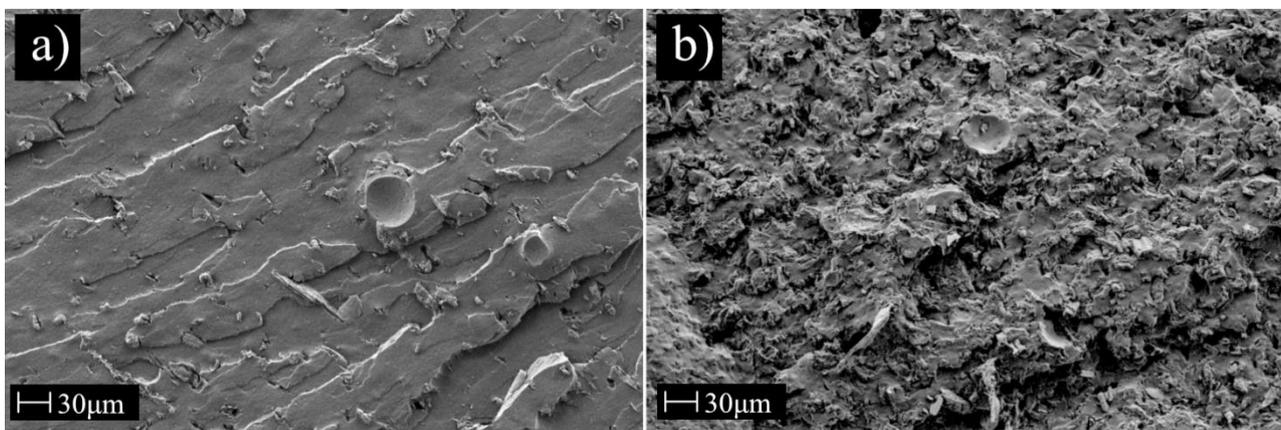


Figure 6. FESEM micrographs taken from the fracture surface of H2 composites created during tensile testing with filler content of a) 4 % and b) 16 %.

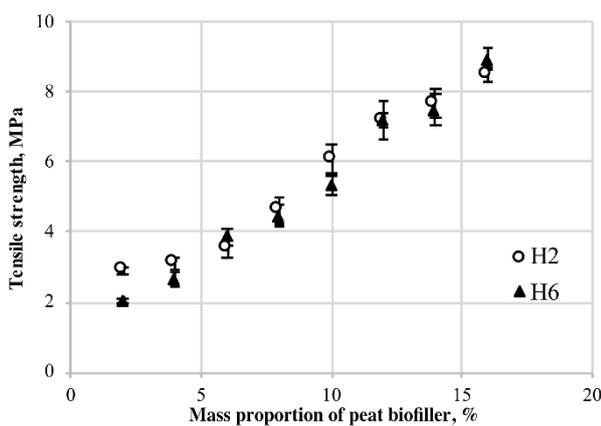


Figure 7. Tensile strength as a function of the mass proportion of biomass in polyurethane.

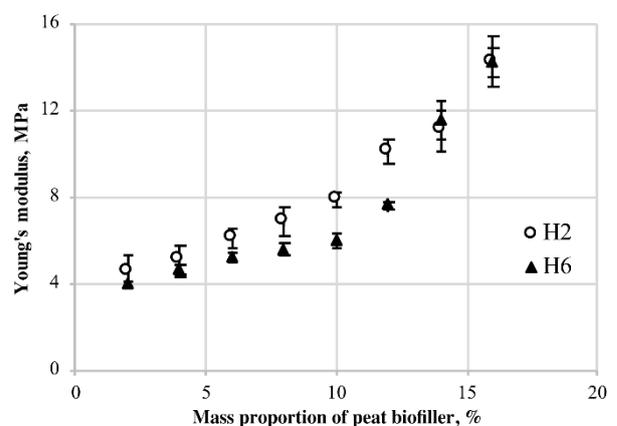


Figure 8. Tensile stiffness (Young's modulus) as a function of the mass proportion of biomass in polyurethane.

much reduction in strain at break. With changing filler proportions, the strain at break of the H2 composites ranged between 80 % and 100 % while for the H6 composites the range was slightly wider, at 75–105 % (Figure 9).

Note that, in Figures 7–9, the bars represent the standard deviation of 5–7 specimens cut from each cast sample. The deviation includes variations due to the structural heterogeneity within the cast sample and to the measurement technique itself. Because replicates of the castings were not made, the reproducibility of the castings could not be confirmed statistically. But the consistent trends of the measurements and their variations as a function of added filler suggest the results are reliable and reproducible.

DISCUSSION

DMA analysis

In general, DMA provides information on the viscoelastic properties of materials such as viscoelastic moduli, storage and loss modulus and 'tan delta'. In DMA, materials are deformed under a small sinusoidal stress. DMA is most commonly used to measure a material stiffness (modulus) and glass transition temperature (T_g) in which transition of a polymeric material from a hard and relatively brittle glassy state into a viscous or rubbery state occurs. The quantity 'tan delta' is a measure of the energy damping ability of a material and T_g , the glass transition temperature, can be observed as a peak value in the curve (Crompton 2013).

In the biopolyurethane composites tested here, the movement of 'tan delta' toward higher temperatures with an increasing amount of biofiller shows that the filler and the polyurethane matrix interact strongly. The hydroxyl groups of the filler react with isocyanate, bonding the filler and matrix to each other chemically. Thus, filler particles stiffen the structure by restricting the segmental motion of the flexible matrix. The result is consistent with the findings for wood flour (Casado *et al.* 2009) and particulate Kraft lignin (Tavares *et al.* 2016).

The height of the 'tan delta' peak decreased with increasing filler content. The effect can be explained by the decreasing proportion of the PU matrix that takes part in relaxation with an increasing filler content. Additionally, the filler reduces the damping capability of the composite, i.e., the ability to dissipate mechanical energy. Particulate biomass fillers - wood flour and Kraft lignin - have often been reported to broaden the 'tan delta' peak (measured at the half height of the peak), which is attributed to the

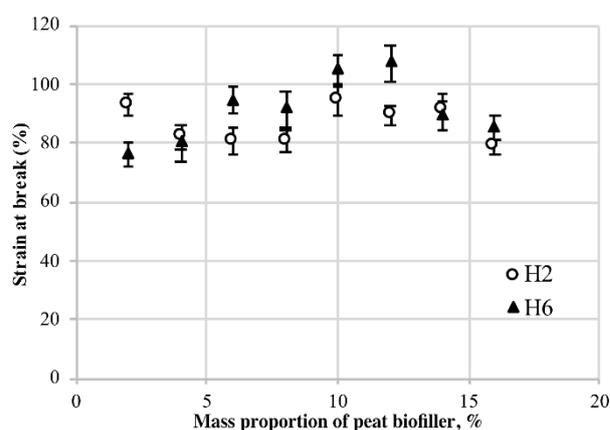


Figure 9. Strain at break as a function of the mass proportion of biomass in polyurethane.

heterogeneity of the matrix (Casado *et al.* 2009). In our case, the peak widths were almost constant for both the H2 and H6 filler grades. Thus, the filler in the PU matrix seems to form a homogeneous structure, which may result from the small size and hydrophobicity of the filler, enabling its efficient dispersion within the matrix.

The effect of the biofillers in the bioPUs was a result of the abundant hydroxyl groups, which react with pMDI leading to a cross-linked filler reinforced structure with good interfacial bonding. But the hydroxyl values of the biofillers did not seem to be an explanatory factor for the dynamic mechanical properties of the biopolyurethanes. The hydroxyl value of the more humified grade (H6) was clearly greater than that of the less humified one (H2) but the properties of the bioPUs were identical at a given filler proportion as seen in Figures 4 and 5. The reason may originate from the chemical compositions of the Sphagnum grades. In Sphagnum, as in wood lignin for example, both aliphatic and phenolic hydroxyl groups exist. However, phenolic hydroxyl groups have much lower reactivity with isocyanate compared to primary and secondary hydroxyl groups (Ionescu 2005). During humification, the fractions of polysaccharides decrease while the share of complex phenolic compounds (lignohumic substances) increases, causing phenolic hydroxyl groups to increase as well, at the expense of non-aromatic hydroxyl groups. On the other hand, it is reasonable to assume that not all hydroxyl groups of a biomass are reactive or available in polyurethane synthesis and that only those on the surface take part in the polymerisation reaction. Due to the high viscosity of the liquid body, isocyanate cannot easily diffuse into particles via micropores and nanopores. On the other hand, due to the high reactivity of isocyanate,

polymerisation reactions take place on the surface layer of filler particles and may thus form an impenetrable shell preventing the diffusion of isocyanate into the particles. Because of their lower hydroxyl value, the thickness of the reactive layer may be somewhat greater for H2 particles than for H6 particles, which would compensate the difference between the cross-linking densities, resulting in almost identical DMA properties for both fillers.

The rôle of reinforcement filler in tensile properties

The Sphagnum filler reinforced the castor oil-based biopolyurethane samples considerably. At the same biofiller proportions, the mechanical properties of bioPU composites with Sphagnum fillers were similar to those of similarly made bioPUs with wood microfibrils ground from mechanical pulp. In the latter case, biofiller dosing was limited to a maximum of 5 %, because fibrillary wood particles with a high aspect ratio increased viscosity due to their strong tendency toward agglomeration (Visanko *et al.* 2017). In contrast, Sphagnum filler could be used in proportions over three times more than wood microfibrils.

The addition of filler is generally known to improve the mechanical properties of elastomers, especially stiffness. It has been proposed that the improvements can be mainly explained by the hydrodynamic effect and the interphasial reinforcement effect (Jiang 2014). The former effect refers to the fact that the addition of filler results in a composite material whose mechanical properties are a weighted average of the properties of the soft PU matrix and the rigid fillers. The latter refers to the effect in which the attaching of polymer chains onto the filler forces the chains into conformations that differ substantially from those in the bulk matrix. The thin interphases formed may be much stiffer than the bulk matrix, especially because polymer chains are chemically connected to the filler surface via its hydroxyl groups.

During tensional stressing of PU composites, failure at the filler-polymer matrix interface may be due to debonding of the interphase polymer chain from the filler surface, debonding and disentanglement of the interphase polymer chain from the bulk polymer matrix, or breaking of the interphase polymer chain. Increasing the filler proportion reduces the distance between filler particles, thus causing larger stress on the polymer chains between particles during stretching. As a result, debonding of the polymer chains from the filler surface could be expected to happen at lower strain (Jiang 2014). This kind of behaviour was not

seen in this study but the strain at break remained almost unchanged. The reason may be the interphase layer, already described, that allows molecular level stretching around the particles. There may also be an additional explanation. The filler particles had a flat, slightly elongated shape and were probably mostly randomly oriented within the PU matrix. Those rigid particles not oriented in the stretching direction, however, could avoid the debonding of polymer chains during stretching of an elastic sample because of the simultaneous dimensional changes in the sample. This orientation might compensate for the increased stress due to the shorter surface-to-surface distance between particles with increasing filler proportion. Finally, during casting into the mould, filler particles might have become partially oriented in an uncontrolled way due to the flow of the mixture, which could explain the observed differences in strain at break values with different filler proportions.

We have shown that Sphagnum moss particles serve as an efficient reinforcement filler in castor oil based biopolyurethane composites. The glass to rubber transition temperature increases with an increasing filler mass proportion, indicating strong cross-linking between matrix and filler. Due to their hydrophobicity, dry filler particles are dispersed homogeneously within the polyol enabling efficient reaction with isocyanate and resulting in a PU matrix having a narrow cross-link distribution at a wide range of filler proportions. Tensile strength can be increased to more than fivefold and stiffness over fourfold by replacing 28 % of the polyol with Sphagnum filler. Interestingly, stretch (at around 90 %) seems to be almost independent of the filler mass proportion. Sphagnum as a filler has substantial promise.

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