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# **Lignin as a functional additive in a biocomposite: Influence on mechanical properties of polylactic acid composites**

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## **Keywords:**

Composite

Esterification

Lignin

Deep Eutectic Solvent (DES)

Construction and Demolition Waste (CDW)

Polylactic acid (PLA)

## **ABSTRACT**

In this research, lignin and modified lignin were used as a biobased additive in the manufacturing of biocomposites. The biocomposites were produced from polylactic acid (PLA) and wood. Lignin used in this study was recovered both from spruce and from construction and demolition waste (CDW) by extracting it with a deep eutectic solvent (DES), and part of the recovered lignin was modified in esterification with maleic anhydride. The implementation of lignins on biobased composites in filament extrusion was tested and the influence of lignin on the composite manufacturing process and mechanical characteristics of the produced biocomposites was evaluated and discussed. The results showed that lignin compounds can be used as a part of biocomposites based on PLA and wood material, because the lowest tensile strength was achieved with samples which did not contain any commercial coupling agent compounds. Lignin was found to act in the biocomposites more as a coupling agent than as a lubricant, and the coupling agent strength effect of esterified lignin was comparable to the commercial coupling agent used in these experiments. The best specific tensile strength of filaments achieved in this study were 7.68 and 7.71 MPa for materials that included commercial coupling agent and esterified lignin, respectively.

## **1. Introduction**

Sustainable practices are a growing trend, and the availability of many existing materials will be limited in the future due to the increasing competition for scarce resources. Therefore, alternative solutions for current materials are needed, especially in cases where nonrenewable materials are presently used. Composites made at least partly from renewable materials or even from wastes are interesting and promising materials to replace for instance plastics in many different products and applications. Thus, based on recently published research papers there is a growing interest in them (John and Thomas, 2008; Koronis et al., 2013; La Mantia and Morreale, 2011; Mohanty et al., 2002; Satyanarayana et al., 2009).

Wood polymer composites (WPCs) consist of both non-renewable plastics and renewable material (wood fibers). Usually, due to the incompatibility of hydrophobic plastic and hydrophilic wood, the manufacturing of the WPCs require coupling agents and lubricants that will improve their inner connections and facilitate the manufacturing process. In addition to plastics, the raw materials of the matrix and fibers might be based on bioplastics, such as polylactic acid (PLA). However, although in those cases the main part of the composites is made from the renewables (PLA and wood fibers), the required coupling agents and lubricants still generally originate from fossil fuel based processes. This restricts the achievement of a perfect renewable character for composites and creates the need for novel biobased coupling agents and lubricants.

Polylactic acid (PLA) is a biodegradable thermoplastic polyester made from renewable resources, derived from the fermentation of polysaccharide sources. Due to its advantageous properties, such as biodegradability, processability and mechanical strength, it has become popular in many applications recent years, such as in the manufacturing of composites (Csikós et al., 2016; Ding et al., 2016; Faludi et al., 2013; Fortunati et al., 2010; Spiridon and Tanase, 2018). Instead of the biodegradability advantages of PLA, it also has some limitations as a material for

composites, such as a narrow thermal processing window, high moisture sensitivity and a price several times higher than that of non-biodegradable options in industrial applications (Holcapkova et al., 2017). Due to the costs, it is reasonable to combine PLA and wood fibers as fillers in the composites. However, there are still unsolved questions on how to improve the interface between wood fibers and PLA (Delgado-Aguilar et al., 2018). A certain option might be the chemical modification of components which was improved the feature of wood-PLA composite (Joffre et al., 2017). Thus, the modification of the components or good biobased coupling agents are needed to improve the properties and quality of these biobased composites.

Lignin is considered as the second most abundant natural polymer, making it a potential candidate for use as a reinforcing material or as a functional additive in biocomposites (Cicala et al., 2017). This is a result of its high number of reactive functional groups, high carbon content, good stability, and good mechanical properties due to the presence of aromatic rings. Lignin can reportedly be blended with several materials, such as proteins, starch and cellulose (Doherty et al., 2011; Nagele et al., 2002). The composition of lignin varies depending on the delignification procedure and origin of the lignocellulosic biomass. Nowadays, lignin is mostly produced as a byproduct of the paper/pulp industry, where it is usually considered as waste or an energy source. However, novel solvents, such as deep eutectic solvents (DES), enable the recovery of sulfur-free lignin fractions from wood. The use of DES-based processes would make it an interesting option to produce a biobased lignin-additive for composites for instance from waste wood fractions such as saw dust and construction and demolition waste (CDW).

The main objective of the present study was to examine if lignin and modified lignin could be used to replace oil-based additives in biocomposites. Moreover, the aim was to determine the functionality of lignin in the composites and how its use affects the mechanical properties of the produced biocomposite.

## **2. Materials and methods**

### *2.1. Materials*

PLA used in the manufacturing of the biocomposites was a NatureWorks LLC product, PLA polymer 3051D. The manufacturer announces that its density is 1.25 g/cm<sup>3</sup> and melt index 10–25 g/10 min (at 210 °C and 2.16 kg). The glass transition temperature and crystalline melt temperature of this PLA resin are between 55 and 65 °C and 150 and 165 °C, respectively. Arbocel B 800 was used as cellulose fibers in the biocomposites. It is supplied by J. RETTENMAIER & SÖHNE GmbH+Co KG. The cellulose content of Arbocel B 800 was approximately 99.5% with a specific gravity of 1.5 g/cm<sup>3</sup>. The average fiber length and thickness were 130 µm and 20 µm, respectively. As the reference coupling agent and lubricant, the commercial DuPont™ Fusabond® E226, Mn of 18,239 g/mol, and Mw of 78,201 g/mol (Sánchez-Valdés et al., 2018) and Struktol TPW 113 were used. The density of the commercial coupling agent was 0.93 g/cm<sup>3</sup> with a melt flow rate of 1.75 g/10 min (at 210 °C and 2.16 kg), and the melting point was 120 °C. A lubricant was delivered as a pastille or powder, with a specific gravity of 1.005 g/cm<sup>3</sup> and a dropping point of 70–88 °C. In the development of the new lignin-based additives, spruce wood and CDW wood (class X) were used as the raw material. In the modification of the lignin, 1methyimidazol (99+ sigma), dioxane (from Sigma), maleic anhydride (Sigma), ethyl ether (Acros) were used as received from their manufacturers.

### *2.2. Lignin extraction*

Lignin extraction from both wood and construction and demolition waste (CDW) wood was performed with a DES solution (1:9 choline chloride: lactic acid). At first, 20 g of milled wood of a specific size (~1 mm) was added to 200 g of a prepared DES solution in a 500 ml serum bottle and heated immediately after that to 105 °C in an oil bath. The dispersion was stirred for 18 h at this temperature. Subsequently, the mixture was thoroughly washed with a mixture of ethanol and water (2:1, v/v). After that, the mixture was filtrated through a filter paper in a ceramic Büchner funnel under a vacuum. The wash solution of ethanol and water used for the washing of the treated woody material was collected, and ethanol was then evaporated using a rotary evaporator at 60 °C. Deionized water was added to the concentrate to induce the precipitation of lignin. Finally, the lignin was separated with a centrifuge. The recovered lignin was freeze-dried.

The molecular weight distribution of the lignin was analyzed with gel permeation chromatography in the HPLC system (Shimadzu HPLC, Japan), which included the system controller SCL-10AVP, on-line degasser DGU-14A, low-pressure gradient valve FCV-10ALVP, HPLC pump LC-10ATVP, autosampler SIL-20AHT, and column oven CTO 10ACVP. The system was equipped with a sequentially connected guard column (50mmx 7.8 mm) and two Jordi Gel DVB 500A (300mmx 7.8 mm) columns in series. Separations were run by using THF with 1% acetic acid as an eluent with a constant flow rate of 0.8 mL min<sup>-1</sup>. The detector parameters were an HPLC nebulizer, 40 °C, air pressure 3.5

bar, gain 3, and no-split mode. The injection volume of the autosampler was 50  $\mu\text{l}$ . The oven column was set to 40  $^{\circ}\text{C}$ . Polystyrene standards (Perkin-Elmer, Norwak, Conn., USA) were used to calibrate the columns. Chromatogram evaluation was implemented with commercial software for GPC analysis: CLASS-VP Version 1.03 (Shimadzu). The weight-average ( $M_w$ ) molecular weight of the recovered DES-lignin was 6.544  $\text{g mol}^{-1}$  and a number-average ( $M_n$ ) 2.692  $\text{g mol}^{-1}$ . Furthermore, the DES-lignin displayed a slim polydispersity with a  $M_w/M_n$  of 2.43. These values were close to what is commonly believed to be the natural molecular weight of lignin (Brodin et al., 2012). The purity of the DES-lignin was measured with Klason lignin analysis to account for both acid soluble and insoluble lignin. Furthermore, the carbohydrate amount was analyzed using acid methanolysis followed by GC analysis. The analysis showed that the total lignin purity was 94.5%; only 0.2% of glucose, 0.2% of xylose and 0.5% of ash were found in addition to the lignin.

### 2.3. Esterification of lignin

The DES-lignin was esterified with maleic anhydride. The procedure was based on earlier publications (Schorr et al., 2014; Thielemans and Wool, 2005). To begin, lignin recovered with DES was dried in an oven (60  $^{\circ}\text{C}$ ) to ensure the removal of moisture and possible volatiles left in the lignin. Then, 40 g of the dried DES-lignin, 60 g of maleic anhydride and 200 ml of dioxane were placed into a 500 ml round bottom flask fitted with a condenser. The mixture was heated to 75  $^{\circ}\text{C}$  while being continuously stirred. Then, 25 ml of dioxane containing 2 g of 1-methylimidazol was added dropwise into the mixture over a period of 90 min. After the reaction time of 90 min, the mixture was allowed to cool, and then, 400 ml of ethyl ether was added into the mixture to induce the precipitation of the esterified lignin. After solvent removal by careful decantation, the precipitated product was washed with water (3 x 400 ml). Then, the esterified lignin was first dried at room temperature overnight and subsequently in a vacuum oven at 60  $^{\circ}\text{C}$  overnight.

### 2.4. Confirmation of esterification with Fourier Transform Infrared (FTIR) spectrophotometry

The DES-lignin was analyzed before and after the chemical modification to determine the changes in the chemical structure. The analysis was carried out by using a Perkin Elmer Frontier spectrometer with a universal ATR module (diamond crystal). The FTIR spectra of each sample were measured in the 4000-400  $\text{cm}^{-1}$  wave number range with a resolution of 4  $\text{cm}^{-1}$ . The mass ratios of the p-hydroxyphenyl (H), guaiacyl (G), and syringyl units (S) of DES-lignins was also determined by using pyrolysis-GC-MS. The pyrolysis-GC-MS was carried out on a foil pulse Pyrola 2000 pyrolyzer (Pyrol AB, Lund, Sweden) connected to the GC-MS instrument (Smeds et al., 2016). The analyses were performed as described previously (Smeds et al., 2016, 2012). The tentative identification was mostly based on the mass spectra library created at the Laboratory of Wood and Paper Chemistry at Åbo Akademi University and partly on the Wiley 10/NIST 2012 mass spectral libraries. A sample amount of about 100  $\mu\text{g}$  and one drop of acetone was applied onto the Pt filament, the sample was allowed to dry, and the analysis was started 2 min after the filament was added into the probe.

### 2.5. Manufacturing of the biocomposites

The studied materials were extruded with the Filabot EX2 filament hot-melt extruder with a single screw. The extrusion temperature was 185  $^{\circ}\text{C}$  and the size of the nozzle head was 3 mm. The screw speed of the extruder varied between 0 and 35 rpm depending on the speed of the spooler and the production features of the materials. The extrusion system also includes an airpath device that is located between the filament extruder and spooler devices in the production lines. The compositions of the studied biocomposites are presented in Table 1. PLA production costs can be reduced by using cellulosic fillers. This study employed a cellulose content between 9–10 wt%. The best tensile strength of the PLA filament has been reported with an addition of 10% wood particles (Kariz et al., 2018). Furthermore, 20 wt% of wood flour (average particle size approximately 30  $\mu\text{m}$ ) is based on the earlier studies the critical concentration due to the rheological behavior of PLA during the melt processing (Holcapkova et al., 2017). The analysis has showed that a lignin content of 4% was the most suitable as a PLA reinforcement (Delgado-Aguilar et al., 2018).

The standard applied in the material flow test does not include parameters for a PLA polymer. Before the test, we performed tests to achieve the correct parameters with PLA at a 200  $^{\circ}\text{C}$  temperature with a 2.16 kg load. The results did not show differences between the mass (g / 10 min) and volume (cc / 10 min) in the material flowing test.

**Table 1. The composition of the studied biocomposite samples. Name of the sample is consisted of the included raw materials, such as polylactic acid (PLA), Cellulose (Ce10, Ce9), commercial coupling agent (ca) and lubricant (Lubr.), lignin (DESL), esterified lignin (e-DESL), lignin from construction and demolition waste wood (DESLCDW), and esterified lignin from construction and demolition waste wood (e-DESL-CDW).**

Sample	Bioplastic (PLA) content (%)	Cellulose content (%)	Coupling agent / content (%)	Lubricant content (%)
1. PLA	100	-	-	-
2. PLA / Ce10	90	10	-	-
3. PLA / Ce10 / ca	87	10	ca / 3	-
4. PLA / Ce9 / ca / Lubr.	87	9	ca / 3	1
5. PLA / Ce10 / DESL	87	10	Lignin / 3	-
6. PLA / Ce9 / DESL / Lubr.	87	9	Lignin / 3	1
7. PLA / Ce10 / e-DESL	87	10	Esterified lignin / 3	-
8. PLA / Ce9 / e-DESL / Lubr.	87	9	Esterified lignin / 3	1
9. PLA / Ce10 / DESL-CDW	87	10	CDW lignin / 3	-
10. PLA / Ce9 / DESL-CDW / Lubr.	87	9	CDW lignin / 3	1
11. PLA / Ce10 / e-DESL-CDW	87	10	Esterified CDW lignin / 3	-
12. PLA / Ce9 / e-DESL-CDW / Lubr	87	9	Esterified CDW lignin / 3	1

### 2.6. Analysis of the properties of the biocomposites

The tensile properties (strength and modulus) of the produced biocomposite filaments were analyzed with a testing apparatus Zwick Z020 (Zwick Roell group) based on the ISO 527 standard. The density of the produced biocomposites was determined as an average from 10 tensile test specimens using an immersion method for volume measurement, and the mass was measured with an accuracy of 10–2 g. The density measurement was challenging due to the special characteristics of the material; therefore, the density values were based on the average of ten specimens. The density values can be considered reliable because the achieved density of the PLA polymer deviated only 0.05 g/cm<sup>3</sup> from the value of the raw material. The results indicated that lubricant containing material contribute is significantly denser. The melt index of the studied biocomposites was measured with the laboratory melt indexer (Dynisco LMFI-2NENNNN) according to the standard ISO 1133-1 method A/B. Tensile and melt index results are average of 15 samples per recipe. Statistical significance between the PLA polymer and the composite recipes were tested by using Daniel's XL Toolbox Excel software, performing the one-way ANOVA Bonferroni-Holm post hoc testing algorithm. Additionally, the cross-sectional structure of the produced biocomposite filaments was examined with the scanning electron microscope (SEM) Hitachi SU3500 with the following operation conditions: voltage 10.0 kV, vacuum 100 Pa, and magnification varying between 35 and 500.

## 3. Results and discussion

### 3.1. Esterification of DES-lignin

The esterification efficiency of the DES-lignin was evaluated through FTIR analysis and the mass gain due to the esterification. Fig. 1 shows the FTIR spectra of the DES-lignin and the maleated/DES-lignin. The attribution of the typical FTIR absorption bands for lignin have been reported for instance by Hu et al. (Hu et al., 2015) and Schorr et al. (Schorr et al., 2014). The spectrum for DES-lignin contains an OeH stretching band (3372 cm<sup>-1</sup>), a CHe stretching band (2936 cm<sup>-1</sup>), and aromatic stretching bands (1594, 1512, and 1425 cm<sup>-1</sup>). Moreover, the characteristic absorbance of guaiacyl units were observed at 1265, 1124, 1029, 853, and 813 cm<sup>-1</sup>. The same features can be observed in the spectrum of maleated/DES-lignin. Additionally, the absorption intensity at 3372 and 1029 cm<sup>-1</sup>, corresponding to OeH stretching and COe stretching of primary alcohol, respectively, reduced significantly. Furthermore, the increased peak intensity at 1721 cm<sup>-1</sup> can be attributed to ester groups, and double bonds of maleic anhydride were prominent. Thus, it can be concluded that esterification between DES-lignin and maleic anhydride occurred. The average mass gain of the esterification experiment was 72 ± 2%. This data indicated that the esterification was complete, and other researchers have reported analogous findings (Schorr et al., 2014).

The ratio of the p-hydroxyphenyl (H), guaiacyl (G), and syringyl units (S) of the recovered DES-lignin was determined using pyrolysis-GC-MS and the peak assignment is presented in Figs. 2 and 4. Analytical pyrolysis (Py-GC-MS) data presented here is qualitative since response factors necessary for quantitative measurements were

not determined. Peaks consistent to those usually present in both native spruce and birch, which usually consist of guaiacyl (G) moieties with minor contributions of p-hydroxyphenyl (H) and syringyl (S) phenols, are seen in the py-GC-MS. Peaks are presented in Figs. 2 and 3. These were present in the chromatogram peak of the recovered DES-Lignin from waste wood. Furthermore, there are peaks consistent with the esterification that are present in Figs. 3 and 5. All in all there is a clear picture of that the both lignin sample contain very little amount of carbohydrates which is in line with the results of the Klason lignin analysis.

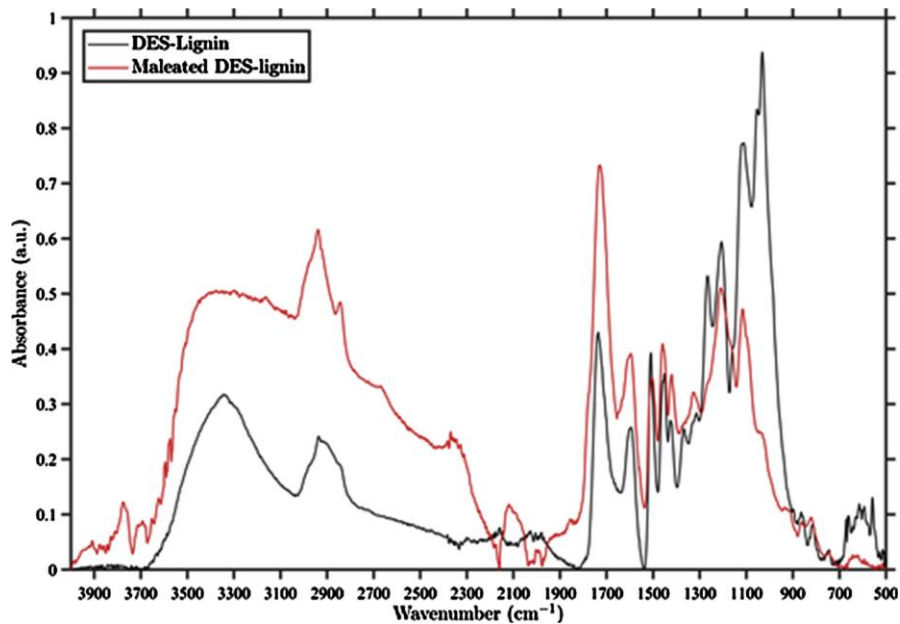


Fig. 1. FTIR spectra of DES-lignin and Maleated DES-Lignin.

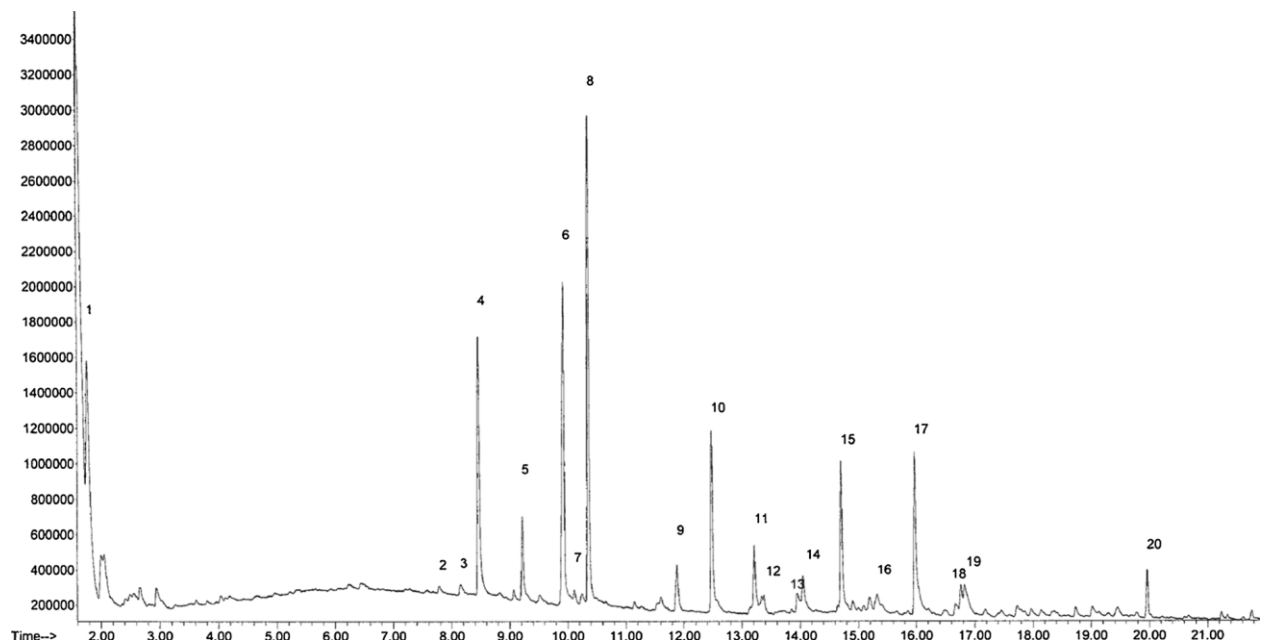
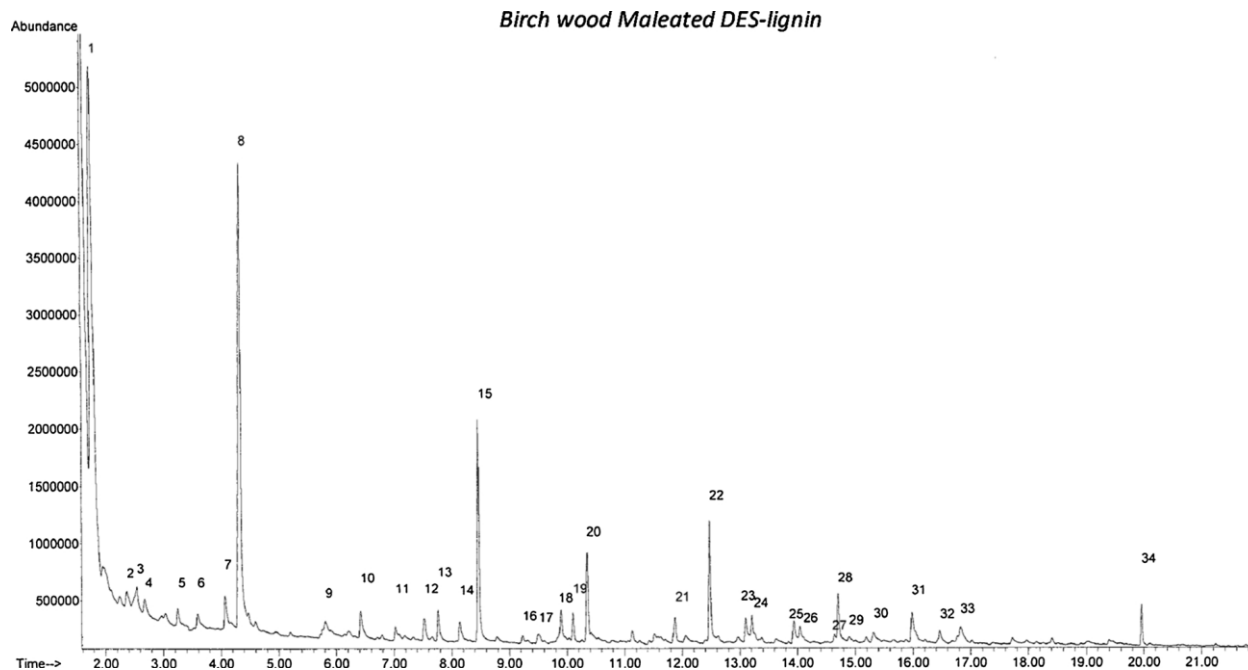
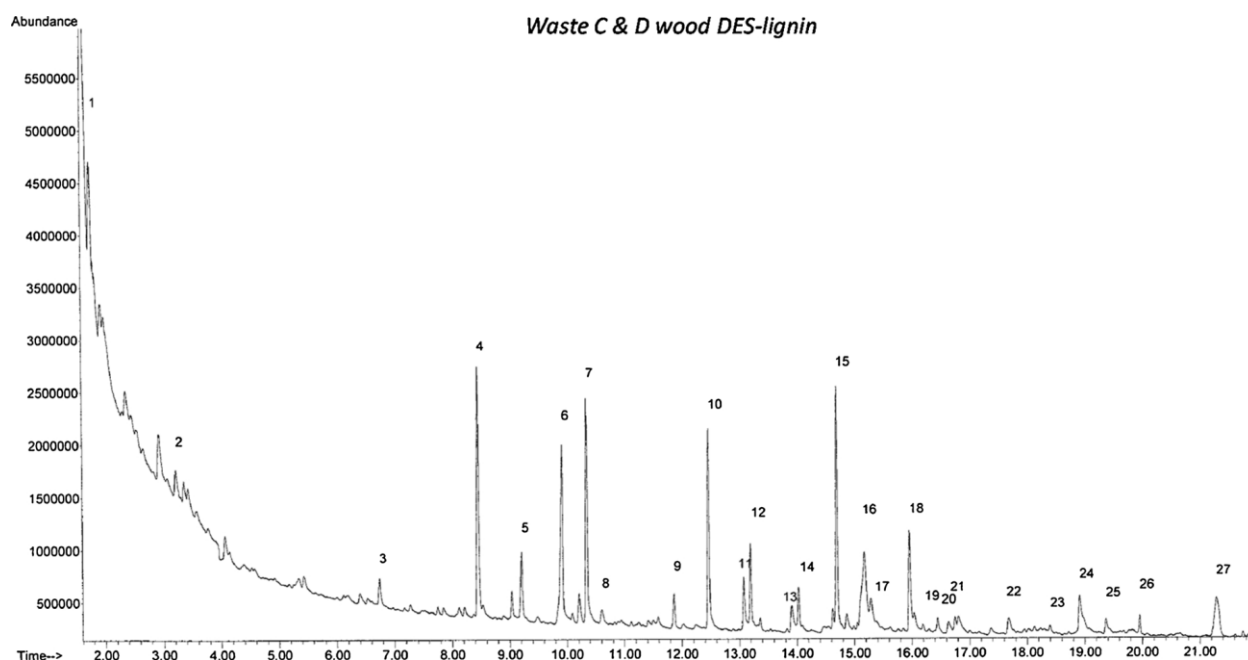


Fig. 2. Birch wood DES-lignin py-GC-MS. Peak assignments 1) acetone; 2) o-cresol; 3) p-cresol; 4) guaiacol (G); 5) and 6) 3,6-dimethyl-1,4-dioxane-2,5-dione; 7) 3-methyl-G; 8) 4-methyl-G; 9) 4-ethyl-G; 10) 4-vinyl-G; 11) eugenol; 12) 4-propyl-G; 13) vanillin; 14) cis-isoeugenol; 15) trans-isoeugenol; 16) acetovanillone; 17) guaiacylacetone; 18) propiovanillone; 19) 4-acetyl-G; 20) isopropylmyristate.

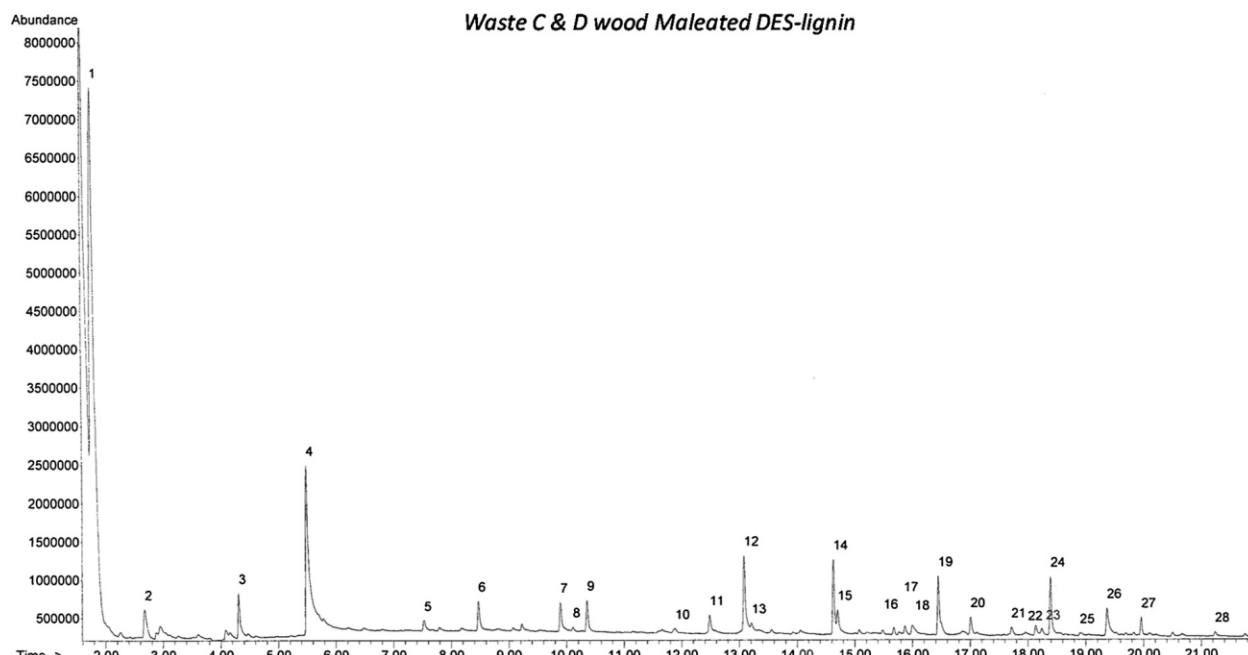


**Fig. 3. maleated birch lignin py- GC-MS. Peak assignments** 1) acetone; 2) benzene; 3) 2-propenoic acid; 4) 1,4-dioxane; 5) 1,3,5-cycloheptatriene; 6) 3,4-dimethyl-2-pentene; 7) 2-cyclopentene-1-one; 8) maleic acid anhydride; 9) methylenesuccinic acid anhydride; 10) phenol; 11) succinic acid anhydride; 12) dimethylmaleic acid anhydride; 13) *o*-cresol; 14) *p*-cresol; 15) guaiacol (G); 16) and 18) 3,6-dimethyl-1,4-dioxane-2,5-dione; 17) 2,4-dimethylphenol; 19) 3-methyl-G; 20) 4-methyl-G; 21) 4-ethyl-G; 22) 4-vinyl-G; 23) syringol (S); 24) eugenol; 25) vanillin +?; 26) *cis*-isoeugenol; 27) 4-methyl-S; 28) *trans*-isoeugenol; 29) homovanillin; 30) acetovanillone; 31) guaiacylacetone; 32) 4-vinyl-S; 33) 4-acetyl-G; 34) isopropylmyristate.



**Fig. 4. (C & D) DES- lignin py- GC-MS. Peak assignments** 1) acetone; 2) 3-hydroxypropanal ; 3) 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one; 4) guaiacol (G); 5) and 6) 3,6-dimethyl-1,4-dioxane-2,5-dione; 7) 4-methyl-G; 8) 1,4:3,6-dianhydro- $\alpha$ -D-glucopyranose; 9) 4-ethyl-G; 10) 4-vinyl-G; 11) syringol (S); 12) eugenol; 13) vanillin; 14) *cis*-isoeugenol; 15) *trans*-isoeugenol; 16) levoglucosan; 17) acetovanillone; 18) guaiacylacetone; 19) 4-vinyl-S; 20) guaiacylpropenal; 21) propiovanillone; 22) dihydroconiferyl alcohol; 23) *trans*-4-prop-1-enyl-S; 24) *trans*-coniferyl alcohol; 25) syringylacetone; 26) isopropylmyristate; 27) 1-docosanol.

### Waste C & D wood Maleated DES-lignin



**Fig. 5** maleated C & D DES-lignin py- GC-MS. Peak assignments 1) acetone; 2) 1,4-dioxane; 3) maleic acid anhydride; 4) 1-methyl-1H-imidazole; 5) dimethylmaleic acid anhydride; 6) guaiacol (G); 7) 3,6-dimethyl-1,4-dioxane-2,5-dione; 8) 3-methyl-G; 9) 4-methyl-G; 10) 4-ethyl-G; 11) 4-vinyl-G; 12) syringol (S); 13) eugenol; 14) 4-methyl-S; 15) trans-isoeugenol; 16) butylated hydroxytoluene; 17) 4-ethyl-S; 18) guaiacylacetone; 19) 4-vinyl-S; 20) 4-prop-2-enyl-S; 21) cis-4-prop-1-enyl-S; 22) and 23) 4-propyne-S; 24) trans-4-prop-1-enyl-S; 25) acetosyringone; 26) syringylacetone; 27) isopropylmyristate; 28) methyl palmitate.

### 3.2. Manufacturing of biocomposites

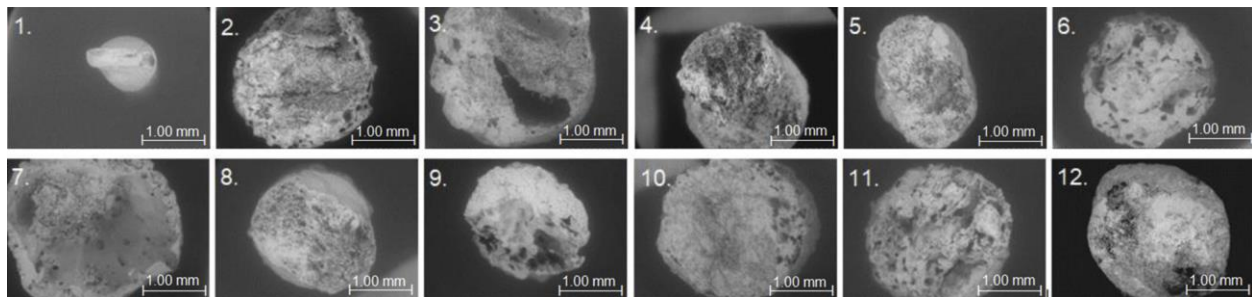
Table 2 shows the effects of the composition of the manufacturing recipe on the production of composites with their measured average densities. The mass flow rates (MFR) and mass volume rates (MVR) are average values from four measurements. The composites, which include esterified lignin and esterified CDW lignin without lubricant, caused some vaporization problems in a material flow test. Thus, their MFR and MVR values are not available. The structure of these composites vaporized during the test, and a uniform material stream needed for the measurement was not possible to achieve. The same vaporization phenomenon caused crackling of the biocomposite filaments when they were manufactured with the extruder. The addition of lubricants enabled the material flow tests, and the results with the recipes containing the lubricants give an idea of the functionality of the esterified lignin materials in the biocomposites. In addition, crackling was not observed in the extrusion step of the biocomposites containing lubricants. The material flow test indicated that even a small amount of component can have a significant influence on the properties of the composite and its manufacturing.

**Table 2.** The melt index of studied materials, mass flow rate (MFR), mass volume rate (MVR) and densities. The MFR and MVR values are reported according to the measured amount for mass gram (g) and volume cubic centimeter (cc) at the temperatures 200 °C with 2.16 kg load.

Sample	MFR g / 10 min	MVR cc / 10 min	Density (g/cm <sup>3</sup> )
1. PLA	14.85	13.39	1.30
2. PLA / Ce10	16.38	13.94	0.75
3. PLA / Ce10 / ca	13.05	10.94	0.86
4. PLA / Ce9 / ca / Lubr.	22.35	17.08	1.32
5. PLA / Ce10 / DESL	15.68	12.02	1.06
6. PLA / Ce9 / DESL / Lubr.	14.69	12.80	1.05
7. PLA / Ce10 / e-DESL	NA	NA	0.74
8. PLA / Ce9 / e-DESL / Lubr.	23.80	17.14	1.33
9. PLA / Ce10 / DESL-CDW	10.39	8.12	0.98
10. PLA / Ce9 / DESL-CDW / Lubr.	21.34	15.55	1.08
11. PLA / Ce10 / e-DESL-CDW	NA	NA	0.85



The manufacture of a biocomposite filament having a homogeneous thickness was difficult. Although a 3mm nozzle head was used, the average diameter of the produced filament series varied between 1.70 and 3.08 mm. Fig. 6 also clearly shows the differences in the diameters. Biocomposite filaments in which the amount of PLA was increased (Samples 1 and 2) had the smallest diameter. However, they also had the smallest cross-section surface due to the large stretch. It has earlier been shown that the increased width of the filament increases the porosity but lowers cohesion, reducing strength (Le Duigou et al., 2016). The structure of the filament containing only PLA is homogenous, but replacing part of the PLA with cellulose made the structure more heterogeneous. Moreover, it could be seen that as the number of components in the structure of the composite increased, the homogeneity of the filament structure decreased. The SEM examination also showed that the cross-section surfaces of the filaments included cavities. In conclusion, insufficient compounding still takes place in the recipes used here. Analogously, the surface of the filament became rougher and more porous, which is in agreement with our findings (Kariz et al., 2018). Previously, SEM pictures have shown that lignin particles have the ability to embed within the matrix (Spiridon and Tanase, 2018) and lignin-PLA matrix has the ability for good adhesion to each other (Spiridon et al., 2015). In addition to the recipes, also the parameters (synchronization between the speed of the screw and spooler) might have had an influence on the varying diameter. The heterogeneous thickness of the filaments has been taken into account in the testing of the mechanical properties of the composites. Figs. 7 and 8 show the tensile strength and modulus, which describe the mechanical properties of the tested biocomposites. The mechanical properties are presented as a white bar chart (an average from 15 measurements) including standard deviations as an error bar. In addition to the mechanical strengths, Figs. 7 and 8 also include grey bar charts, which pay attention to the density of material (presented in Table 2). The density of the pure PLA filament (1.30) was used as the reference value, and the other densities are proportional to it (reference density divided by individual density). Based on the new density ratio, the values of tensile strength are presented as specific results with the black bar charts.



**Fig. 6.** The SEM pictures of tested filaments materials from the cross-section surface of tensile samples. Numbers (1–12) describes the composition of composites that were described in Table 1. SEM pictures of materials from cross-section surface of filaments mechanical strength. The individual SEM picture have been taken with x35 magnification, including 1.00mm scale in the right bottom corner.

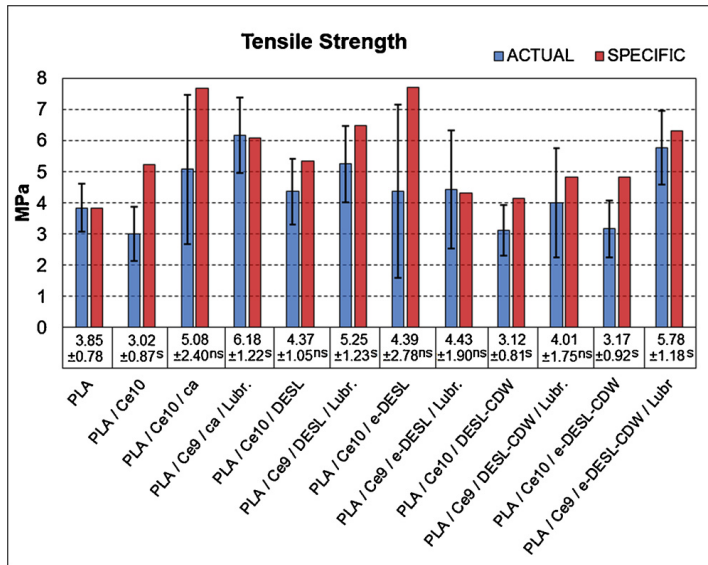


Fig. 7. The results of tensile strength as a blue bar charts with the standard deviations as an error bars. The actual results were also presented by numerically, including finding statistically significant (s) and no significant (ns) changes with 95% confidence level. Red bar charts represents the specific tensile strength with density's effect. The marks of x-axel based on sample name, were presented in a Table 1.

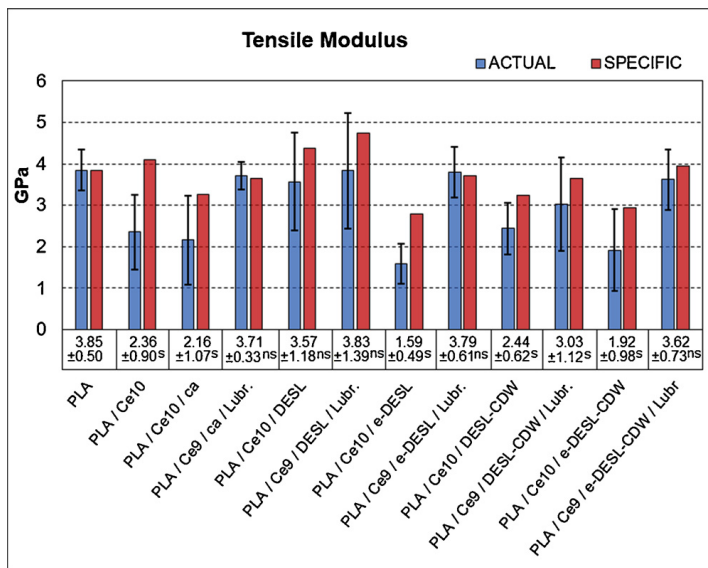


Fig. 8. The results of tensile modulus as a blue bar charts with the standard deviations as an error bars. The actual results were also presented by numerically, including finding statistically significant (s) and no significant (ns) changes with 95% confidence level. Red bar charts represents the specific tensile strength with density's effect. The marks of x-axel based on sample name, were presented in a Table 1.

The temperature of test atmosphere has an influence on the tensile strength of PLA-wood composite (Luedtke et al., 2019) In this study, all the tensile tests were performed under the same conditions. The highest tensile strength values were achieved with biocomposites containing a commercial coupling agent (ca) and lubricant (Fig. 6, sample no. 4). Almost congruent high strength quality was achieved in the biocomposites, in which the commercial coupling agent was replaced by esterified lignin either from virgin wood or from construction and demolition waste (CDW) (Fig. 6, samples no. 7 and 12). This indicates that the commercial coupling agent could be replaced at least to some extent with the esterified lignin. It has also been shown earlier than lignin in the PLA-based composites could have a positive impact on tensile strength. For instance, Spiridon et al. (2015) have shown that lignin increases the tensile strength of lignin-PLA composites when it is used in the composite recipe 7–15 w-%. However, the amount used here was only 3 w-% and the result was still positive. Also Dehne et al. (2016) have shown that the esterification of lignin, which is used in polymer blends, is beneficial for the strength properties of the

blends. This is assumed to result from the increasing length of the ester carbon chain (Dehne et al., 2016). Based on the results in Fig. 7, the use of nonesterified lignin instead of the commercial coupling agent decreases the tensile strength of the biocomposites (Fig. 6, samples no. 5 and 9).

The tensile modulus of the tested biocomposite filaments was found to decrease when esterified lignin was included in the recipe instead of the commercial coupling agents (compare Samples 3, 7 and 9). A phenomenon of this kind has also been reported earlier: the elastic modulus of the PLA matrix was reduced when the dosage of esterified lignin was increased. This was seen especially when spruce-based lignin was used, because it provided greater ability to deform plastically due to its low molecular weight (Gordobil et al., 2016). Wood material from CDW is generally mainly softwood, usually spruce.

Without any coupling agent and lubricant (2.PLA/Ce10), the tensile properties of the produced biocomposite were weak, which might be due to the potentially bounded moisture in the fibers. Based on the literature, the moisture in the PLA fibers could degrade the PLA at high temperatures (Murariu and Dubois, 2016).

The addition of lubricant to the biocomposite production material generally improved the mechanical properties of the biocomposites. This was seen especially in the results measured with the composites containing the lignin originating from CDW (samples 9–12). The review of density values in Table 2 together with the information presented in Figs. 7 and 8 indicated that the use of the esterified lignin produces a porous biocomposite material. This can be discovered also from Fig. 8. The density proportional to strength demonstrates that strength properties are improved with lignin esterification. This can be considered as a significant advantage because lightness with improved strength properties is the desired feature in many applications, such as the packaging and automotive segments.

#### 4. Conclusions

In this work, biocomposite filaments were manufactured from PLA and cellulose and lignin recovered from wood, and construction and demolition waste (CDW) with a “green solvent” (deep eutectic solvent (DES) containing choline chloride and lactic acid) was used as a functional additive. In conclusion, based on the material property tests and SEM images, the esterified DES-lignin originating either from virgin wood or CDW acts as a part of the composite structure. Moreover, adding the esterified lignin as a component in the composites increased the tensile strength in proportion to the lower density. Lignin was also found to act more as a coupling agent in the biocomposites than as a lubricant. Thus, this work demonstrates that a wood-based or a woodwaste-based lignin recovered with DES can replace commercial nonbiobased additives in composite materials and even enable the achievement of a light but mechanically strong structure.

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