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Mechanochemical and thermal succinylation of softwood sawdust in presence of deep eutectic solvent to produce lignin-containing wood nanofibers

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Abstract In this study, the effect of the deep eutectic solvent (DES) based on triethylmethylammonium chloride and imidazole on the mechanochemical succinylation of sawdust was investigated. The sawdust was ball milled in the presence of succinic anhydride and the effects of different amounts of the DES on the carboxylic acid content and particle size were studied with and without post-heating. The carboxylic acid content significantly increased with the addition of the DES and by using 1.5 mass excess of the DES compared to sawdust; milled sawdust with 3.5 mmol/g of carboxylic acid groups was obtained using 60 min post-heating at 100 °C. The particle size was found to depend strongly on DES-to-wood ratio and a change in size-reduction characteristics was

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A. M. Kantola · S. Komulainen NMR Research Unit, University of Oulu, P.O.Box 3000, 90014 Oulu, Finland observed related to fiber saturation point. After mechanochemical milling, three succinylated sawdust samples with different carboxylic acid contents were disintegrated into wood nanofibers and self-standing films were produced. Although the mechanical properties of the films were lower than the cellulose nanofibers, they were higher or in line with oil- and biobased polymers such as polypropene and polylactic acid, respectively. Because of their amphiphilic nature, wood nanofibers were found to be effective stabilizers of water–oil emulsions.

Keywords Wood · Deep eutectic solvent · Succinylation · Ball milling · Nanofibers

Introduction

Deep eutectic solvents (DESs) are a novel class of chemicals used as solvents, reagents, and catalysts (Smith et al. 2014). Importantly, DESs consist of two or more chemical components that have higher melting point individually than as a mixture. The depression in the melting point is related to the interaction between the DES components that prevents the crystallization of the mixture (Meng et al. 2016). The hydrogen bonding appears to be the main interaction mode between the DES components, whereas the influence of other interactions, such as the van der Waals forces, cannot be excluded (Zhao et al. 2018). Although external solvents can be used to prepare DESs, they can be obtained readily in solventfree conditions by heating at a temperature that is lesser than the melting point of the individual components (Zhang et al. 2012). This unique trait allows DESs to be prepared in an atom-economical fashion, as no side products are formed and there is no need for purification steps. In addition, a large number of DESs can be obtained from bulk, biobased chemicals (Dai et al. 2013).

In addition to the sustainable preparation method, DESs are recognized as a potential green and safe alternative to common volatile organic solvents (Liu et al. 2015). Many DESs have negligible vapor pressure and, therefore, do not contribute to the volatile organic component emission and are safer to handle than many common solvents (i.e., minimal exposure to toxic fumes and low flammability). Low or negligible vapor pressure also allows for removal of volatile chemicals from DESs, thus enabling their recycling (Mukesh et al. 2014; Li et al. 2018; Sirviö et al. 2020a). Depending on their chemical constitutions, DESs exhibit low toxicity and are readily biodegradable (Wen et al. 2015). However, it should be noted that some DESs are known to have higher toxicity than the individual components and, therefore, similar to ionic liquids, we cannot generalize on toxicity and degradability (Hayyan et al. 2013). Nevertheless, the use of DESs in chemical synthesis and applications, such as metal and mineral processing, has gained significant attention (Gu et al. 2010; Alonso et al. 2016; Söldner et al. 2019; Anggara et al. 2019).

Because of their sustainable properties, DESs are intensively studied as solvents in the treatment of biomass, especially lignocellulosic materials (Tang et al. 2017; Sirviö and Heiskanen 2017; Chen and Mu 2019). Lignocellulose, mainly comprising cellulose, lignin, and hemicellulose, is a widely available, renewable resource for production of materials, chemicals, and fuels (Brodin et al. 2017; Lorenci Woiciechowski et al. 2020). DESs are investigated as a solvent to disintegrate the recalcitrant nature of the lignocellulose complex to individual components (e.g., in delignification) (Malaeke et al. 2018; Chen et al. 2019; Suopajärvi et al. 2020).

In addition to the separation processes, DESs are used in material preparation, such as production of lignocellulose nanomaterials. Cellulose nanofibers (CNFs) are well-known lignocellulose-based nanomaterials, generally produced from bleached, ligninfree cellulose pulp by using enzymatic, chemical, and mechanical methods, or their combinations (Klemm et al. 2018). In the preparation of CNFs, DESs are used as a swelling agent to obtain non-chemically modified CNFs (Sirviö et al. 2015, 2020a; Li et al. 2017b; Hosseinmardi et al. 2017). The swelling of cellulose fibers results in loosening of the fiber structure, thus allowing for a more efficient CNF production by mechanical disintegration. In the production of chemically modified CNFs, DESs have been used as solvents (Selkälä et al. 2016), catalytic reaction media (Sirviö 2018), and reagents (Sirviö et al. 2019).

Recently, there has been an emerging interest in the production of novel biomass-based nanomaterials, the so-called lignocellulose nanofibers (LCNFs) or wood nanofibers (WNFs) (Solala et al. 2020). Both LCNFs and WNFs refer to the nanomaterials that are produced directly from lignocellulose biomass without or with minor removal of lignin (and hemicellulose). WNFs is a term used exclusively for wood-based lignocellulose nanomaterials (Visanko et al. 2017; Yousefi et al. 2018), whereas LCNFs is a wider term referring to the nanomaterials from any type of lignin- and cellulosecontaining biomass. LCNFs can be produced, for example, from wheat straw (Espinosa et al. 2019) and bagasse (Ninomiya et al. 2018). Due to the exclusion of process steps related to biomass fractionation (e.g., delignification and bleaching), the raw materials in LCNFs can be more cost-effective and have lower environmental impact (i.e., due to the consumption of lesser toxic chemicals). In addition, lignin and hemicellulose can elevate the feasibility of the LCNFs in many applications compared to CNFs, for example, by improving the metal-removal efficiency (Sirviö and Visanko 2020) and providing UV-protection (Wang et al. 2018; Sirviö and Visanko 2019; Liu et al. 2020). However, high crosslinking density (Hanhikoski et al. 2020) as well as hydrophobicity (Figueiredo et al. 2018; Solala et al. 2020) of lignin can hamper the fibrillation effect of materials with high lignin content (Spence et al. 2010), making the production of LCNF generally more cumbersome process compared to CNF.

The chemical modification of biomass can decrease the energy consumption during the nanomaterial production. The introduction of carboxylic acid groups is among the most potential chemical modifications because after neutralization, charged groups are formed, creating electrostatic repulsion and increased osmotic pressure, resulting in the liberation of nanoparticles by mild mechanical treatment (Isogai et al. 2011). Carboxylic acid groups can be introduced by oxidation (Isogai et al. 2011) or carboxymethylation (Naderi et al. 2014) or by using diacids (Sirviö et al. 2016; Bian et al. 2017; Li et al. 2017a) or their anhydrides (Iwamoto and Endo 2015; Sehaqui et al. 2017). Succinic anhydride is a cyclic carboxylic acid anhydride that can react with hydroxyl groups of biomass via the ring-opening reaction to form ester and carboxylic acid groups. Previously, succinic anhydride was used to modify cellulose in dimethyformamide (Sehaqui et al. 2017) and urea-LiCl DESs (Selkälä et al. 2016), cellulose nanocrystals in dimethylformamide (Leszczyńska et al. 2019) and pyridine (Wu et al. 2019), and sawdust in xylene (Doczekalska et al. 2007). Currently, large-scale succinic anhydride is produced from maleic acid, but it can also be obtained from succinic acid, which can be produced from biomass (Bechthold et al. 2008) and industrial side products such as glycerol (Carvalho et al. 2014) via fermentation.

A good reaction efficiency was observed when succinylation of wood (spruce groundwood pulp) was studied using DES based on triethylmethylammonium chloride (TEMACl) and imidazole (IMI), possibly due to the similar catalytic effect of IMI on the acylation of lignocellulose (Nawaz et al. 2013) compared to the commonly used pyridine (Bhandari and Singhal 2002). However, because of the swelling of lignocellulose in DESs, a 25-time excess of DES compared to biomass was used. In this study, we investigated the mechanochemical succinylation of sawdust followed by post-heating in order to decrease the DES consumption. During the mechanochemical modification, size reduction and chemical modification can occur simultaneously. Mechanochemical modification has been previously applied in chemical modification of sawdust with sulfamic acid-based DESs. However, chemical modification of lignocellulose with sulfamic acid is a one-step reaction in which the DES component (sulfamic acid) acts as a reagent, whereas imidazole-catalyzed succinylation is a two-step reaction in which an active intermediate is formed between the DES component and succinic anhydride (Sirviö and Visanko 2017). Therefore, the present study aims to investigate whether the succinvlation of sawdust occurs in mechanochemical milling without the use of excess DESs and additional solvents. In addition, the selected succinylated sawdust samples were disintegrated into WNFs to further examine for film preparation and emulsion stabilization.

Experimental

Materials

Spruce sawdust was obtained in the never-dried from Keitele Forests Oy. The sawdust was oven-dried (24 h at 60 °C) and sieved with a 2-mm mesh. The proportions of lignin (TAPPI T222), alkali-soluble (TAPPI T222) and insoluble polysaccharides (ISO 1762), and acetone-soluble extractive (TAPPI T280) contents of the sawdust were 29.4 %, 14.2 %, 54.5, 1.6 %, respectively.

TEMACl (98.0 %), IMI (98.0 %), and succinic anhydride (95 %) used for mechanochemical succinylation of the sawdust were obtained from TCI (Belgium). Soybean oil and methyl methacrylate (MMA, 99.0 %) were obtained from Sigma Aldrich (Germany), 0.1 M NaOH and 0.1 M HCl from FF-Chemicals (Finland), and NaCl (99.5) from Merck (Finland). For all steps requiring water, deionized water was used.

Mechanochemical and thermal succinylation of sawdust

The sawdust was milled using a planetary ball mill (Retsch PM200, Germany) with a 125-mL jar equipped with seven milling balls (diameter of 20 mm). A jar was charged with 5 g of sawdust together with 1, 2.5, or 5 g succinic anhydride and 1, 2.5, 5, 7.5, or 10 of DES. The molar ratio between TEMACl and IMI was 3:7. DES was added to the jar as individual components and was allowed to form during the milling by mechanical energy (Crawford et al. 2016; Li et al. 2019). After 15-min milling, the thermal posttreatment was followed, that is, the jar was placed into an oven at 100 °C for 15, 30, or 60 min. After the desired reaction time, the sawdust was washed using either 1000-mL deionized water (for particle size analysis) or 100 mL of 0.1 M HCl followed by washing with 1000 mL of deionized water (for carboxylic acid group determination and

nanofibrillation). All the samples were stored at 4 °C before analysis.

For reference samples, sawdust was milled without chemicals or together with individual DES components. The reference samples were also obtained without subjecting them to post-heating in an oven. All the reaction conditions that were applied are presented in Table 1.

Carboxylic acid content analysis

The carboxylic acid content of the samples was measured by conductometric titration using Mettler Toledo Excellence T5. For the measurement, an acid-washed sample with a dry mass of 0.5 g was measured in a sample cup. Next, 10 mL of 0.01 M NaCl solution and deionized water were added until the total mass of the suspension reached 70 g. The pH of the suspension was adjusted to 3 by using 0.1 M HCl. The sample was then titrated using 0.1 M NaOH. The carboxylic acid content was calculated from the plateau area of the

conductivity curve. All the samples were measured in duplicate.

Particle size analysis and fractionation

The particle size of the water-washed samples was measured using the Beckman Coulter LS 13 320 (USA) laser diffraction particle size analyzer. Before analysis, 300 mL of 0.2 wt% dispersion was prepared by manually mixing the sample with the desired amount of water.

Infrared spectroscopy

Chemical characterization of sawdust before and after succinylation were investigated using diffusion reflectance Fourier transform (DRIFT) infrared spectroscopy using Bruker Vertex 80v spectrometer (USA). The spectra were collected in the range of $4000-600 \text{ cm}^{-1}$ using resolution of 2 cm^{-1} with number of scans being 40 per sample.

Table 1 Chemicals and post-heating conditions used in mechanochemical succinylation of sawdust

Entry	Succinic anhydride (g)	DES (g)	Post-heating time (min)	Carboxylic acid content (mmol/g)	Mean particle size (µm)	
1	-	_	_	0.13 ± 0.01	59	
2	5	-	-	0.14 ± 0.00	84	
3	5	_	30	0.37 ± 0.00	91	
4	5	5	-	0.69 ± 0.01	157	
5	5	5	15	0.67 ± 0.00	90	
6	5	5	30	0.98 ± 0.02	111	
7	5	5	60	2.73 ± 0.02	75	
8	5	1	30	1.13 ± 0.05	32	
9	5	2.5	30	0.75 ± 0.01	396	
10	5	2.5	60	1.44 ± 0.00	395	
11	5	7.5	15	1.21 ± 0.03	42	
12	5	7.5	30	2.42 ± 0.03	44	
13	5	7.5	60	3.47 ± 0.04	46	
14	5	10	15	0.98 ± 0.00	58	
15	5	10	30	2.42 ± 0.01	52	
16	5	10	60	3.55 ± 0.01	52	
17	1	7.5	30	0.44 ± 0.00	73	
18	2.5	7.5	30	1.07 ± 0.00	69	
19	5	_c	30	0.82 ± 0.02	347	
20	5	_ ^d	30	0.63 ± 0.01	254	

Mass of the sawdust in all the samples was 5 g and the milling time was 15 min

^a Weight weighted fiber length. ^{b,c} IMI and ^dTEMACl were used instead of DESs

Nuclear magnetic resonance

The solid-state ¹³C cross polarization-magic angle spinning nuclear magnetic resonance (CP-MAS NMR) spectra were measured from the original sawdust and the freeze-dried wood nanofibers using a Bruker Avance III 300 spectrometer having a ¹³C resonance frequency of 75.5 MHz. Prior the measurements, original sawdust was ground using Ultra Centrifugal Mill ZM 200 (Retsch, Germany) using a sieve size of 250 mm. The samples were packed into 7-mm zirconia rotors, and the spinning frequency was 5 kHz. Tetramethylsilane at 0 ppm was used as an external standard. Spectra were acquired with 16 384 scans, 4 s repetition rate, 1.5 ms variable amplitude contact pulse, and SPINAL-64 decoupling during the acquisition.

Fabrication of wood nanofibers

Nanofibrillation of the succinylated sawdust was performed using a microfluidizer (Microfluidics M-110EH-30, USA). First, the samples were diluted to 1 % consistency with deionized water. Next, 0.1 M NaOH solution was added with a 1:1 molar ratio between carboxylic acid content of the sample and NaOH. Finally, the suspension was diluted to 0.5 % consistency and passed two times through a 400- μ m premixing chamber without the interaction chamber and then six times through 400- μ m premixing and 200- μ m interaction chambers at a pressure of 1000 bar.

Transmission electron microscope

Transmission electron microscope (TEM, JEOL JEM-2200FS, Japan) was used to investigate the morphology of WNFs. The sample was prepared by adding 7 μ l of a diluted poly-L-lysine solution, 7 μ l of a diluted WNF suspension, and 7 μ l of 2 % uranyl acetate on a carbon-coated copper grid. Between adding the chemicals, each of these solutions was allowed to remain on the grid for approximately 30 s and, after that, were dried with filter paper.

Preparation of wood nanofiber films

The WNF films were produced by the vacuum filtration method. The WNF suspension containing

0.33 g WNF as the dry matter was first diluted to 110 g, followed by mixing with a magnetic stirrer for 3 min and degassing with an ultrasonic bath for 10 min. The obtained suspension was then filtrated through a polyvinylidene fluoride membrane (Merck Millipore) with a pore size of 0.65 μ m. After all the visible water was removed by filtration, the film was dried in a vacuum drier (Rapid Götzsch, Germany) for 9 min at 93 °C under a gauge pressure of – 900 mbar.

Scanning electron microscopy

Scanning electron microscopy (SEM, Zeiss Zigma HD VP, Germany) was used to characterize the surface morphology of WNF films. Samples were clued to carbon tape and imagined using the accelerating voltage of 2 kV. Cross-section images were acquired from platinum coated tensile test strips using Zeiss Ultra Plus (Carl Zeiss SMT AG, Germany) field emission scanning electron microscope (FESEM) with the accelerating voltage of 2 kV.

Tensile strength test of films

The tensile strength test was conducted using a universal testing device (Instron 5544, USA) according to ISO 1924-2 standard. All the samples were conditioned at 23 °C and 50 % relative humidity for 48 h, and the measurements were performed under these conditions. After conditioning, the samples were cut into 70-mm long and 5-mm wide strips, and the average thickness was measured with a thickness gauge (Precision Thickness Gauge FT3, Hanatek Instrument, UK). For tensile measurement, a 2-kN force sensor, a gauge length of 40 mm, and a strain speed of 5 mm/min were used. Five samples of each film were measured.

Emulsion preparation and analysis

Before preparing the emulsion, 10 mL of 0.1 wt% WNF dispersion was prepared. Next, the dispersion was mixed with 1 g of soybean oil or MMA for 15 min using Ultra-turrax homogenizer with 7000 rpm at room temperature. The droplet size of emulsion was then directly analyzed using Beckman Coulter LS 13 320 (USA) laser diffraction particle size analyzer within 30 min after preparation of emulsion. The "span" was taken as a measurement of the width of the

particle size distribution. Span was calculated as follows: span = (D(0.9) - D(0.1)/D(0.5)), where D(0.9) is the droplet diameter for which 90 % of the droplets are smaller than this size, D(0.5) is the droplet diameter for which 50 % of the droplets are smaller than this size, and D(0.1) is the diameter for which only 10 % of the droplets are smaller than this size (Laitinen et al. 2017). Reference emulsions were produced used 1 g of oil or MMA with 10 mL of water.

Thermogravimetric analysis

The thermal properties of the original sawdust and WNFs were investigated using a thermal analyzer (Netzsch STA409, Germany) under a nitrogen at a constant rate of 60 ml/min. Before thermogravimetric analysis (TGA) WNFs were freeze-dried to obtain aerogel. Then, approximately 50 mg of dry sample was weighed in an aluminum oxide pan and heated from 40 to 950 °C at a rate of 10 °C/min. The first derivate curves of TGA (DTG) were recorded using OriginPro 2019 software.

Results and discussion

Mechanochemical and thermal succinylation of sawdust

A grinding media mill (grinding media are usually balls or beads) is a type of fine grinding mill that is used to produce wood floor. The fibrous structure of biomass is destroyed when the particles are under the impact either between the grinding balls and the mill casing or between the colliding grinding balls (Karinkanta et al. 2018). Ball milling has previously been used in the production of cellulosic nanomaterials (Piras et al. 2019). However, long milling times, ranging from few hours to several days, are generally used, as the liberation of nanosized particles needs a significant amount of energy. In this study, we used planetary ball milling to intensify the succinvlation of sawdust; however, our aim was not to produce WNFs directly using ball milling, but to improve the succinvlation efficiency of sawdust. Although the surface of sawdust can be chemically modified using reactive DESs, the disintegration before chemical modification is required to facilitate the production of WNFs (Sirviö and Visanko 2019). Therefore, simultaneous size reduction and chemical modification of the sawdust was studied. A schematic illustration of the mechanochemical succinylation is presented in Fig. 1. A 15-min treatment time was chosen for the ball milling, as this duration was observed to be appropriate to reduce the large sawdust particles into a fine powder. The mean particle size of the sawdust after 15 min of milling was 59 μ m (Table 1, entry 1). The carboxylic acid content of the milled sawdust was determined to be 0.13 mmol/g, mainly originating from hemicelluloses (Khazraie Shoulaifar et al. 2012).

Size reduction of wood in the used mechanochemical system depended primarily on the physical conditions, whereas chemical conditions played a minor role. The DES-to-wood ratio had the most important role in size reduction and there was the ratio, where dry grinding was switched to wet (or semi-wet) grinding.

Dry wood was efficiently ground to small particle sizes (Table 1, entry 1). When a small amount of DES was added, grinding became more efficient (entry 8). Although the exact effect of DES on size reduction is unknown, it can be postulated that DES might act as a swelling agent for sawdust and together with succinic anhydride might chemically enhance the size reduction by creating repulsion between the particles. Without DES, succinic anhydride (entry 3) together with IMI (entry 19) or TEMACI (entry 20) added to the grinding causes the particle size to increase, as the impact energy per wood decreases with increasing total solids.

Size-reduction characteristics were found to change dramatically when DES-to-wood ratio was increased from 0.2 (entry 8) to 0.5 (entry 9) and the particle size increased abruptly from 45 to 350 µm. The phenomenon probably addresses the fiber saturation point, that is, the cell walls of sawdust became saturated with liquefied DES, being a transition between dry grinding and (semi-)wet grinding. In wet grinding near the fiber saturation point (DES-to-wood ratio of 0.5, entries 9 and 10), size reduction was poor and the particle size remained large. Under these conditions, the free liquid presented may form inter-particle liquid bridges, which increase the cohesiveness of the powder. For this reason, sawdust does not mix properly and tends to stick to the surfaces of the grinding media and bowl, preventing the size reduction. On increasing the DES-



Fig. 1 a Schematic illustration of mechanochemical succinvlation of sawdust and \mathbf{b} reaction mechanism of hydroxyl groups of sawdust with succinic anhydride in the presence of imidazole

to-wood ratio to 1 (entries 5–7), additional free liquid begins to break the bridges, improving the mixing and flow of particles within the ball mill and thereby aiding in size reduction. At the DES-to-wood ratio of 1.5 (entries 11–13), the rheology of the slurry enhances further. An increase of the ratio to 2 (entries 14–16) does not have an additional effect on size reduction, indicating that the liquid medium is more or less continuous already.

Decreasing succinic anhydride loading slowed down the size reduction slightly. With the doses of 5 g (entry 12), 2.5 g (entry 18), and 1 g (entry 17), the particle sizes were 44, 69, and 73 μ m, respectively. This may indicate that chemical conditions also have a role in size reduction.

The degree of succinylation was associated with the particle size. At a given post-heating time, succinylation increased with decreasing particle size. With decreasing particle size, the specific surface area of particles increased, thus providing more hydroxyl groups for succinylation reaction. Additionally, decreasing particle size is an indication of increasing absorbed energy by the system that facilitated the reaction between succinic anhydride and hydroxyl groups of wood. Furthermore, post-heating had a crucial effect on the succinylation yield. A short postheating time (15 min) did not show noticeable increase in the carboxylic acid content (Table 1, entry 4 and 5), however, increase of heating time to 30 and further to 60 min gradually increased succinylation efficiency. Despite the size reduction of sawdust during the milling, the succinylation is solid-state reaction on the surface of sawdust and longer reaction times at elevated temperature are beneficial for the reaction.

Milling of sawdust together with succinic anhydride without the DES at a mass ratio of 1:1 demonstrated no increase in the carboxylic acid content compared to the original sawdust (Table 1, entry 2). This indicates that during the short milling time, there was not enough mechanical energy (or heat due to the friction) to facilitate the reaction between the succinic anhydride and hydroxyl groups of the sawdust. Post-heating of the sawdust milled with succinic anhydride at 100 °C for 0.5 h increased the carboxylic acid content 2.5-fold, from 0.14 to 0.37 mmol/g (Table 1, entry 3). By adding a small amount (1 g) of DES (entry 8), the carboxylic acid content increased to 1.13 mmol/g. Thus, it can be concluded that for the effective reaction with wood, succinic anhydride requires the presence of a DES, which acts as a catalyst in the succinylation reaction.

A transition from dry grinding to wet grinding appears to decrease the succinvlation efficiency, from 1.13 mmol/g (entry 8) to 0.75 mmol/g (entry 9). However, in wet grinding conditions, the increase in the DES-to-wood ratio stepwise from 0.5 to 1.5 increases the carboxyl content almost linearly, then levels off with the DES-to-wood ratio of 2. The amount of carboxyl acid contents depended strongly on the post-heating time; a decreasing time led to lower carboxyl acid content. The DES-to-wood ratio from 0.5 to 2 with post-heating of 60 min produced carboxyl acid content from 1.44 mmol/g (entry 10) to 3.55 mmol/g (entry 16), respectively, whereas with post-heating time of 30 min, the carboxyl acid content varied from 0.75 mmol/g (entry 9) to 2.73 mmol/g (entry 7). At the DES-to-wood ratio from 1 to 2 with post-heating of 15 min, the carboxyl acid content varied from 0.67 mmol/g (entry 5) to 1.21 mmol/g (entry 11). In comparison with the results of previous studies, the level of carboxylic acid content of 2.73 mmol/g (Table 1, entry 7) was similar to the results reported previously with groundwood pulp at the same succinic anhydride-to-biomass mass ratio, but with 25 times higher DES content,(Sirviö and Visanko 2017) whereas the carboxylic acid content of 3.48 mmol/g was close to the value reported for succinylation of cellulose in dimethylformamide (Sehaqui et al. 2017).

The degree of succinylation is strongly dependent on the amount of succinic anhydride. The carboxylic acid content seems to be directly proportional to the amount of succinic anhydride: the decrease in the succinic anhydride from 5 g (entry 12) to 2.5 g (entry 18) reduces the carboxyl acid content from 2.42 to 1.07 mmol/g, respectively. Further decrease of the succinic anhydride to 1 g (entry 17) reduces the content to 0.44 mmol/g.

The use of individual DES components, IMI (entry 19) and TEMACl (entry 20), also demonstrated an increase in the carboxylic acid content compared to the reaction with only succinic anhydride (entry 3). Pure IMI had higher effect on the carboxylic acid content than TEMACl, which could be attributed to the (partial) melting of IMI during the reaction.

Infrared spectroscopic analysis

Sawdust milled without any chemicals exhibited a typical infrared spectrum of wood materials containing cellulose, hemicellulose, and lignin (Horikawa et al. 2019), and no difference was observed when compared to the original sawdust (Fig. 2). The sawdust had a carbonyl stretching peak at 1734 cm^{-1} , originating from the ester from the acetyl group of hemicellulose and ester linkage of the carboxylic groups in the ferulic and p-coumaric acids of lignin/ hemicellulose (Jonoobi al. 2009). et After mechanochemical succinvlation and acid washing, the carbonyl stretching shifted to a slightly higher wavenumber (1740 cm^{-1}) and the intensity of the peak was increased notably. The changes in the carbonyl region is due to the addition of the ester and carboxylic acid groups to the sawdust by the reaction with succinic anhydride. After neutralization of carboxylic acid with sodium hydroxide, the carbonyl stretching peak was further shifted to a higher wavenumber, whereas the new peak appeared around 1600 cm^{-1} , corresponding to the antisymmetric stretching of the carboxylate anions. Therefore, the DRIFT spectra provide further evidence that sawdust is efficiently modified chemically by the mechanochemical succinvlation.



Fig. 2 DRIFT spectra of (a) original sawdust, (b) sawdust milled without chemicals, and acid-washed succinylated sawdust (carboxylic acid content of 0.44 mmol/g) (c) before and (d) after NaOH neutralization

Solid-state nuclear magnetic resonance analysis

The further chemical characterization of original sawdust and succinylated samples (Table 1, entries 17, 18, and 13) were done using solid-state ¹³C CP-MAS NMR. At the spectrum of the original sawdust, the characteristic peaks of aromatic lignin carbons can be observed at range of 110-160 ppm (Santoni et al. 2015) (Fig. 3). Small peak of the methoxy group of lignin is observed at 55 ppm. The most dominant feature of the NMR spectrum of sawdust is the aliphatic carbohydrate carbons at region of 65-105 ppm. The most intensive peaks at 72 and 74 ppm are associated to carbon C2, C3, and C5 of cellulose and hemicellulose. The anomeric carbon at C1 position of carbohydrate is observed at 105 ppm. Typical methyl and carboxylate carbon peak of hemicellulose are presented at ppm of 21 and 172, respectively.

After succinylation, all peaks related to original sawdust are still visible, indicating that there was not notable removal of wood constituents during the chemical treatment. On the other hand, strong peaks can be observed at carbonyl region at ppm of 175 and 180 and they can be associated to ester and carboxylate carbon of the succinic acid monoester group (Ribeiro-Viana et al. 2016). Furthermore, methylene peak of succinyl group can be seen at 31 ppm (Xin et al. 2017). The NMR results further indicates that mechanochemical and thermal succinylation using DES is efficient



Fig. 3 ¹³C NMR spectra of (a) original sawdust, and succinylated sawdust with carboxylic acid content of (b) 0.44, (c) 1.07, (d) 3.47 mmol/g

method for chemical modification of sawdust without notable removal of original wood constituents.

Wood nanofibers from mechanochemically succinylated sawdust

Three succinylated samples with a carboxylic acid content of 0.44, 1.07, 3.47 mmol/g (Table 1, entries 17, 18, and 13) was investigated for WNF production by microfluidization and the samples were designated as WNF1, WNF2, WNF3, respectively. From the TEM images, it can be seen that all the samples exhibited a heterogonous size distribution (Fig. 4) (more TEM images can be seen in Supporting Information). The size of the fibrillated fibers ranged from individual, elemental fibrils of few nanometer wide to large, several hundred nanometer-wide aggregates. The large deviation in the fiber size is characteristic for LCNFs and WNFs with a high lignin content, as the lignin acts as a matrix to bind microfibrils together, reducing the fibrillation efficiency (Solala et al. 2020). Similar to the previous reports (Sirviö 2018; Li et al. 2019; Sirviö et al. 2020b) with WNFs, some individual, coarse nanoparticles can also be observed (Fig. 4f), associated with the amorphous materials originating from lignin and hemicellulose.

Wood nanofiber films

One possible application of nature-based nanomaterials is in the replacement of plastic packaging and wrappings. In addition, they can be used as reinforcement, for example, in paper and cartonboard (Boufi et al. 2016; Sanchez-Salvador et al. 2020). The WNF films obtained from the mechanochemical succinylated sawdust exhibited relative low mechanical properties, for example, specific tensile strength ranged from 63 to 32 kNm/kg (Table 2). For the CNF films obtained from bleached cellulose, the specific tensile strength over 200 kNm/kg has been reported (Salajkova et al. 2013; Yang et al. 2020; Sirviö et al. 2020a). In addition, although films produced from WNFs with a high lignin content usually have lower mechanical properties than CNFs, specific tensile strengths of 83 (Sirviö and Visanko 2017), 90 (Ämmälä et al. 2019), and 134 kNm/kg



Fig. 4 TEM images of WNF1 (a and b), WNF2 (c and d), and WNF3 (e and f) (higher quality images are presented in Supporting Information)

Sample	Density (g/cm ³)	Specific strength (kNm/kg)	Strain (%)	Specific modulus (MNm/kg)	Work capacity (J/ kg)	Citation
WNF1	0.79	63 ± 9	1.7 ± 0.3	5.5 ± 0.3	650 ± 220	This work
WNF2	0.67	32 ± 5	1.2 ± 0.2	3.8 ± 0.6	210 ± 50	This work
WNF3	0.75	32 ± 3	3.2 ± 0.5	2.2 ± 0.2	670 ± 140	This work
Holo-CNF	1.47	218	4.8	14.3	6667	Yang et al. (2020)
WNF (lignin content of 31 %)	0.51	55	-	10	4313	Spence et al. (2010)
Cationic WNF	0.53-0.77	79–134	4.0–5.7	4.6–7.5	-	Sirviö et al. (2020b)
Polylactic acid	1.21–1.25	16.8–48.0	2.5-6	0.28-2.80	-	Callister and Rethwisch (2012)
Polylactic acid	1.24-1.30	40.0-66.8	3.0-10.0	2.23-3.85		Farah et al. (2016)
Polypropylene	0.9	28–44	-	-	-	Farah et al. (2016)

Table 2 Density and mechanical properties of WNF films and their comparison with selected CNF, WNF and polymeric materials

(Sirviö et al. 2020b) have been previously reported. The tensile test results indicate that mechanochemical succinylation is not ideal for production of highstrength biobased materials. Nevertheless, the mechanical properties of WNF films produced from the succinylated sawdust are higher than common

plastics, such as oil-based polypropylene (Callister and Rethwisch 2012) and biobased polylactic acid (see Table 2) (Farah et al. 2016).

When comparing the films produced from different mechanochemical succinylated sawdust, it can be noticed that WNF1 with the lowest carboxylic acid content exhibited the highest specific tensile strength and modulus. The WNF2 and WNF3 had similar specific tensile strengths, although the strain of WNF3 was more than two times higher than WNF2. Therefore, the work capacity of WNF3 was higher than WNF2, and in similar range to WNF1, despite the significant difference in specific tensile strength between WNF1 and WNF3. Therefore, tensile test results indicates that mechanical properties of WNFs could be adjusted by changing the carboxylic acid content and for high tensile strength material, relative low succinvlation degree is desirable. On the other hand, higher succinvlation degree decreased brittleness of the films that is, making it more ductile. Although the strain value of 3.2 % is still lower compared to many cellulosic and synthetic materials, it might be possible to adjust the ductility of WNF films by optimizing the succinvlation degree as well as by using different counter-ion instead of sodium. For example, tetraalkylammonium cations have been shown to increase the strain as well as the hydrophobicity of carboxylated CNFs (Shimizu et al. 2014). Furthermore, the higher carboxylic acid content slightly improved the transparency of the films, as the image below WNF3 film was slightly more visible compared to the other films (Figure S4). However, all the films were practically opaque, which is typical to the films produced from high-lignin containing lignocellulose nanomaterials (Ewulonu et al. 2019).

The morphology of the films might have a significant impact on the mechanical properties and the SEM images of the surface of the films were uneven and rough (Fig. 5). Especially the WNF1 film with the lowest carboxylic acid content contained a significant amount of large, non-disintegrated fibers. Nevertheless, it can be assumed that the presence of large fibers provided moderate mechanical strength to the film and the presence of nanosized fibers acted as reinforcement and a gluing agent to bind larger fibers together. Therefore, the WNF1 film exhibited the highest tensile properties of all the films.

The WNF2 sample also showed the presence of large fibers, although in lesser extent compared to WNF1. Only a few large fibers were embedded in the network of small nanofibers on the surface of the film produced from WNF3. Furthermore, presence of large fibers is evident in cross-section of WNF1 and WNF2 films, as they showed notable amount of protruding large fibers. On the other hand, SEM images of the cross-section of WNF3 exhibited relatively smoot surface and layered structure typical to lignocellulose nanomaterials films, although layers were not as prominent as they are in typical CNF films (Benítez et al. 2013). The visible reduction in the amount of large fibers indicates that higher carboxylic acid content could have enhanced the fibrillation efficiency. However, the mechanical properties of WNF2 and WNF3 films were notably lower than those of WNF1. From the SEM images, it can be observed that despite the presence of few large fibers, the surfaces of the WNF2 and WNF3 films were uneven and porous. Therefore, the bonding between the fibers were reduced and, as there were no large fibers to support the film structure, the mechanical properties were observed to decrease when compared to WNF1. It should also be noted that especially the WNF3 contains a significant amount of non-lignocellulose materials, that is, the amount of sodium succinate groups significantly contributes to the mass of the films (around 42 % compared to the 13 and 5 % of WNF2 and WNF1, respectively). The sodium succinate group might act as an internal plasticizer (Zhang and Fang 2000; Jia et al. 2018), improving the strain of WNF3 film. The plasticizing effect is also supported by the lowest specific modulus of WNF3 compared to other two samples.

Wood nanofibers as an emulsion stabilizer

Lignocellulosic nanoparticles are also potential biobased materials for Pickering emulsions, wherein the solid particles create a physical barrier between emulsion droplets, preventing them from merging on collision; that is, it allows for the production of stable emulsion (Yang et al. 2017). This approach has been studied for oil-spill treatments (Ojala et al. 2016; Doshi et al. 2018), in food applications,(Sarkar et al. 2018; Sanchez-Salvador et al. 2019) and in emulsion polymerization to make the composites (Saelices et al. 2019; Mabrouk et al. 2020). Cellulose is described as



Fig. 5 SEM images of the surface of WNF1 (a and d), WNF2 (b and e), and WNF3 (c and f) at two different magnification

an amphiphilic material that is able to interact with both the aqueous and oil phases (Costa et al. 2019). Chemical modification has been used to enhance the amphiphilic properties of the cellulose nanomaterial (Visanko et al. 2014; Ojala et al. 2018), and nanofibers produced from partially delignified wood has been used in as reinforcement of polystyrene via emulsion polymerization (Ballner et al. 2016). Here, the soybean oil represents the vegetable oil used, for example, in medical application in emulsion (Dai et al. 2016), whereas the MMA is a common monomer for emulsion polymerization (Ballard et al. 1984).

The water–soybean oil emulsion without WNFs had a particle size of 11.3 μ m and a span value of 34.1 (Table 3), indicating a relatively large droplet size and wide size distribution. The addition of WNFs resulted in a significant drop in the particle size and span value

of emulsion. Especially when WNF3 was used, the particle size was decreased almost 10-fold to 1.96 µm. In case of MMA, an emulsion could not be formed using water without WNFs, whereas the presence of WNFs allowed for the production of stable emulsion. When comparing the WNF samples, WNF3 again exhibited the highest efficiency to produce emulsion with the smallest particle size and lowest span value, although the particle size was higher than soybean oil. The differences between the particle size of emulsion formed with soybean and MMA might originate from lower viscosity of MMA, requesting a stronger barrier between the emulsion droplets to prevent collision. Nevertheless, WNFs could potentially be used in emulsion polymerization instead of environmentally undesirable petroleum-based surfactants, and higher carboxylic acid content seems to correlate with

 Table 3
 Particle size and span value of water-oil emulsions produced with pure water and with water-WNF suspensions (water-to-oil mass ratio 10:1)

Sample	Soybean oil		Methyl methacrylate (MMA)		
	Particle size (µm)	Span value	Particle size (µm)	Span value	
Water	11.3	21.5	_a	_a	
Water + 0.1 % WNF1	3.6	34.1	16.9	67.5	
Water + 0.1 % WNF2	9.4	33.7	23.9	80.1	
Water + 0.1 % WNF3	2.0	5.8	14.7	51.8	

*No stable emulsion was obtained with pure water and MMA

emulsion stabilization effect. However, more studies are warranted to optimize the emulsion formation.

Thermal properties of wood nanofibers

Many chemical modifications of lignocellulose materials are known decrease their thermal stability due to the introduction of labile and acidic functionalities (de Britto and Assis 2009; Fukuzumi et al. 2010). In addition, chemical and mechanical (e.g., grinding and microfluidization) modifications can damage the crystalline part of the lignocellulose (mainly cellulose) and decrease the polymerization degree of polymers, causing in decline in thermal properties (Nair et al. 2014). Previously, succinylation of sawdust in xylene has reported to decrease the thermal stability of both softwood and hardwood sawdust (Doczekalska et al.



Fig. 6 a TGA and b DTG curve of the original sawdust and WNFs

2007). From Fig. 6 it can be seen that the thermal degradation of WNFs occurs at slightly lower temperature compared to original sawdust: onset degradation temperature of sawdust was at 312 °C, whereas the onset degradation temperature of WNFs were in range of 264-278 °C. There was no notable difference between onset temperatures of different WNF samples. In addition, WNF1 and WNF2 exhibited similar, monomodal degradation curves than original sawdust and according to the first derivate TG curves (Fig. 6b), their degradation rates were similar. However, the initial degradation rate of WNF3 was slower compared to other samples and it has minor second degradation rate peak 440 °C (Fig. 6b). It can be assumed that different degradation behavior of WNF3 is due to its significantly higher succinvlation degree. Degradation of succinic functionality result in release of acid groups upon degradation, which in turn causes the carbonization of lignocellulose material, thus creating insulating barrier decreasing the degradation rate. However, due to the weak acidity of carboxylic acid, carbonization is only observed with sample having high succinic group content (i.e., WNF3).

The thermal stability of the lignin-containing nanofibers are reported to be high compared to similar material produced from low-lignin containing pulp (Ewulonu et al. 2019). It has been shown that nanofibers prepared from lignin-containing exhibits better thermal stability compared to the low-lignin containing pulp (Nair and Yan 2015). The prolonged mechanical disintegration did not decrease the onset temperature of lignin containing nanofibers, whereas the thermal stability of low-lignin containing nanofibers gradually decreased after increased mechanical treatment. Although in current study, the thermal properties of sawdust decreased after the mechanochemical succinilation and mechanical disintegration, the thermal stability of WNFs produced are relatively high. For example, succinylated CNFs with carboxylic acid content similar to WNF3 has reported to have onset temperature at 254 °C (Sehaqui et al. 2017), being 10 °C lower compared to WNF3. Furthermore, the carboxylated, high-lignin containing nanofibers, with charge density of 0.857 meq/g (in between WNF1 and WNF2) has reported to have onset temperature at 230 °C (Herrera et al. 2018). Lower thermal stability of oxidized samples are generally attributed to the presence of aldehyde functionalities

(Ewulonu et al. 2019), which are absent in carboxylated lignocellulose produced by esterification with cyclic anhydride.

Conclusions

The highly consistent mechanochemical succinylation of sawdust was efficiently achieved and the use of the DES significantly improved the reaction efficiency. The moderate excess of DES (1.5 times the amount of sawdust) was found to be most efficient for yielding a high carboxylic acid content; however, even the use of 25 wt% of the DES compared to sawdust was able to promote the succinvlation reaction. Although the succinvlation had already occurred during the milling, the post-heating demonstrated a notable effect on the succinvlation and a maximum of 3.5 mmol/g of carboxylic acid content was achieved after 1 h postheating at 100 °C. The amount of the DES had a notable effect on the particle size, due to the transition from dry milling to the (semi-)wet grinding. WNFs with a wide size distribution could be prepared from the mechanochemical succinylated sawdust microfluidization and they could be used to produce selfstanding films and stable water-oil emulsions. Although increase in carboxylic acid content had adverse effect on strength of films, the WNF with highest carboxylic acid content was found to be best emulsion stabilizer. Therefore, by adjustment the reaction conditions (e.g., amount of reagents and post-heating time) can be used to design the WNF to fit properties of target application.

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Declarations

Conflict of interest All authors certify that there is no conflict of interests in this study.

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