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Preparation of Flame-retardant Lignin-containing Wood Nanofibers Using a High-consistency Mechano-chemical Pretreatment

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Highlights

- Mechano-chemical pretreatment was developed to produce anionic wood nanofiber.
- Deep eutectic solvent worked both as reactive agent and medium for the reaction.
- The reaction consistency of wood biomass was greatly improved (up to 60 wt%).
- Anionic wood nanofibers obtained high sulfate group contents (up to 3.1 mmol g⁻¹).
- Multi-functional films can be fabricated from anionic wood nanofibers.

Graphical abstract

ABSTRACT:

Deep eutectic solvents (DESs) can be used as green media for lignocellulosic nanofiber production. However, typically, a high liquid-to-lignocellulose ratio is required (i.e. the consistencies of biomass are low, usually limited from 1 to 5 wt%), which greatly reduces the sustainability of DES use. In the present work, wood sawdust was first anionized using a reactive DES (formed from sulfamic acid and urea) at a high mass consistency (with gradually increased sawdust consistencies up to 60 wt%) in the pre-milling and post-heating processes. Anionic sawdust nanofibers (ASNFs) were then produced after mild nanofibrillation (two passes) using a microfluidizer. The processes of producing ASNFs were fast (1 h of pretreatment) and the

ASNFs was obtained with high sulfate group contents (up to 3.1 mmol g⁻¹). Besides, the ASNFs possessed a well-individualized structure with a homogeneous size distribution (3–5 nm in width). More importantly, films fabricated from ASNFs achieved strong flame resistance and good mechanical strength. Due to the presence of lignin, ASNF films were able to block over 90% of UV light (at a wavelength of 200–400 nm). The investigated functionalities of ASNFs led the lignocellulosic biomass residuals to be converted to high value-added bioproducts. Therefore, the reactive DES treatment combined with milling and heating process offers a practical and sustainable route for multi-functional biomaterial production, which can be potentially utilized, even at an industrial scale.

KEYWORDS: Flame-retardant; deep eutectic solvents; anionization; milling; film

1. Introduction

Wood sawdust is an attractive lignocellulose resource owing to its low cost (sometimes even freely available from timber yards), global abundance, renewability and carbon neutrality.[1] Traditionally, sawdust is used directly in energy or charcoal production.[2] Nowadays, higher value-added applications based on sawdust have also been developed, such as green composites made from recycled plastic,[3] biotemplates for catalytic systems[4] and packaging materials reinforced by sawdust nanofibers.[5] Unlike solely cellulose-based nanofibers (known as nanocelluloses) that are conventionally produced from more expensive bleached pulp, wood nanofibers use mechanical pulp or even wood sawdust as a starting material. This approach provides many advantages, e.g. it reduces costs notably, has a high yield of 85–95% and avoids the toxic chemicals used in delignification.[6] Moreover, the lignin in wood sawdust nanofibers

can be utilized to formulate protective barriers that absorb UV light,[7] eliminate free radicals and are resistant to flame,[8] which all enrich the functionalities of sawdust nanofibers.

However, due to the hydrogen-bonded and compacted structure of cellulose fibers that are embedded in a strong lignin matrix,[9] the liberation of nanofibers from woody biomass is a cumbersome process (e.g. causing device clogging)[10] and requires a significant amount of energy. Thus, conventional pretreatment approaches based on enzymatic,[11] thermal-mechanical[12] and acid hydrolysis[13] are mostly applied before mechanical nanofibrillation. Nevertheless, wider applications, such as water purification additives to remove e.g. positively charged toxic heavy metals,[14] usually require chemical functionalities on the surfaces of nanofibers. More importantly, hydroxyl groups are rich in all major components of wood (i.e. cellulose, hemicellulose and lignin); therefore, strategies based on the chemical modification of hydroxyl groups can disrupt and loosen the hydrogen bonding networks, e.g. by introducing repulsive charges.[15] This is a crucial factor that promotes the liberation of nanofiber constituents[16] and reduces energy consumption during biomass disintegration.

Recently, deep eutectic solvents (DESs)[17–19] have been used as pretreatment mediums in production of functionalized ground wood nanofibers.[6,20] DESs, which typically consist of a binary system of hydrogen bond donors and acceptors, are known for their beneficial properties in comparison to many traditional solvents:[21] they are easy to prepare, readily available at a fairly low cost and biodegradable with a relatively low toxicity.[22,23] An obvious disadvantage of using DESs in biomass modification is that a high solvent-to-lignocellulose ratio has typically been used due to the very high solution viscosity.[19] Previously, the mass consistency of lignocellulosic biomass in DES systems has often been limited from 1% to 5% in the production of non-derivatised[24] and functionalised[6,20] nanofibers, respectively. The high amount of

chemical consumption and the required long reaction times in turn reduce the sustainability of DES use.

In this study, anionic sawdust nanofibers (ASNFs) were produced through the sulfation of wood sawdust in DESs under simultaneous milling, followed by nanofibrillation using a microfluidizer (Figure 1). The reactive DES components, including sulfamic acid and urea, were pre-mixed with sawdust (with gradually increased sawdust consistencies up to 60 wt%) under mechanical milling (at room temperature for 0.5 h). Then, the sawdust–DES mixtures were post-heated to accelerate the anionization reaction (at 105°C for 0.5 h). Conventionally, sulfation of lignocellulosic biomass using sulfamic acid usually requires additional medium (e.g. dioxane,[25] N,N-Dimethylformamide and diglyme[26]), which can cause chemical pollution and waste during the preparation of sulfated biomaterials.[27] Nevertheless, sulfamic acid composed DES was reported for sulfation of cellulose without using any external solvent.[28] The efficiency of sulfation was monitored by both elemental analysis (sulfur and nitrogen) and polyelectrolyte titration. The aim was to monitor mechano-chemical sulfation and its effect on nanofibrillation and nanofiber properties. The morphologies, crystallinities and viscosities of ASNFs were characterized using transmission electron microscopy (TEM), X-ray diffractometry and rheometry, respectively. Moreover, ASNF films were fabricated using a vacuum filtration method, and their structural features, UV shielding performances, thermal stabilities (including flame-retardant properties) and mechanical properties were investigated by field emission scanning electron microscopy (FESEM), ultraviolet–visible light (UV–Vis) spectroscopy, thermogravimetric analysis and a universal material-testing machine, respectively.

Figure 1. The flowchart and highlights in the preparation of flame-retardant wood nanofiber films from sawdust.

2. Materials and methods

2.1 Materials

Spruce timber sawdust with a diameter of ca. 2 mm (obtained from Pölkky Oy, Finland, and sieved with 2 mm mesh) was oven-dried at 105°C for 24 h. Standard methods were used to analyze the compositions of raw materials: the lignin content with a TAPPI T 222 om-02, the acetone-soluble extractives with a TAPPI T 280 pm-99 and the hemicellulose and degraded cellulose portions with a TAPPI T 212 om-02. The hemicellulose, lignin and extractive contents were 28.6, 19.7 and 1.2%, respectively. Urea (97%) was obtained from Borealis Biuron (Austria), and sulfamic acid (98%) and polylysine were obtained from Sigma–Aldrich

(Germany). All chemicals were used as received, and deionized water was used throughout the experiments.

2.2 Mechano-chemical Pretreatment of Sawdust in DESs

DES chemicals (sulfamic acid and urea with a molar ratio of 1:2) were weighted together with sawdust, and DES was formed directly during milling. The total mass of the sawdust–DES mixture was 10 g, and the mass consistencies of sawdust were 20, 30, 40, 50 and 60 wt%. Mechanical milling was conducted using a planetary ball mill device (Retsch PM200, Germany) with a 125-mL jar equipped with 7 milling balls (diameter of 20 mm). The milling time was 30 min and the rotational speed was 500 rpm. After milling, the sawdust–DES mixture was collected and evenly spread on a glass petri dish (diameter of 10 cm).

2.3 Heat Treatment of Milled Sawdust

The sawdust–DES mixture was transferred to an oven to promote further the sulfation reaction. The heating temperature and duration were 105°C and 30 min, respectively. After the heat treatment, the sample was diluted with 500 mL of deionized water and was washed using a centrifuge until the pH of the sample suspension was neutral. The sulfated sawdust was collected and stored at 4°C.

2.4 Fabrication of Anionic Sawdust Nanofibers

Sulfated sawdust samples were diluted with deionized water (1 wt%), followed by mechanical nanofibrillation using a microfluidizer (Microfluidics M-110EH-30, Westwood, MA, USA). Before nanofibrillation, sample suspensions were first dispersed using an Ultra-Turrax mixer (IKA T25, Staufen, Germany) at 11,000 rpm for 1 min. Then, the suspensions were passed once

through 400–200 μm and 400–100 μm chambers at 1,000 and 1,500 bars, respectively, which resulted in gel-like ASNF suspensions. ASNFs produced from different sawdust mass concentrations during milling (in sawdust–DES mixtures), i.e. 20, 30, 40, 50 and 60% (w/w), were coded as ASNF20, ASNF30, ASNF40, ASNF50 and ASNF60. The mass yields of ASNFs were calculated as weight percentages of dry matters between ASNFs and starting sawdust.

2.5 Elemental Analysis of ASNF

Dried ASNF samples (at 105°C for 24 h) were analyzed by PerkinElmer CHNS/O 2400 Series II elemental and LECO CS-200 carbon-sulfur analyzers for the determination of nitrogen and sulfur contents, respectively.

2.6 Polyelectrolyte Titration

The surface charge densities of ASNFs were determined through the polyelectrolyte titration method using a particle charge detector (BTG Mutek PCD-03, Germany). In total, 10 ml of the well-dispersed ASNF suspension (at 0.01 wt%) was titrated by polydadmec, and the charge density was calculated based on the consumption of polydadmec.

2.7 Viscosity

The viscosities of the ASNF suspensions were measured using the TA Instruments Discovery HR-1 hybrid rheometer (Germany), equipped with cone-plate geometry (cone diameter of 40 mm and cone-plate angle of 1.999°). ASNF samples were prepared at the same consistency of 0.5 wt%. All measurements were conducted at 25°C and at a shear rate of 0.1–1,000 1/s.

2.8 Preparation of ASNF Films

Nanofiber films (80 g m^{-2}) were prepared by the conventional vacuum filtration method.[29,30] The ASNF suspension was at first diluted with deionized water into a consistency of 0.25% and then homogenized with a magnetic stirrer for 10 min before filtration. A filter membrane with a pore size of $0.65 \mu\text{m}$ (Millipore, USA) was applied to obtain a condensed ASNF cake, and this was followed with a vacuum drying process at 93°C for 10 min using a Rapid-Köthen sheet former (Estanit, Germany). ASNF films were stored at a constant temperature and humidity condition ($23 \pm 1^\circ\text{C}$ and $50 \pm 2\%$, respectively).

2.9 X-ray Diffraction

The crystalline structures of pristine sawdust and ASNFs were investigated using wide-angle X-ray diffraction. The Rigaku SmartLab 9 kW rotating anode diffractometer (Japan), equipped with a Cu K α radiation source ($\lambda = 0.1542 \text{ nm}$), was set at 45 kV, 200 mA. All the oven-dried samples were pressed into tablets with a thickness of 1 mm. Scans were taken over a 2θ (Bragg angle) range from 5° to 50° and at a scanning speed of $2^\circ \text{ s min}^{-1}$ using steps of 0.05° . The degree of peak intensity of the main crystalline plane (200) diffraction was set at I_{200} . The peak intensity associated with the amorphous fraction of cellulose was coded as I_{am} . Crystallinity index (CrI) values were calculated according to the empirical Segal method.[31]

$$\text{CrI} = \left(\frac{I_{200} - I_{\text{am}}}{I_{200}} \right) \times 100\%$$

2.10 TEM

The morphological characteristics of ASNFs were analyzed with TEM using the JEOL JEM-2200FS (JEOL Ltd., Tokyo, Japan). ASNF samples were highly diluted (0.03 wt%) by deionized water before imaging. A tiny droplet ($7 \mu\text{L}$) of polylysine[32] was dosed on the top of a carbon-

coated copper grid and kept for 1 min. Filter paper was applied to remove the residual polylysine. Similarly, 7 μL of the ASNF sample solutions was then dropped and removed from the grid. Finally, a solution of uranyl acetate (2% w/v) was applied as a negative stain agent using the same procedure. The stained ASNF samples were imaged at 100 kV under standard conditions. Images were taken by a Quemesa CCD camera. The widths of the individual nanofibers were measured using the iTEM image analysis software (Olympus Soft Imaging Solutions GMBH, Munster, Germany). The width of each ASNF sample with standard errors was calculated based on over 100 individual nanofibers.

2.11 FESEM

Both surfaces and cross sections of ASNF films were imaged by field emission scanning electron microscopy (FESEM; Zeiss Sigma HD VP, Oberkochen, Germany). The cross sections were captured by snapping the frozen (liquid nitrogen) film strips. ASNF film samples were fixed to a carbon-coated carrier and were sputter-coated with platinum (with thickness of 5 nm). An accelerating voltage at 5 kV was applied during imaging.

2.12 UV-Vis Spectroscopy

UV-Vis spectra of ASNF films were measured using the Shimadzu UV-2600 spectrophotometer (Japan).

2.13 Thermogravimetric Analysis

Thermogravimetric analyses (TGAs) of ASNF films and original sawdust were carried out using a thermal analyzer (Netzsch STA 449F3, Germany) under two separate atmospheres, nitrogen flow and air flow (dynamic air), at a constant rate of 60 mL min^{-1} . Approximately 5 mg of the

room temperature-dried sample was carried by an aluminium oxide pan and was heated from 30 to 900°C with a heating rate at 10°C min⁻¹.

2.14 Limiting Oxygen Index (LOI)

The flame-retardant properties of ASNF films were represented by LOI values using a JF- 3 oxygen index meter (Jiangning Analysis Instrument Company, China). Based on the ISO 4589-1996 standard, film samples were pre-cut as narrow strips (130 mm × 3 mm) and were ignited with the required oxygen percentage.[33]

2.15 Tensile Test

The mechanical properties of ASNF films were measured with a universal material testing machine (D0724587; Zwick, Switzerland), equipped with a 100-N load cell. Films were always kept in constant temperature and humidity conditions (at 23 ± 1°C and 50 ± 2%, respectively) during sample preparation and measurement. The thickness of each specimen was measured by a precision thickness gauge (Hanatek Instruments, East Sussex, UK) to determine an average value of three random locations on the sample strip. For tensile testing, a 40-mm gauge length was set under a manual pre-strain of 0.05–0.1 N. The strain rate was controlled at 4 mm min⁻¹. After the stress–strain curve was plotted, Young's modulus was calculated from the initial linear slope.

2.16 Statistical Analysis

Mechanical properties were determined using values from more than five strips in each sample for tensile strength, maximum strain and Young's modulus. The one-way analysis of variance (ANOVA) was applied with (★) $p < 0.05$, suggesting a significant difference, and with (★★) $p < 0.01$, providing a critical assessment.[34]

3. Results and discussion

3.1 Anionization of Sawdust in DES

Sulfamic acid is a stable, non-hygroscopic and solid sulfating agent that has been used in the esterification of alcohols.[25,26] Compared with aggressive sulfuric or chlorosulfonic acid, sulfamic acid is milder and easier to handle. However, owing to the high melting point (ca. 205°C) and low reactivity of sulfamic acid, high reaction temperatures (e.g. 150°C was set for the sulfation of cotton cellulose[35]) are usually required. Nevertheless, the presence of urea can improve its sulfation efficiency and reduce the reaction temperature.[25] Therefore, a strategy using sulfamic acid and urea to form an effective DES (through a hydrogen bonding interaction[17]) was schemed.[28] In the current study, sulfamic acid, applied as part of reactive DES, reacts with OH groups of sawdust forming corresponding ammonium salt of sulfate ester (Scheme 1). As the mass ratio between DES and sawdust was low and raw sawdust was applied in a large size (ca. 2 mm in length), mechanical milling was used simultaneously to disintegrate the sawdust into fine powder and to promote the reaction efficiency. When sawdust was milled together with solid DES components at a relatively low consistency (e.g. 20 wt% of sawdust), a homogeneous muddy mixture was obtained, indicating that DES was formed during milling, and it was enabled to wet and penetrate within the sawdust structure. However, with the increase in sawdust consistency, the sawdust–DES mixtures became gradually drier in their appearance (Figure S1. in the Supporting Information). Moreover, sequential mechanical nanofibrillation of these samples was difficult (occurrence of chamber

clogging). To optimize the reaction efficiency, a post-heating process was then applied to the milled mixtures.

Scheme 1. Sulfation of hydroxyl with sulfamic acid.

3.2 Production of ASNFs

After the post-heating process, all anionized sawdust sample suspensions passed through chamber pairs of the microfluidizer successfully without clogging, which was benefited by both mechanical pre-milling (to obtain smaller-sized particles) and sulfation with DES (anionically charged groups loosened the sawdust's internal structure due to charge repulsion). The aqueous suspensions of ASNF20–50 (1 wt%) showed a homogenous, stable and highly gel-like status (Figure 2B). Sample of ASNF60 was slurry-like and started to form sediment after standing for 24 h at room temperature, whereas other ASNFs (e.g. ASNF50) maintained as a stable gel even after three months (Figure S2 in the Supporting Information). With the increased consistencies of sawdust in the reaction, the colours of the ASNF water suspensions changed from green-yellowish to yellow-brownish (from ASNF20 to ASNF60, Figure 2A). These visual differences in nanofibers in water are usually due to their newly introduced functional groups and/or the transformation of their morphologies (e.g. dimensions, liberation of fiber aggregates) from

pristine sawdust. Herein, the charge densities and morphological properties of ASNFs were investigated in more detail.

Figure 2. Visual appearance of the aqueous suspensions of ASNFs (ASNF20–60) at the 1 wt% concentration (A). Highly viscous, gel-like appearance of ASNF20 at the 1 wt% concentration (B).

3.3 Sulfate Group Contents and Mass Yields of ASNFs

The sulfate group contents in ASNFs were measured by elemental analysis (based on the weight percentages of N and S, respectively) and were further confirmed by polyelectrolyte titration. As shown in Figure 3 (detailed data can be found as Table S1 in the Supporting Information), sulfate groups were introduced successfully to the sawdust with high contents. Depending on the analysing methods, the contents of the sulfate groups in the same sample differed slightly. Nevertheless, similar trends (as a function of sawdust consistency) verified that the increase in sawdust consistency (during reaction) decreased the sulfate group contents almost linearly.

Theoretically, the N content associated with ammonium salt should be equal to the S content of the introduced sulfate groups (Scheme 1). However, the N contents were noted to be higher than

the S contents, mostly because of the occurrence of a side reaction (carbamation) between urea and cellulose, which increases the N content due to carbamate formation (Scheme S1 in the Supporting Information).[36–38] On the contrary, polyelectrolyte titration presented lower values in terms of charge density. This is assumed to be because only charged groups on the surface of sawdust were detected.

In addition to high sulfate group contents, all the ASNFs obtained an over 90 wt% of mass yields, with ASNF30–50 having even > 95 wt% (Table S1 in the Supporting Information). It is likely that the addition of large molecular weight anionic groups to the sawdust during the reaction resulted in the mass increase.

Figure 3. The contents of sulfate groups in ASNFs, represented by elemental analysis (N and S) and polyelectrolyte titration, respectively.

Generally, these results indicate a high reaction efficiency associated with the milling-assisted sulfation in a DES medium (i.e. short reaction times with a high mass yield and sulfate group contents were obtained). The high treatment consistency proved to provide clear benefits. For

example, compared with ASNF20, which had the highest sulfate group contents of 3.1 mmol g^{-1} , ASNF50 consumed three times fewer chemicals (per gram of sawdust) but still possessed a high quantity of the sulfate group (1.98 mmol g^{-1}). Besides, wood components become more soluble in water with an increase in sulfate group content and thus were partially removed during washing,[39,40] which also has a negative influence on their final mass yields.

3.4 Morphological Properties of ASNFs

TEM images confirmed the formation of nanosized and elongated sawdust fibers. All the ASNFs had well-individualized structures with a homogeneous size distribution (Figure 4A-E), from 2.4 ± 0.7 to $5.4 \pm 1.7 \text{ nm}$ (Figure 4F), which aligns with the description from the literature that wood elemental fibers have a typical width of 3–5 nm (TEM image of ASNF40 with a larger magnification can be found as Figure S3 in the Supporting Information).[41–43] The dimensions of the ASNFs differed from previously reported lignocellulosic nanofibers in which the containing fiber aggregates have large widths. For example, nanofibers from citrus waste,[11] bamboo chips[44] and hemp[45] had reportedly larger widths of c.a. 10, 50 and 200 nm, respectively. These results suggest that current pretreatment approaches are capable of leading lignocellulosic biomass to produce tiny elementary fibers. Of the samples, ASNF20 and ASNF60 showed the smallest and largest widths, respectively. It should be noted that ASNF60 also included more fiber aggregates than the other ASNF samples in the TEM analysis (Figure 4E). It is probable that the high sawdust-to-liquid ratio of ASNF60 restricted the DES penetration and wetting of sawdust completely, thus reducing the reaction efficiency. Consequently, the existence of both fiber aggregates and individual nanofibers led to the sedimentation of ASNF60 in a water suspension (Figure S2 in the Supporting Information).

Figure 4. TEM images of ASNF individual nanofibers: ASNF20 (A), ASNF30 (B), ASNF40 (C), ASNF50 (D), ASNF60 (E) and their measured widths (F).

In addition to nanofibers, lignin was also expected to be presented in ASNFs as a separate fraction. In the case of ASNF60, there existed irregular structures among the nanofibers, which were similar to previously reported lignin structures (Figure 5).[46] However, based on TEM images of ASNF20–50, similar irregularly shaped (amorphous) lignin/hemicellulose particles were not observed that much. This might be because of more effective (when comparing with ASNF60) mechanical milling and chemical modification were occurred in ASNF20–50, in which the amorphous structures of lignin and hemicelluloses were severely disintegrated and thus difficult to be visualized in the TEM analysis.

Figure 5. TEM image of ASNf60. Amorphous lignin or hemicellulose structures (arrow) are shown among individual nanofibers.

3.5 Rheological Features of ASNf Water Suspensions

In a nanofiber suspension, viscosity usually represents the most fundamental and common fluid rheological property that is critical to advanced applications, such as using nanofibers as bio-ink/rheology modifiers in fluidic high-resolution 3D printing.[47,48] Hereby, ASNfs were diluted in water at low consistencies of 0.5 wt%, and their viscosities were compared as a function of the shear rate at room temperature.

All the ASNf samples easily dispersed in water, which is important to aqueous-based applications, as non-derivatized lignin is naturally hydrophobic and therefore is often problematic

in water dispersing.[12,49] The results (Figure 6) indicated that the viscosities of the ASNF suspensions decreased as a function of the shear rate, suggesting the typical shear thinning behavior of the nanofiber suspension.[50,51] Among all the ASNF samples, ASNF40 showed the highest viscosity, which resulted from homogeneous fibrous network structure, whereas ASNF60 obtained the lowest and most water-like viscosity (because of its lower charge density and presence of more fiber aggregates). Overall, ASNF suspensions showed generally lower viscosity values than that of, for example, TEMPO-oxidised[52] and mechanical-grinded[53] cellulose nanofibers at a similar concentration. This may be due to the presence of more hydrophobic,[12] shorter and irregularly shaped lignin particles (when compared to cellulose).

Figure 6. Viscosities of ASNF water suspensions at consistencies of 0.5 wt%.

3.6 Crystallinity

It is well known that both mechanical and chemical treatments can affect the crystalline characteristics of cellulose-dominated lignocellulose fibers.[42,54] However, chemical treatment

using organic solvents can also dissolve the amorphous parts of cellulose,[55] hemicelluloses[21,42] and/or lignin,[56] which may in turn result in an increased crystallinity. Here, ASNFs were produced with a small amount of reactive DES, which may have decreased the influence caused by the dissolution of amorphous fragments.

In general, all the ASNFs retained their cellulose I crystalline structure without the occurrence of other cellulose polymorphs. The corresponding CrIs of the ASNFs were (Figure 7B) calculated from their X-ray diffractograms (Figure 7A). The CrI of the samples was found to increase as a function of the sawdust contents (from ASNF20 to ASNF50). ASNF20 showed the lowest CrI value at 27.4%, which is most likely because severe mechanical pretreatment was applied to a small mass of sawdust. In addition to the influence caused by mechanical disintegration, highly chemically modified ASNF20 contains many functional groups (i.e. sulfate and carbamate groups) that can be detected as amorphous regions and thus negatively affect their CrI values. Overall, with the increased amount of pretreated sawdust, more crystal structures can be protected from mechanical forces (ASNF20–50) and chemical damage. Nevertheless, ASNF60 obtained a lower CrI value than ASNF50, which was probably caused by a higher amount of amorphous hemicelluloses, and lignin was reserved in the fiber aggregates/bundles of ASNF60.

Figure 7. X-ray diffractogram (A) and calculated crystallinity indices (B) of ASNFs and pristine sawdust.

3.7 Surface Properties of ASNF Films

Wet film cakes were first obtained from the ASNF aqueous suspension by dewatering using vacuum filtration. ASNFs were homogenously distributed in the film cake (Figure 8A). After vacuum drying the cakes, ASNF films with smooth surfaces were fabricated with different visual transparencies (Figure 8B).

Figure 8. Wet ASNF20 film cake before drying (A) and the dried ASNF films (numbers refer to ASNF20–60) (B).

The surfaces and cross sections of ASNF films were analyzed by FESEM. ASNF20–30 (Figure 9A–B) showed a relatively rough surface with visible fibrous structures, whereas ASNF40–60

(Figure 9C–E) had a smoother appearance. In addition, all the ASNF films showed a multi-layered structure in their cross sections (Figure 9A'–E') without any visible porous structure. Nevertheless, ASNF30–50 (Figure 9B'–D') seemed to have more compacted layers than ASNF20 and ASNF60.

Figure 9. FESEM images of the ASNF films' surfaces (A–E) and their cross sections (A'–E').

3.8 UV Shielding Performance of ASNF Films

All the ASNF films were able to block 90% of UV-A (320–400 nm) and 100% of UV light below 320 nm (covered UV-B and UV-C ranges) (Figure 10), which is comparable to hybrid films prepared by e.g. ZnO-nanocellulose[57] or graphene oxide-cellulose acetate,[58] yet is much better than biohybrid films made from natural tannin extract and cellulose nanofibers.[59] The transmittances of ASNF films started to increase differently after a wavelength of ca. 350

nm. Specifically, at a wavelength of 400 nm, the transmittances of the films made from ASNF40 and ASNF50 increased similarly to 10%, whereas the ASNF20 film maintained 99% UV protection. In general, ASNF films achieved a good UV shielding performance, which was similar to other research that previously reported on cellulose-lignin film.[7]

More importantly, the presence of chromophore UV absorbents usually has a negative impact on the optical transparency of a film. However, in the visible wavelengths (400–750 nm), ASNF films had a good visible light transmission. Compared with a highly transparent PVA film having 3 wt% of lignin, which showed a significant reduction in transparency,[60] the ASNF films obtained 41–68% transmittance at wavelengths of 600 nm, which is similar to the reported cellulose nanocrystals–lignin hybrid film.[61] ASNF films are optically variable, because they are built from different sizes of fiber strands, which have a significant impact on light scattering.[62,63] Among ASNF films, films made from ASNF30–40 had much better optical transmittances than the ASNF20 film; this also verified the visible appearances of the ASNF films shown in Figure 8B. ASNF films with a good UV blocking performance combined with optical transparency are demanded to be utilized in advanced applications, such as optical lenses[64] and solar cells.[65]

It should be noted that although lignin has been known as natural UV blocker,[61] adding lignin to emulsions (e.g. sunscreen) can be problematic because high content of lignin may demulsify the sunscreen.[66] However, emulsions can be well stabilized by nanocellulose.[67] Therefore, lignin-containing nanofibers like ASNFs can be potentially applied as UV blocking agents in emulsion applications.[68]

Figure 10. Total transmittance of ASNF films.

3.9 Thermal Stability of ASNF Films

The thermal behaviors of ASNF films were analyzed by TGA in both N_2 and air atmospheres. The original sawdust particles were applied as reference samples in the TGA test.

TGA curves (Figure 11A–A') indicated clearly that all ASNF films had similar onset decomposition temperatures (T_{Onset}) at ca. 145 (N_2) and 130 (air) $^{\circ}C$, which were lower than what the pristine sawdust obtained T_{Onset} , at ca. 265 (N_2) and 235 (air) $^{\circ}C$, respectively. Previously, other researchers had noted that chemical- and/or mechanical-based approaches usually reduce the size and increase the surface area of cellulose fibers, and thus decrease their thermal stability.[69] Besides, reduced crystallinity of cellulose has also negative effects on decomposition temperature.[70] These explanations are also suitable here, whereas the mechanism is more complicated than only altering fiber dimensions and decrease in cellulose crystallinity. The decreased thermal stability of sawdust was greatly affected by DES sulfation:

the introduced sulfate groups on the ASNF films led to the formation of sulfuric acid during the degradation of ASNF films at an elevated temperature. Sulfuric acid, in return, worked as a catalyst that activates the dehydration reaction (through a reaction with hydroxyl groups) of ASNF films into char (does not burn) and non-flammable gases (like water and carbon dioxide).[71,72] In addition to sulfate esters, the formation of ammonia gas (from ammonium sulfate and possibly also from carbamate) can also improve the flame-retardant properties, as ammonia is a non-flammable gas and thus dilutes the oxygen concentration.[73,74] These factors explain why ASNF films achieved 61–78% more char residuals (at 600°C, N₂ atmosphere) than non-sulfated pristine sawdust in which more flammable volatiles were generated.[75] Therefore, the introduced sulfate groups (as well as ammonium salts)[76] can be utilized to act as flame retardants and thus highlight the functionality of ASNF films.[77] In addition to sulfated sawdust, a similar thermal performance and mechanism were also noted with solely cellulose nanocrystal and microcrystalline cellulose after the introduction of acidic sulfate groups.[78]

In the N₂ atmosphere, the parent sawdust showed monomodal maximum mass loss rates (T_{max}) at ca. 365°C, whereas ASNF films showed two separated pyrolysis processes at a temperature range of 190–250°C, including the primary pyrolysis of ASNF films catalyzed by sulfate groups and the char formation of solid residue (Figure 11B). In the air atmosphere, combustion occurred for all samples at 400–435°C (Figure 11B'), which was also confirmed by the DSC result, with a sharp exothermic peak at a corresponding temperature range (Figure 11C'). The temperatures of the exothermic peaks of the ASNF films were approx. 30°C lower than pristine sawdust with air flow; however, they were higher than that of the reported wood cellulose nanopaper (320–350°C)[79] and bacterial nanopaper (320–380°C).[80] More importantly, DSC curves from both the N₂ and air atmospheres showed an exothermic peak at 200°C for ASNF films, but not for

unmodified sawdust, which confirms the occurrence of a dehydration reaction (Figure 11C and Figure S4 with a large magnification in the Supporting Information)

Figure 11. TGA (A–A'), DTG (B–B') and DSC (C–C') curves of ASNf films and pristine sawdust. A–C and A'–C' were conducted in the N₂ and air atmospheres, respectively.

During the burning test, film stripes were ignited and compared by their required minimum concentration of oxygen to support combustion of the sample, which is represented by the LOI value. A higher LOI value indicates lower flammability of the sample. For example, the oxygen concentration in the air atmosphere is about 21%; therefore, samples with a LOI value less than 21% are likely burnt directly in the open-air condition. In the test, both non-derivatizing nanocellulose film (without lignin)[79] and wood nanofiber film (with lignin)[12] were applied as reference samples A and B (Ref. A and B), respectively.

Figure 12 indicated that ASNf films in general achieved a great flame-resistant ability, that is, the LOI values of ASNf films were 46–108% higher than nanocellulose film and even 31–87% higher than lignin-reserved nanopaper. Lignin is known as a natural flame retardant owing to its phenolic backbones, which are able to produce a mass of char residue upon heating at an elevated temperature.[81,82] The presence of unmodified lignin in Ref. B showed only a slightly higher LOI value than Ref. A. Similar to lignin-containing Ref. B, clay has been reported to act

as a fire retardant for carboxylated nanocellulose films to reduce their flammability. However, the addition of 10 wt% of clay was only able to slightly improve the LOI value of pure film from 18.3% to 23.1%.[83] Herein, the dominant reason for the improved flame-resistant performance of ASNF films was assumed to relate to the introduction of sulfate groups, which are able to form char layers that prevent the formation of flammable volatiles and further combustion, as explained before. Of the ASNF films, ASNF40 had the best flame-resistant performance, with an LOI value of 40.9%, whereas other ASNF films had similar LOI values at 28.6–33.5%, which was 18–30% lower than the LOI of ASNF40. A balance between chemical modification (sulfate group contents) and mechanical disintegration (morphology) is most likely responsible for the optimized flame resistance, as the burning test is also related to the bulk properties of materials.[84] To visualize and practically verify the flame-retardant properties of ASNF films, films made from ASNF40 and wood nanofiber (Ref. B) were ignited and compared with a recorded video in an open-air situation (presented in the Supporting Information). The video shows that Ref. B was burnt smoothly, with visible ash residuals and a minor amount of char residuals, whereas the ASNF40 film could not even be ignited. In addition, the flame-extinguishing ability of ASNF film was observed when the fire resource (match fire) was removed from the igniting of the ASNF films, suggesting a strong flame-retardant property.

Overall, these results indicate that raw sawdust and ASNF films have different degradation mechanisms, mostly caused by the introduction of acidic sulfate groups. It degrades sawdust significantly through a dehydration reaction, leading to lower thermal stability. On the other hand, it acts as a flame retardant by improving the char fraction from flammable tars. In addition, the formation of ammonia gas dilutes the oxygen concentration, which further protects the films from being burnt. Also, the existence of lignin had positive influence on the high LOI values of

ASNF films. The burning test indicated that ASNFs could be used as a flame-retardant agent, for example, in packaging and composite materials.

Figure 12. LOI testing results of ASNF films with a previously reported reference film. Ref. A and Ref. B are a nanocellulose film (without lignin) and wood nanofiber film (with lignin), respectively.

3.10 Mechanical Properties of ASNF Films

Lignin-containing cellulose nanopapers often have a lower mechanical strength than solely nanocellulose films owing to the fact that lignin can prohibit the hydrogen bonding of cellulose nanofibers.[85] However, the reported high tensile strengths of nanocellulose films usually represent their ultimate tensile strengths, whereas the yield strengths of cellulose nanopapers are actually lower. For example, a film made from cellulose nanofiber was reported to have a tensile strength of 214 MPa, whereas the yield strength was 91 MPa.[86] Tensile strength before yielding holds practical meaning, as it determines how much load that film materials can bear before deforming/being damaged permanently, which is of vital importance for applications that

require the original shape after being elongated. ASNF films were observed with only an elastic region in the tensile strength test, which indicated a strong non-yielding performance (Figure S5 in the Supporting Information). All the ASNF films had good tensile strengths (Figure 13A), and film made from ASNF50 achieved the highest tensile strength at 64.7 ± 6.8 MPa, which is comparable to the maximum tensile strengths of previously reported films fabricated from almond shell (65 ± 3 MPa)[87] and rice straw (66 ± 4 MPa).[88] Interestingly, the trend in the tensile strength of ASNF films is in line with their CrI values, and similar behavior (i.e. linear relationship between tensile strength and CrIs) has been reported with cellulose nanopaper.[89] For example, ASNF20 with the lowest CrI value had also the weakest tensile strength when it was in a film form. ASNF20–50 had a gradually improved tensile strength, whereas ASNF60 started to decrease, which was probably caused by large fiber aggregates (Figure 4E) and residual lignin structures (Figure 5). However, thermal pressing can likely be applied to soften the lignin and form a more compact structure;[90,91] thereby enhancing the mechanical performance of the film by improving the adhesion and strength of the bonds between the nanofibers.[12]

Figure 13B suggested that all the ASNF films achieved a similar strain at ca. 1.8%, which is in general lower than cellulose-based (e.g. nonderivatising[79] or TEMPO-oxidised[92]) nanopapers. The results from the elastic modulus followed similar trends in their tensile strength and distribution of CrIs (Figure 13C). ASNF50 had the highest value at 5.0 ± 0.5 GPa, which is comparable to the films made from grinded wood nanofibers (5.1 ± 0.5 GPa) and even pure nanocellulose (6 ± 1 GPa).[93] ASNF20 had the lowest elastic modulus at 3.6 ± 0.2 GPa, whereas there was no significant difference between ASNF50 and ASNF60. In general, ASNF

films obtained a good tensile strength and elastic modulus, and the CrIs of ASNFs were able to have a significant influence on their film's mechanical properties.

Figure 13. Tensile strength (A), Young's modulus (B) and strain (C) of nanofiber films. Data presented as mean $\pm$ standard error and analyzed using a one-way ANOVA, (★) $p < 0.05$; (★★) $p < 0.01$.

4. Conclusion

DES synthesized by sulfamic acid and urea was successfully applied for the production of highly anionically charged sawdust nanofibers with flame resistance. The pretreatment including pre-milling and post-heating processes were able to improve greatly the reaction consistencies of sawdust from a conventionally low consistency (1–5 wt%) to the current 60 wt%. All ASNFs obtained a homogenous size distribution at 3–5 nm in width, and the sulfate groups newly introduced on ASNFs act as strong flame retardants by promoting a dehydration reaction and forming non-flammable char layers. Due to the reservation of lignin, films made from ASNFs were also able to block over 90% of UV light; meanwhile, the optical transparencies of ASNF

films were still competitive with hybrid films. These features mean sawdust, a biomass residual, can be used in high value-added applications. In general, the combination of DES sulfation with milling and heating is an effective, productive and chemical-saving approach in functional nanomaterial production. Nevertheless, as a new form of DES application, the parameters in mechanical milling (e.g. milling time, sizes and number of milling balls and spinning speed) and the recycling of DES still deserve further study to optimize the sustainability of ASNF production.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Highlights

- Mechano-chemical pretreatment was developed to produce anionic wood nanofiber.
- Deep eutectic solvent worked both as reactive agent and medium for the reaction.
- The reaction consistency of wood biomass was greatly improved (up to 60 wt%).
- Anionic wood nanofibers obtained high sulfate group contents (up to 3.1 mmol g⁻¹).
- Multi-functional films can be fabricated from anionic wood nanofibers.