

Microemulsion Systems for Fiber Deconstruction into Cellulose Nanofibrils

Carlos A. Carrillo,^{*,†,‡} Janne Laine,[§] and Orlando J. Rojas^{*,†,§,||}

[†]Department of Forest Biomaterials, North Carolina State University, Raleigh, North Carolina 27695, United States

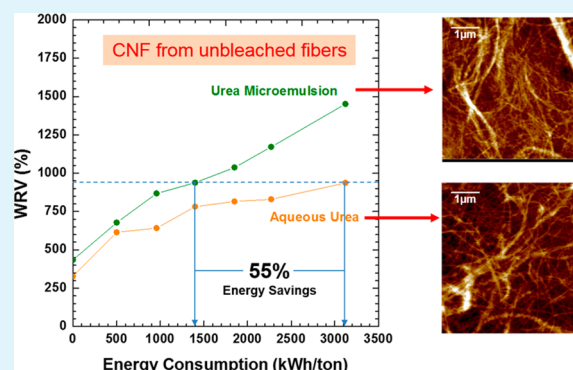
[‡]Escuela de Ingeniería Química, Universidad de Los Andes, Mérida 5101, Venezuela

[§]Bio-based Colloids and Materials Group, Department of Forest Products Technology, School of Chemical Technology, Aalto University, 02150 Espoo, Finland

^{||}Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina 27695, United States

ABSTRACT: A new method to produce cellulose nanofibrils (CNF) is proposed to reduce the energy demand during deconstruction of precursor fibers suspended in aqueous media. Microemulsions were formulated with aqueous solutions of urea or ethylenediamine and applied to disrupt interfibril hydrogen bonding. Compared to typical fibrillation of lignin-containing and lignin-free fibers, pretreatment with microemulsion systems allowed energy savings during microfluidization of 55 and 32%, respectively. Moreover, microemulsion processing facilitated smaller-scale CNF structures (higher degrees of deconstruction), with higher water retention value (WRV) and surface area. Urea-containing microemulsions were found to be most effective in reducing energy consumption and in weakening the cellulosic matrix. Films prepared from CNF processed after pretreatment with urea-containing microemulsions presented a more uniform fiber network and produced films with smoother surfaces compared to those based on ethylenediamine. The lignin-containing CNF (LCNF) produced denser films than those obtained from lignin-free CNF. The mechanical properties of films obtained after application of microemulsion pretreatment were compared, and the benefits of the proposed approach were further confirmed. Overall, fiber deconstruction after microemulsion treatment is a step toward energy-efficient production of nanocellulose.

KEYWORDS: deconstruction, microfluidization, cellulose nanofibrils, microemulsions, pretreatment, energy consumption



INTRODUCTION

Replacement of synthetic composite reinforcing agents by biobased materials has captured renewed attention because they can reduce costs while taking advantage of their availability and biodegradability.^{1–4} Cellulosic fibers are particularly remarkable because they have exceptional mechanical performance when used as reinforcement^{3,5} and represent the most abundant natural polymer on earth.^{3,6} However, a drawback in the application of cellulosic fibers, especially when they are processed into the micro- and nanoscales, is the high mechanical energy demanded during their deconstruction.⁷

By using different cellulosic sources, e.g., wood fibers, bacterial cellulose, etc., it is possible to produce cellulose nanofibrils (CNF) via mechanical disintegration (microfluidization, homogenization, or grinding).^{8,9} CNF manufacture involves water suspensions of cellulosic fibers that undergo high shear in order to break the linkages that hold the fibrillar network together. The CNF produced via mechanical disintegration usually have high aspect ratio and diameters from 10 to 100 nm.^{10,11} The high energy consumed during

defibrillation via microfluidization, reported to be of the order of ~1000 kWh/ton,⁷ can have a dominant, negative impact in CNF cost structure. Thus, new approaches to reduce the energy consumed and efficiency of fiber deconstruction are required to make it more cost-effective while maintaining the morphological and mechanical properties of the produced CNF.

Different pretreatments have been proposed to weaken the fiber structure and ease the fibrillation process; these include alkaline treatment, acid and enzymatic hydrolysis, (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO) oxidation, or a combination of the same.^{8,12} These approaches have been shown to increase the degree of fibrillation, mainly by reducing hydrogen bonding. The same observations apply to lignin-containing fibers to produce lignocellulose nanofibrils (LCNF). The presence of lignin in the form of hydrophobic domains

Received: September 30, 2014

Accepted: December 2, 2014

Published: December 2, 2014

smear out on the surface of precursor fiber is expected to affect the wettability and degree of deconstruction in aqueous media.^{7,13–15} The role of the hydrophobic faces in crystalline domains of cellulose is also expected to affect the interactions with deconstruction media, a factor that has not been studied in detail. Overall, more effective ways to deconstruct or to deliver agents for fiber pretreatment or processing are required.

We propose a new method for lignocellulosic fiber deconstruction that effectively delivers agents to facilitate the process. The approach is based on microemulsion systems that are able to penetrate capillary structures, for example, similar to that in wood impregnation or flooding at atmospheric pressure and room temperature.^{16,17} In fiber deconstruction, the microemulsions systems are proposed to be effective media to overcome the physical and chemical heterogeneities naturally present in lignocellulosic biomass while facilitating shear transfer and friction. Here, we refer to microemulsions, as first described by Winsor, as thermodynamically stable dispersions of two immiscible fluids that form spontaneously in the presence of a surfactant that reduces the interfacial tension between the two phases to ultralow values. The microemulsion systems were also applied to deliver active agents that reduce hydrogen bonding, which is responsible for holding together the cellulosic fibrils, and to improve the energy efficiency in the production of CNF or LCNF.

MATERIALS AND METHODS

The organic phase in the microemulsions was R-limonene (Fluka, St. Louis, U.S.A.), and the surfactant and cosurfactant used were sodium dodecyl sulfate (SDS) (Sigma-Aldrich, St. Louis, U.S.A.) and *n*-pentanol (Acros Organics, New Jersey, U.S.A.), respectively. Reverse osmosis water was used in all the experiments, and sodium chloride was used as a formulation variable to attain the phase behavior conditions corresponding to a microemulsion (Sigma-Aldrich, St. Louis, U.S.A.). Urea (Sigma-Aldrich, St. Louis, U.S.A.) and ethylenediamine (EDA) (Sigma-Aldrich, St. Louis, U.S.A.) were used as the active components in the microemulsions.

Lignocellulosic Fibers. Two different types of cellulosic fibers, with different lignin contents, were evaluated to determine the influence of residual lignin in the extent of deconstruction. The fiber materials were obtained from Kraft digestion of eucalyptus (unbleached, lignin-containing fibers) and from spruce after bleaching (lignin-free fibers). The moisture content of the fibers was 67 and 69% in the case of eucalyptus and spruce fibers, respectively.

Microemulsion Formulation. The surfactant (S)–oil (O)–water (W) system (SOW system) selected for the synthesis of the microemulsions consisted of SDS–R-limonene–water, and their phase behaviors were determined by following previous reports.¹⁶ Two active components for deconstruction were used: urea and ethylenediamine (EDA). These active agents were selected for their ability to weaken the hydrogen bonding between the cellulosic fibrils and to solubilize cellulose under extreme conditions.^{18–21} It is expected that by using these components under mild conditions the hydrogen bonding that holds together the fibers can be disrupted and a reduction in energy consumption for deconstruction of the fibers into CNF or LCNF can be achieved. A SOW system was selected according to an optimization of the formulation variables and included the incorporation of the given active component (see Table 1).

The order of component addition was as follows: First, the surfactant was mixed with water and the sodium chloride solution. The active agent was then introduced followed by limonene and pentanol addition. A magnetic stirrer was used for 1 min to mix the system, producing a clear, thermodynamically stable, isotropic liquid microemulsion.

Fiber Processing and Deconstruction. The cellulosic fibers were dispersed in 100 mL of microemulsion (for final 3% solids). The fibers were left to equilibrate in the microemulsion medium for 12 h at

Table 1. Microemulsion Compositions (Reported As wt %)

	system I	system II
SDS	3.0	3.0
NaCl	2.7	2.7
water	67.7	78.2
limonene	8.0	8.0
<i>n</i> -pentanol	3.1	3.1
urea	12.5	
NaOH	3.0	
ethylenediamine		5.0

room temperature and atmospheric pressure. The fibers were then filtered under vacuum and washed with excess water to remove any residual chemical after filtration.

The fibers were redispersed in water (1.5% solids content) using an Ultra Turrax system at 20 000 rpm for 15 min. Following the homogenization, the fiber slurry was defibrillated in a microfluidizer (Microfluidics M-110P) at 2 000 bar for 7 passes. In the microfluidizer, the samples flow through an intensifier pump that increases the pressure and go through two interaction chambers connected in series with orifice diameters of 200 and 100 μm , respectively. Before the first pass and after each of the passes, a sample was taken to evaluate the fibrils. A control sample was obtained by pretreatment with solutions of the given active components (free of surfactants and oil) at identical concentrations as those in the respective microemulsion, and applied following the same procedure described before. **We note that it was not possible to fibrillate the fibers if no pretreatment was applied.** Likewise, pretreatment of the cellulosic fibers with a microemulsion in the absence of any of the active agents (urea or EDA) was not successful. In both cases clogging of the microfluidizer prevented the process.

Energy Consumption during Fibrillation. The energy consumed during the process of fibrillation with the microfluidizer was calculated using the following eq 1:²²

$$E_m = \varepsilon \frac{V\rho}{1000} \left(\frac{V}{V_{\text{micro}}} t_{\text{res}} N \right) \quad (1)$$

where E_m is the total energy consumed, ε is the turbulent energy dissipation rate, V is the volume processed, ρ is the density of the dispersion, V_{micro} is the volume of the mixing chamber, t_{res} is the residence time, and N is the number of passes through the microfluidizer.²² The turbulent energy dissipation rate is the energy associated with turbulent eddies in fluid flow that break until they are ultimately converted into heat by viscous forces. We used the value indicated in ref 22 (see also references contained therein) of 1×10^7 W/kg, which is usually assumed for the micromixing chamber of the M-110P microfluidizer. Thus, the calculated energy should be used here as an approximation to determine relative differences in energy consumed.

CNF and LCNF Characterization. The morphology and dimensions of the nanofibers was studied by atomic force microscopy (AFM). For this purpose, a drop of a diluted dispersion of CNF or LCNF in water (0.05 wt %) was deposited on the surface of clean mica, and it was left to dry overnight. The images were taken with a Nanoscope IIIa Dimension 3000 atomic force microscope operated in tapping mode (Santa Barbara, CA, U.S.A.).

The water retention value (WRV) of the CNF or LCNF was measured as an indication of the degree of fibrillation of the material.^{12,23,24} The procedure used was adapted from TAPPI standard UM 256 to make it applicable to CNF. In short, 10 g of nanocellulose sample with 1.4% solid content were subject to centrifugation at 900g for 30 min. The wet pat obtained after centrifugation was dried overnight at 105 $^{\circ}\text{C}$, and the WRV was calculated using eq 2,

$$\text{WRV} = \frac{W_w - W_d}{W_d} \times 100 \quad (2)$$

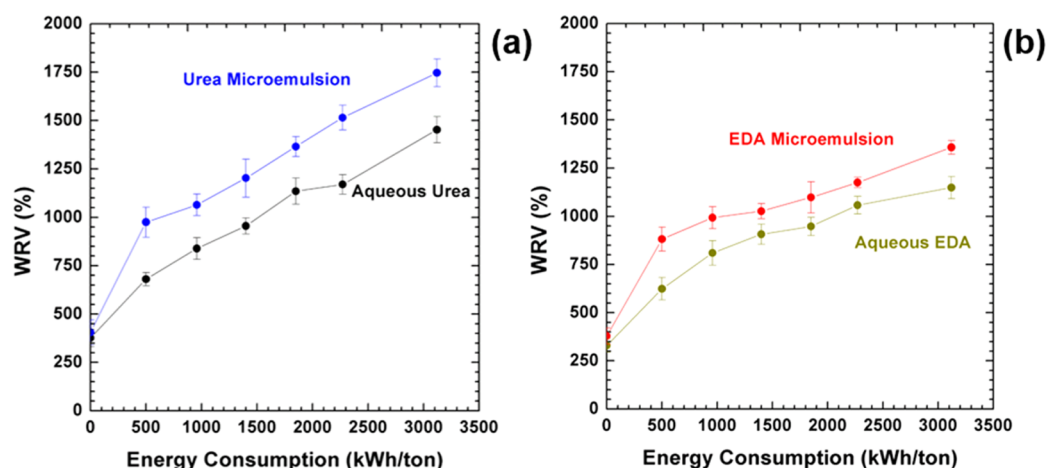


Figure 1. Water retention value (WRV, %) as a function of the calculated energy consumption in the microfluidizer during processing of lignin-free fibers pretreated with urea (a) and ethylenediamine (b), delivered from either aqueous or microemulsion systems. Note that fibers pretreated with only water or an active-agent-free microemulsion were not suitable for microfluidization due to clogging.

where W_w is the weight of the sample after centrifugation and W_d is the weight of the sample after drying at 105 °C overnight. The WRV was calculated for samples taken after each pass through the microfluidizer in order to follow the evolution of the degree of fibrillation.

Preparation and Characterization of CNF or LCNF Films.

After CNF or LCNF were obtained from the different pretreatments, films of the respective samples were prepared to study their topography and structural and mechanical properties. The films were produced by vacuum filtration under 2 bar pressure using a polycarbonate membrane with a pore size of 0.1 μm . The films were dried at 80 °C overnight and were stored in a desiccator. For the characterization of the films, field emission scanning electron microscopy (FE-SEM, JEOL 6400 microscope) with an accelerating voltage of 5 kV and a working distance of 20 mm was used to explore the microstructure and morphology of the films. The images analyzed corresponded to the cross sections of the films that were obtained after cryofracture of the frozen samples. The mechanical properties of the films were obtained by using a dynamic mechanical analyzer (DMA, Q800 from TA Instruments). The samples were cut from the films as 5.5 \times 9.0 mm probes. The data were obtained from a stress/strain procedure, isothermal at 29 °C and 50% humidity. The force was ramped up to 18 N with a speed of 3.0 N/min. The effective length was determined by the instrument, and the thickness was obtained from the SEM images of the cross sections of the films.

RESULTS

Water Retention and Energy Consumption. The water retention value (WRV) was determined after each microfluidizer pass as an indicator of the evolution of the degree of fibrillation of the cellulosic material (Figure 1). WRV profiles as a function of the energy consumption in the microfluidizer were constructed for lignin-free fibers pretreated with aqueous solutions of urea as well as microemulsions containing the same agent.

The same applied to the case of ethylenediamine (EDA) as active agent. It was observed that the WRV increased with the extent of fibrillation, as has been also reported elsewhere.^{12,23,24} For a given energy consumption in the microfluidizer, and compared to the WRV of the fibrils obtained after treatment with the aqueous solution of the respective active agent, higher WRV was measured after pretreatment with the microemulsions. This difference in WRV is an indication that the material pretreated with the microemulsions was fibrillated more extensively.

The fact that higher WRV was obtained when the microemulsion was used as a pretreatment indicates that this pretreatment medium was effective in reducing the energy consumed during deconstruction. The reason for this improvement is related to a better impregnation of the precursor fibers during pretreatment and a more efficient delivery of the pretreatment agent. These results are in agreement with previous findings that indicated an improved impregnation of woody biomass with the application of microemulsions at atmospheric pressure and room temperature.^{16,17}

Higher WRV was obtained after pretreatment with urea-based media (Figure 1a) compared to those based on EDA (Figure 1b), i.e., a higher fibrillation degree was obtained in the presence of urea. These findings indicate that, under the conditions of the pretreatment, urea is more effective for weakening the cellulosic matrix and to facilitate fibrillation. The energy required to obtain a given WRV after seven microfluidization passes after pretreatment with urea microemulsions was ca. 32% lower compared to that from urea solution pretreatment. In the case of EDA, an energy reduction of ca. 30% was observed if the respective systems are compared.

When the fibers were directly suspended in water without any pretreatment, the resulting suspension completely clogged the microfluidizer during the first pass. Likewise, the fibers pretreated with microemulsions in the absence of the active-agent clogged the microfluidizer and prevented fibrillation. Therefore, it is apparent that the microemulsion alone (with no active agent) is not enough to disrupt hydrogen bonding; the active agent is essential to the proposed process.

The WRV as a function of the energy consumption in the microfluidizer for the lignin-containing fibers is presented in Figure 2 corresponding to pretreatment with urea solutions and microemulsions. As was the case of lignin-free fibers, microemulsion pretreatment of lignin-containing fibers is more effective than the pretreatment with the respective aqueous solution. Noticeably, compared to the case of lignin-free fibers, the WRVs is lower in the case of lignin-containing fibers: the extent of fibrillation is lower, i.e., the presence of residual lignin might reduce the efficiency of fibrillation.

For the given WRV obtained after seven passes, the lignin-containing fibers required almost 55% lower energy if urea-based microemulsions are used; this energy saving level is comparatively larger than that observed for lignin-free fibers.

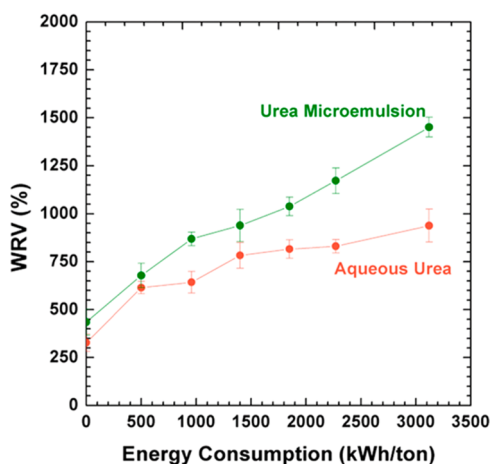


Figure 2. Water retention value of LCNF and CNF obtained after (microemulsion and solution) pretreatment with urea from lignin-containing fibers.

Thus, the microemulsions seem to be more effective in the presence of residual lignin. This may be explained by the fact that more hydrophobic domains exist in lignin-containing fibers, which may prevent water from fully impregnating the substrate if the aqueous solutions are used.

Morphology of CNF and LCNF. The CNF and LCNF prepared using the different pretreatments were characterized to determine the morphology and dimensions of the nanofibers by using atomic force microscopy (AFM). Images of CNF and LCNF obtained from lignin-free and lignin-containing fibers after pretreatment and microfluidization with urea as active agent are included in Figure 3. Parts a and b of Figure 3 correspond to the lignin-free CNF after pretreatment with aqueous solutions or microemulsions containing urea, respectively. Parts c and d of Figure 3 correspond to the respective lignin-containing LCNF. CNF obtained after

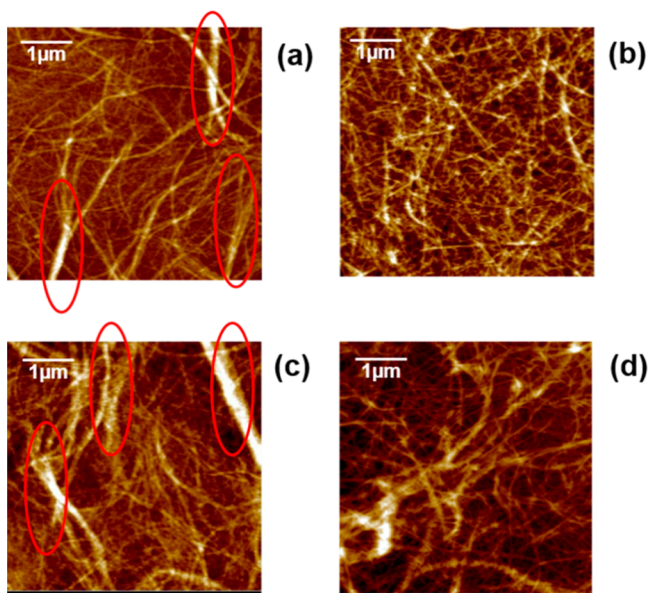


Figure 3. AFM images of the CNF obtained from lignin-free fibers (a and b) and lignin-containing fibers (c and d) pretreated with urea. Images (a) and (c) correspond to the pretreatment with an aqueous solution of urea and (b) and (d) correspond to the pretreatment with microemulsions containing urea.

pretreatment with aqueous urea (Figure 3a and c) indicate nanofibers with larger widths if compared to nanofibers obtained after pretreatment with urea-containing microemulsions (Figure 3b and d). Also, the amount of fibril bundles in both cases, lignin-free and lignin-containing nanofibers (red circles in the images), is lower after seven passes through the microfluidizer when the fibers were pretreated with a microemulsion system.

The effects on nanofibril width for samples pretreated with the aqueous solutions and with the microemulsions are more notorious for LCNF if compared to the respective CNF. These observations are in agreement with the WRV, which highlight the more pronounced effect of microemulsion pretreatment in the case of lignin-containing fibers.

CNF and LCNF Films. Films of CNF and LCNF were prepared using the different pretreatments. Films obtained after pretreatment of lignin-free fibers with microemulsion containing EDA and urea are presented in parts a and b of Figure 4, respectively. Similarly, the fibrils from respective pretreatments are presented in Figure 4 c and d for LCNF.

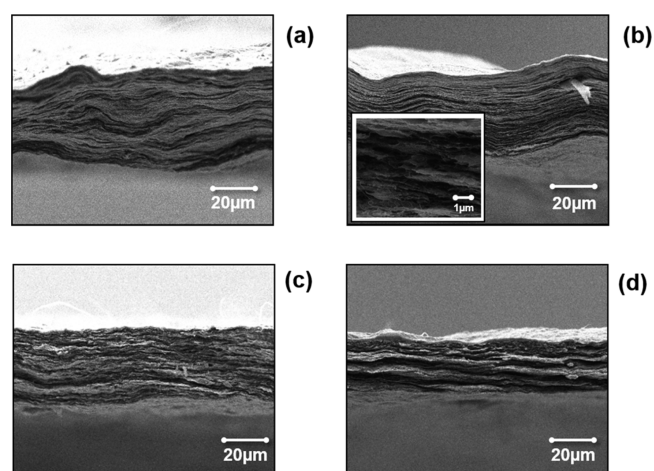


Figure 4. SEM images of the films prepared from lignin-free fibers pretreated with a microemulsion containing EDA (a) or after pretreatment with a microemulsion containing urea (b). The case of LCNF from lignin-containing fibers pretreated with urea in aqueous solution (c) or in microemulsions (d) are also presented. The inset in (b) is a magnified view to appreciate the fibrillar structure in the layers of the film.

The SEM images indicate that the films were formed as a layered structure of CNF or LCNF. The inset with higher magnification of Figure 4b shows that these layers were composed of collapsed fibrillar structures. By comparing the images of films obtained from lignin-free fibers after microemulsion pretreatment using the two active ingredients (Figure 4a and b), it can be observed that the pretreatment with urea yielded a more compact layering of CNF in the film and thus produced a reduced thickness. The better packing can be explained by the fact that urea pretreatment produced smaller fibril widths, which promote a more compact packing.

The films prepared after pretreatment of lignin-containing fibers with urea microemulsions were thinner if compared to those from lignin-free fibers (compare parts b and d of Figure 4). The presence of residual lignin in the nanofibers enhanced the packing of the nanofibers in the film, producing a thinner film.

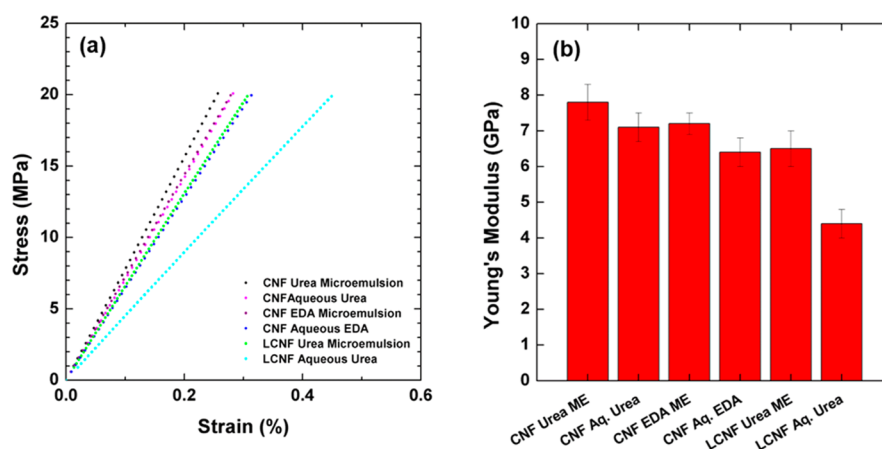


Figure 5. Mechanical properties of the CNF and LCNF films prepared with fibers pretreated with the methods considered in this study, as indicated. Stress–strain curves (a) and calculated Young's modulus (b) at 25 °C.

It can be observed that the film obtained from lignin-containing fibers pretreated with urea aqueous solution was thicker than that obtained from the microemulsion system (parts c and d of Figure 4, respectively). The reason for this difference in thickness is related to the fibril size. The fibrils obtained from the aqueous pretreatment presented larger sizes after microfibrillation and thus produced thicker films. The effect of fiber morphology on the mechanical properties of the films is discussed next.

Mechanical Properties of CNF and LCNF Films. The mechanical properties of CNF and LCNF films were analyzed by using a dynamic mechanical analyzer (DMA) (Figure 5).

The values of Young's modulus of the given films obtained from microemulsion pretreatment were slightly higher than those obtained from aqueous solution pretreatment. In the case of LCNF, the differences between the microemulsion and the aqueous pretreatments are more evident. Clearly, the microemulsion pretreatment did not affect negatively the modulus of the resultant CNF or LCNF films.

Negligible differences in Young's modulus are noted if one compares the effect of the active agent used in pretreatment of the given fiber, urea or EDA. However, the presence of residual lignin causes a reduction of the film modulus, probably because the bonding between fibrils is negatively affected by lignin, as has been observed by other authors.¹³

CONCLUSIONS

Microemulsions are demonstrated as effective media to pretreat lignocellulosic fibers as they drastically reduced the energy consumed during microfluidization to obtain cellulose nanofibrils and yielded finer fibrils and less bundling. Energy savings of up to 55 and 32% were achieved upon microfluidization of lignin-containing and lignin-free fibers, respectively. It is also demonstrated that active ingredients in the microemulsions, urea and ethylenediamine, disrupted hydrogen bonding of the fibers and facilitated deconstruction. The films obtained from lignin-containing cellulose nanofibrils (LCNF) were thinner and had lower Young's modulus values compared to those from lignin-free fibrils (CNF). Moreover, the pretreatment with microemulsions did not affect the mechanical performance of the obtained films; on the contrary, a gain in stiffness was achieved if compared to pretreatment with aqueous solutions of the given active agent.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: cacarril@ncsu.edu.

*E-mail: orlando.rojas@aalto.fi.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was partially supported by the Academy of Finland Centres of Excellence Programme (2014–2019) and South-eastern Sun Grant Initiative (U.S.A.).

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