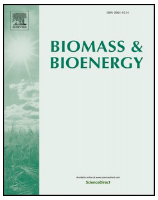
Biomass and Bioenergy 153 (2021) 106214

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: www.elsevier.com/locate/biombioe



# Binderless films from lignin-rich residues of enzymatic saccharification

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ARTICLE INFO

*Keywords:*
Self-bonding
Wet strength
Compostability
Co-product
Waste valorization

ABSTRACT

The goal of this study was to examine the conversion of lignin-rich residues from (hard)wood cellulosic sugar production into films without adding binders. Enzymatic hydrolysis was conducted on alkaline pretreated aspen wood to attain saccharification (liberation of monomeric sugars). Non-converted lignin-rich residues in the solid waste stream were fibrillated and formed into films with the aid of micro/nanofibrillated wood (non-saccharified). The films were hotpressed to activate the adhesive characteristic of the lignin *in situ*. Results showed that hotpressing drastically improved water resistance and wet strength. These effects, not attributable to densification alone, are judged to have arisen from heat-induced hydrolytically stable bonding and hydrophobization. The fully biobased films, even at highly moist (98% RH) conditions, are comparable in strength and stiffness, and tested significantly more biodegradable compared to polystyrene polymer. Overall, this study offers a simple route for converting wood saccharification residues without pre-refining for lignin, thereby favoring cost efficiency of a coproduction strategy in the cellulosic sugar production.

## 1. Introduction

Production of biobased chemicals and alcohol fuels via the cellulosic sugar platform could play a significant role in an emerging bioeconomy, but this conversion route often leaves behind lignin-rich residues. Saccharification is a process of liberating sugars from the polysaccharide portion of plant biomass. The polysaccharides of lignocellulosic biomass are strongly associated with lignin, which acts as a "shield" against the access of hydrolytic enzymes or reagents, thereby partially contributing to incomplete saccharification. This issue can be circumvented by prefractionation, through which the main polymeric components (cellulose, lignin, and hemicelluloses) of the biomass are chemically isolated into a range of product streams for separate valorization. The other solution, which is probably less capital-intensive, is pretreating lignocellulosic biomass to partially dissociate the linkages among and within the cell wall polymers, thereby facilitating subsequent hydrolysis to monomeric sugars. This latter approach results in increased saccharification levels, but a portion of unreacted (polysaccharide) materials remains within a matrix of lignin [1]. Therefore, valorizing such residues would add value to lignocellulosic biomass and generate additional revenue for the bioeconomy.

Efforts in utilizing lignin-rich compounds, non-specific to enzymatic residues, often entail pre-isolation of lignin to improve processability in subsequent conversions which are realized via one of the two pathways. The first of these is converting the extracted lignin to low molecular weight compounds, such as benzene, toluene, and other aromatics used in bulk quantities for industrial processes [2]. The second conversion pathway is using lignin as a precursor for advanced materials [2], for instance in the production of phenol-formaldehyde resin [3] and polyurethane foam [4] as a partial substitute of phenol and polyol, respectively. Other potential products under this second pathway include carbon fiber [5] and lignin-based plastics up to 100 wt% lignin content [6]. Although lignin isolation for valorization affords the flexibility for conversion into a host of products, the need for pre-refining signifies additional cost in utilizing saccharification residues. This could impede industrial realization of the valorization process, thereby hampering its intended purpose in supporting the sugar platform for converting lignocellulosic biomass.

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https://doi.org/10.1016/j.biombioe.2021.106214
Received 2 March 2021; Received in revised form 30 June 2021; Accepted 10 August 2021

Converting saccharification residues without pre-refining for lignin would potentially increase cost efficiency of the valorization process. However, there have only been few published studies tapping such opportunities. Among these attempts, lignocellulosic residues in an ethanol-focused process were used to partially (50 wt% optimum) substitute phenol for the synthesis of phenol-formaldehyde resin, an exterior-grade plywood adhesive [7]. In another application, lignin-rich saccharification residues of lodge-pole pine were blended (10–20 wt%) into Kraft pulp as a cost-reducing bulking agent [8]. For soil amendment, rice straw saccharification residues were demonstrated successful as a raw material for biochar with 30 wt% conversion yield [9]. Collectively, these existing studies, though limited in number, showed possibilities of utilizing saccharification residues without having to first pre-refine for lignin. Further opportunities for materials of both high-yield conversion and products with high contents of saccharification residues remain under-explored.

Molded materials capitalizing on the self-bonding of lignin moieties could be a potential option in large-quantity utilization of lignin-rich saccharification residues. Under this concept, plant elements are re-constituted into boards or films by thermal compression molding without the use of an external binder. This concept has been demonstrated for plant biomass (without saccharification) of both wood (hardwood or softwood) and herbaceous origin, as reviewed in the literature [10]. The heat-induced bonding is plausibly a result of covalent bonding formed either among the thermally depolymerized lignin moieties or between lignin fragments and the thermal degradation products (e.g. furfural) of hemicelluloses [10,11]. The strength properties of these molded products could be improved by thermal or mechanical (or combined) pretreatments of the particles such as steam explosion and grinding, which likely improve their conformability (deformability) for more intimate contact or/and their surface area for enhanced area of bonding [11], when plasticization [12] and plastic deformation are induced in the subsequent hotpressing step. Interestingly, similar pretreatments are also practiced prior to the enzymatic saccharification of lignocellulosic biomass as reviewed earlier in this section. It is therefore rational to examine the production of binderless molded products, taking advantage of the pretreatment in the main process line, and tapping the high presence of lignin in the solid residue for its self-bonding capability. This strategy circumvents part of the pretreatment cost which would typically be incurred when native (non-saccharified) materials are used instead for the (binderless) products.

The objective of this study was to examine the mechanical and water-resisting properties of binderless films produced from wood saccharification residues without pre-refining for lignin. Utilizing such residues for binderless products has rarely been attempted for either wood or herbaceous biomass. A published paper [13] which focused on moisture sorption, reporting that the (binderless) hotpress moldings of saccharification residues were less hygroscopic than those of the non-saccharified wood. Other relevant attempts merely examined the use of biorefinery lignin as a bonding agent for molded products of wood particles and pulp fiber [14,15]. Hence this present study would be one of the earliest attempts in unravelling the potential of utilizing lignin-rich saccharification residues as a major constituent of binderless products without lignin pre-refining. To allow a (more) thorough discussion, a streamlined experimental design was opted by focusing on aspen wood as a representation of (hard)wood biomass. Aspen is a fast-growing hardwood species known to have desirable properties as both a bioenergy crop [16] and raw material for re-constituted panel and paper products [17] for which binder-free bonding was to be enabled in this study. Aspen is also of global significance owing to its native distribution across the northern hemisphere covering North America, Eurasia, North Africa, and East Asia [17]. It is hoped that this research would engage further studies channeled to saccharification residues of other botanical origins.

The strategy deployed in this study was intended to harness the synergy between enzymatic saccharification and binder-free bonding. Specifically, this study used a relatively mild alkaline pretreatment prior to enzymatic saccharification of hardwood particles to retain much lignin and partially preserve its xylan [18] hemicellulose which, as reviewed earlier, could also play a role in self-bonding. Similar alkaline pretreatments were reported to also improve the glucose yield in saccharification of both hardwood and softwood [18]. Post saccharification, a fibrillation step was adopted to further improve the particle surface area for bonding, which in turn, would favor strength properties of the consolidated material. It is anticipated that findings from this study would benefit the bioenergy and bioeconomic sectors by generating the much lacking data on a likely feasible value-adding strategy that effectively utilizes wood feedstock and/or processing waste.

## 2. Materials and methods

### 2.1. Materials

The woody biomass source for this study is quaking Aspen (*Populus tremuloides*). The wood in the form of chips was donated by the Cloquet mill (Minnesota) of Sappi group. The sodium hydroxide (Sigma-Aldrich, Saint Louis, MO) for pretreatment was used as received. The enzyme mixture used for saccharification was Celluclast® 1.5 L (Sigma-Aldrich; endoglucanase and exoglucanase from *Trichoderma reesei*) and Novozyme 188 (Sigma-Aldrich; β-glucosidase of *Aspergillus niger*).

### 2.2. Sample preparation

The comminution and pretreatment steps were performed using a previously established protocol that had been proven to facilitate defibrillation of wood biomass [19]. Briefly, wood chips were milled to particles (10-mesh pass; 20-mesh on). The resulted particles were pretreated with sodium hydroxide (NaOH 10% w/v) at 1:6 wood-to-liquor ratio and 100 °C for 2 h in an autoclave. The pretreated residue was rinsed to neutral pH, and air-dried. Small samples were withdrawn for determination of moisture content in order to dose the intended amount of sample in the subsequent saccharification step. Another batch of samples were taken for lignin content determination in accordance to TAPPI T222 OM-06 [20], and carbohydrates isolation followed by quantification (as peak area) using high-performance liquid chromatography (1200 series HPLC, Agilent Technologies) as detailed elsewhere [21].

To enzymatically saccharify the pretreated substrate, a cellulase mixture of endoglucanase and exoglucanase (in Celluclast 1.5L) along with β-glucosidase (in Novozyme 188) were loaded at respective activities of 60 filter paper units (FPU) and 64 p-nitrophenyl β-O-D-glucopyranoside units (pNPGU) per gram of cellulose in the (alkaline-pretreated) sample, following NREL Technical Report NREL/TP-510-42629 protocol [22]. The saccharification was conducted at 50 °C for up to 9 days in a mixer whose rotor was set to rotate at 1.13 Hz (revolutions per second). A preliminary saccharification run was used to first determine the saccharification rate. The rate curve generated was then used to target harvest points along this continuum that would yield maximum possible glucose yield (which turned out to be 80%) in the main saccharification runs. At the end of saccharification, the solid (residue) fraction was recovered by filtration, rinsed with distilled water until pH-neutral, and stored at 5 °C without pre-drying for further steps.

The saccharified residue in aqueous suspension (2% solid in water) was ground in accordance with the protocol established in the investigators' laboratory for alkaline pretreated wood [19]. In brief, the grinding was conducted using an ultra-fine friction grinding machine (MKCA6-2; Masuko Sangyo Co.) equipped with a 1.5 kW motor and two ceramic grinding stones (MKG-C 120 grit size), one (static) above another (rotating). The stone rotation was set at 25 Hz (revolutions per second), and the clearance for sample flow-through between the stones was adjusted to attain the intended grinding intensity. Samples of pretreated sample (without going through saccharification) were also ground for comparisons. Hence there were two types of samples for grinding: one was non-saccharified (pretreated only), while the other one was saccharified (pretreated and then saccharified). These two types of particles were separately ground at similar cumulative energy input of 10–11 kWh/kg. This involved grinding at a series of gap closure of −25, −50, −100, and −125 μm, successively with two passes each. Here, it is worth noting that the gap size was negative in values because the two stone disks were compressed against each other after a slight contact. For the saccharified sample, the grinding was extended to a narrower clearance of −175 μm (also two passes) for the cumulative energy input to approximate the case of non-saccharified sample. This cumulative value was obtained by summing up the input energy for each grinding pass. The particle grinding energy in each pass, per kilogram basis, was estimated from the operation voltage of the grinder, electrical current read during grinding, residence time in the grinder and mass of infeed particles:

Specific grinding energy *(Wh/g or kWh/kg)* = voltage *(V)* × current *(A)* × time *(h)*/mass *(g)*

For film sample preparation, 2 g (dry weight equivalent) of the aqueous suspension of ground particles were withdrawn, mechanically stirred, and poured into a filtration funnel that was connected to a vacuum pump (Welch Vacuum 2522B-01). The vacuum filtration was conducted through two layers of filter paper of 185 mm in diameter, one (crepe) with 15 μm pore size on top of the other with 1 μm pore size (both supplied by Whatman group). The resulted paste together with the (wet) filter paper was removed from the filtration funnel for a subsequent blotting step aimed at removing excess water. Before blotting, a well-polished stainless-steel plate was placed on top of the paste, while blotter papers were placed below the wet filter paper. The assembly was pressed under a slight pressure of 345 kPa first for 5 min and then (after detaching filter paper and replacing wet blotters) another 2 min, employing the standard press apparatus specified in TAPPI T205 [23] for handsheet forming. The resulted blot-dried sample, supported by the attached stainless-steel plate, was then mounted onto standard handsheet drying rings for drying at 23 ± 1 °C and 50 ± 2% RH for 2 days. The air-dried circle sheets with diameter of 165 mm were then removed from the plates and stored in a desiccator as starting paper substrates for further treatments.

Some of the paper substrates were hotpressed between two well-polished stainless-steel plates using an automatic benchtop press (Carver Auto C-PL,H) at 5.4 MPa and 190 °C for 20 min to induce self-bonding. The hotpressing temperature was selected in consideration of sample burning risks [10] while the pressing time was earlier optimized from a preliminary trial based on an applied force (115,000 N) that was held below 90% of the machine capacity. Other paper substrates were cold pressed (ambient temperature) using the same procedure described above. Thus, there were three types of films: hotpressed films (190 °C; 5.4 MPa) along with two others for reference purposes – cold pressed films (ambient; 5.4 MPa) and paper (starting) substrates referred as “unpressed films”.

### 2.3. *Test methods*

#### 2.3.1. *Water retention value (WRV)*

The WRV measurement is based on centrifugal dewatering of a sample of aqueous slurry or water-saturated particulates. The protocol used in this study was adopted from TAPPI UM256 standard [24] with some modifications as reported in an earlier study [19]. In brief, the test involves centrifuging a sample amount (dry weight equivalent) corresponding to 790 g/m$^2$ (instead of the specified 1400 g/m$^2$) based on the screen area of the filter disk. The wet sample was centrifuged (Sorvall Biofuge Primo, Thermo Scientific) at a relative centrifugal force (RCF) of 2,700 times the acceleration of Earth’s gravity (as opposed to 900 RCF specified for pulp fiber). These modifications were made considering the (higher) water retaining ability of the fibrillated substrates and capacity of the centrifugal filter. The centrifugal dewatering was conducted for 30 min at room temperature as specified in the standard method. After centrifuging, the sample was removed to measure weights, and then oven dried at 103 °C until reaching a constant mass. The WRV was calculated as the percent ratio of water remained in the sample after centrifuging, relative to its dry weight.

#### 2.3.2. *Tensile test*

To prepare for tensile test specimens, the films were cut to strips with width of 9.5 mm and length of 63.5 mm in compliance with ASTM D882-12 standard [25]. Before testing, specimens of hotpressed films were conditioned at 23 ± 1 °C and 50 ± 2% RH for at least 40 h to achieve equilibrium. Test specimens of both paper and cold pressed samples were dried in a forced air oven at 50 °C up to seven days to adjust moisture content to similar levels as the hotpressed specimens. After conditioning and drying, some specimens were subject to tensile testing while others were used for either water soaking (24-h) or high humidity exposure tests (98% RH in desiccator for 60 days), both at 23 °C. At the end of their exposure period, the wet specimens were removed one at a time to be promptly tensile tested. Prior to each tensile loading, the mass and dimensions of the specimen were recorded for later determination of moisture content (expressed as a percent of ovendry mass) and specific gravity (based on volume after environmental exposure and dry mass after ovendrying).

Tensile tests were performed at 23 ± 1 °C and 50 ± 2% RH with a displacement-control loading of 5 mm/min using a universal testing machine (Instron 5542) equipped with a 500 N load cell. The recorded load-displacement data, along with specimen dimensions and initial (grip) span, were used to obtain stress-strain curves for determination of tensile strength, Young’s modulus, and strain at break. At least five specimens were tested for each sample according to the ASTM D882-12 standard for tensile testing [25]. Values for replicates of each type of treatment were averaged and its standard deviation was calculated.

#### 2.3.3. *Scanning electron microscopy (SEM)*

Scanning electron microscopy was used to examine the morphology of ground samples which constituted the film products. To allow this microscopic observation, samples were freeze-dried and then sputtered with platinum before loaded into an JSM 6700F (JEOL, Japan) Field Emission Scanning Electron Microscope (FESEM). Imaging was made at 5 kV acceleration voltage.

For imaging of film samples, the FESEM was of SIGMA (Zeiss, Germany). The film samples were also sputtered with a layer of platinum (*ca.* 10 nm thick) which were sufficiently thin but still allowed revealing of morphological features at nanometer scale. A relatively short working distance (2.8 mm) was used to obtain images at a low acceleration voltage (2 kV).

#### 2.3.4. *Compost test*

The protocol for compost tests was adopted from the ISO 20200 method [26]. The synthetic waste used consisted of aspen saw dust (40%), rabbit feed (30%), ripe compost (10%), corn starch (10%), saccharose (5%), corn seed oil (4%), and urea (1%) pre-sieved to below 2 mm in size. Film specimens pre-cut to 25 mm$^2$ squares totaling to about 1 g in weight (ovendry equivalent) were mixed into 100 g of wetted synthetic waste (pre-adjusted to 55% water content). The mixture was then placed in a 118 mL round plastic container with its opposite sides punctured with holes of 2 mm × 3 mm in size to allow aeration. Three replicates were tested for each sample.

The compost tests were conducted at 58±2 °C for 50 days, and 25±2 °C for the subsequent 40 days. The mixture (film specimen + synthetic waste) was re-wetted (by adding water) to maintain 100% of original weight for the first 30 days, 80% of weight for the next 30 days, and 70% for the final 30 days. Mixing was performed periodically within the first 14 days, then on day 30 and day 45. After 90 days, the compost mixture was dried at 58 °C for two days. The dried compost was carefully sieved through 10-mm, 5-mm, and 2-mm screens successively. Residues of test specimens that remained after screening were carefully washed with distilled water and ovendried for two days before recording the final weight. These ovendry weight readings allowed calculation for weight loss by subtracting from the initial specimen weight (before compost test). A degree of disintegration could then be quantified from the ratio of weight loss relative to the dry weight of the initial specimens.

## 3. Results and discussion

### 3.1. *Enzymatic saccharification: effects on chemical composition and ease of fibrillation*

Table 1 shows the chemical composition of aspen wood upon alkaline pretreatment followed by enzymatic saccharification. Pretreatment with sodium hydroxide at 100 °C did not noticeably alter the content of lignin. This pretreatment temperature is moderate compared to that typically used (e.g. 170–180 °C) in the alkaline (Kraft) pulping of wood. With the same 100 °C and 2-h conditions, Mirahmadi and coworkers [18] observed some lignin removal from birch (hardwood) wood powder after an alkaline treatment (7% NaOH solution), but this removal was much less compared to that of hemicelluloses (from 28 to 8%). Similarly, the content of xylan (major hemicelluloses in hardwood) in the present study was also reduced by more than half (from 19 to 8%), while other hemicelluloses in the pretreated sample were found in small amounts of less than 1%. The hemicellulose removal was due to a combination of peeling and alkaline hydrolysis reactions [11]. On the other hand, the glucan content, which is primarily of cellulose, remain similar which is agreeable to the observation of Mirahmadi et al. [18]. Upon enzymatic hydrolysis, about 80% of the glucan content of pretreated (non-saccharified) sample was removed, resulting in an increase in the weight fraction of lignin and xylan within the solid residue. More specifically, the hydrolysis residue contained lignin in quantity that was higher than cellulose and xylan combined, with relative presence of 54:26:20 among the three components in the order of their mention.

Although the saccharified sample is rich in lignin, which is more hydrophobic than cellulose or xylan, it exhibits a higher water retention value (WRV) compared to the non-saccharified (pretreated) sample (205 vs. 153%; Table 2). This can be explained by the higher accessibility of water molecules to the saccharified sample because more voids are made available upon glucan removal. Related to this explanation, previous research [27] revealed an increased pore volume in saccharification residues (of aspen wood) that was about three times of the (dilute acid) pretreated, non-saccharified sample. This increased porosity, and thus surface area, would facilitate water retention in saccharified samples.

Despite having a higher water retaining capacity in the starting material (unground), the saccharified sample is more difficult to defibrillate. At similar energy input (10–11 kWh/kg), the WRV of saccharified particles is only about half of the value of non-saccharified (pretreated) particles (843 versus 1594%; Table 2). In defibrillation treatments, WRV is indicative of the degree of fibrillation [28]. The defibrillation difficulty inferred from WRV data is supported by images from scanning electron microscopic (SEM) studies (Fig. 1). The pretreated sample after grinding shows distinct fibrils of high aspect ratio. On the contrary, the ground particulates of saccharified samples appear much less filamentous, with most fragmented elements low in aspect ratio and irregular in shapes. Using a micro grinder for defibrillation of wood pulp, Hoeger et al. [29] also reported a lower degree of fibrillation with the presence of lignin. They obtained fewer nanofibrils with mechanically refined wood pulp even at a higher grinding energy when compared to bleached pulp (lignin largely removed). In the present study, the impaired defibrillation of saccharified samples could additionally relate to their low content of cellulose, which is known to exist as microfibrils in plant cell walls.

### 3.2. *Tensile properties of films containing lignin-rich residue*

In consistent with SEM observations, the film-forming property of the saccharification residue turned out to be poor but this issue can be remedied by blending with non-saccharified biomass. Films made of ground particles of the saccharification residue were too brittle to be handled and thus of any valuable use. This adversity is attributable to the low aspect ratio of the ground particles, and presumably also the low molecular weight of the cell wall polymeric substances after enzymatic hydrolysis. For remedy, this study adopted findings from an earlier study about using fibrillated particles of alkaline pretreated wood in supporting film formation of a brittle (electrically conductive polymer) material [30]. Conveniently, this film-forming substrate could be obtained in the proposed coproduction scheme since alkaline pretreated particles are the intermediate material for the enzymatic saccharification process. Upon blending and filtration, a self-standing film could be formed from the slurry of the mixed particles for hotpressing treatments.

Fig. 2 shows how the resulted films, after hotpressing, responded to elongation. The stress-strain behaviors are typical of brittle materials. The ductility showed a subtly rising trend as the presence of non-saccharified fibrillated particulates was increased from 30 to 40 and

**Table 1**

Chemical composition (without normalization) of untreated, alkaline pretreated, and alkaline pretreated followed by enzymatically-saccharified biomass.

| Sample | Lignin (%) | Glucan (%) | Xylan (%) | Galactan (%) | Arabinan (%) | Mannan (%) | Mass loss (%) |
|---|---|---|---|---|---|---|---|
| Untreated | 20.4 | 44.7 | 19.0 | 1.2 | 0.28 | 1.4 | |
| Alkaline-pretreated | 21.7 | 45.1 | 8.29 | 0.45 | 0.26 | 0.12 | 8.2 |
| Alkaline-pretreated and enzymatically-saccharified | 36.8 | 17.8 | 14.1 | 0.87 | 0.51 | 0.21 | 53 |

Note: Extractives and inorganic ash are also present but not tested.

**Table 2**

Water retention values of particles resulted from ultra-fine friction grinding, with Wiley-milled particles (10-mesh pass; 20-mesh on) as starting material for pretreatment.

| Sample | Ultra-fine friction grinding in successive steps with 2 passes through each gap clearance (μm) | Cumulative specific grinding energy (kWh/kg) | Water retention value (percent of dry mass) |
|---|---|---|---|
| Alkaline pretreated | None | – | 153 (2)[a] |
| | −25/-50/-100/-125 | 9.9[a] | 1594 (22)[a] |
| Alkaline pretreated and then 80% saccharified | None | – | 205 (16) |
| | −25/-50/-100/-125/-175 | 11 | 843 (11) |

Note: values in parentheses are standard deviations of the respective means.

The clearance sizes are negative in values because the grinding stones were brought closer to push against each other beyond gap closure.

[a] Data previously reported [19].

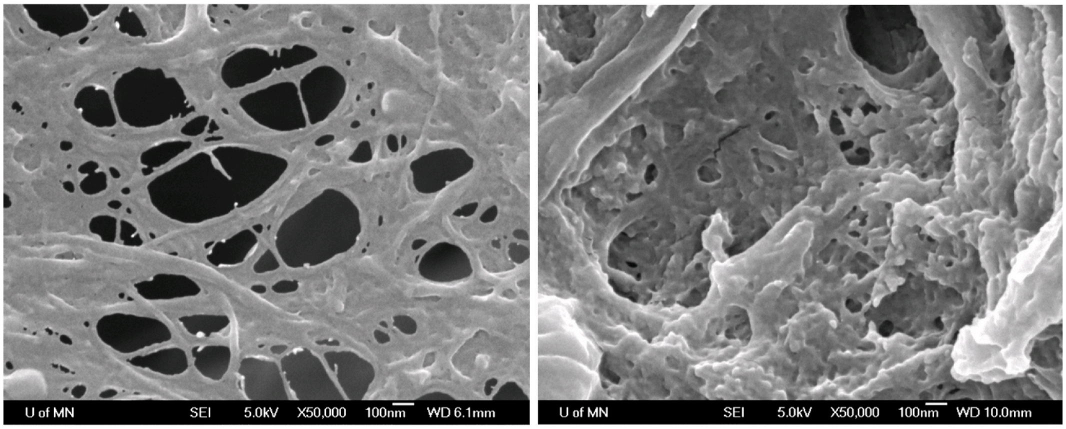


**Fig. 1.** SEM images (HFW = 2.4 μm) of ultra-fine friction ground particles of non-saccharified (alkaline pretreated) sample (left) and saccharified sample (right). HFW: horizontal field width.

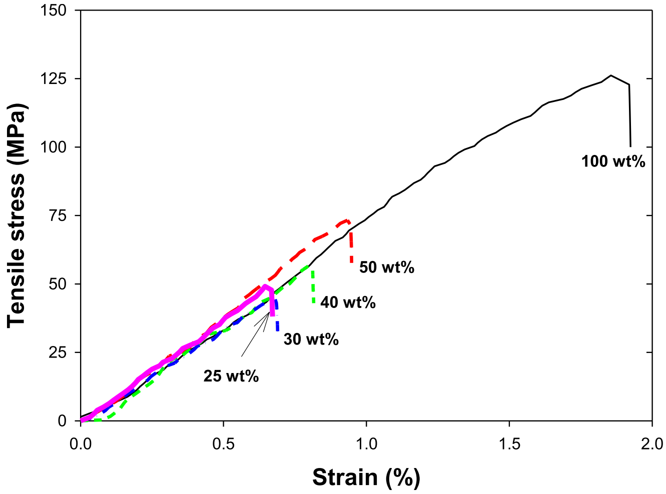


**Fig. 2.** Stress-strain curves of 20-min hotpressed films of saccharification residues, with different addition levels (mass fraction) of non-saccharified (but alkaline pretreated) particles in the blend. E.g., 30 wt% means the blend by weight consists of 30% non-saccharified and 70% saccharified particles (both fibrillated). 100 wt% means consisting entirely of fibrillated, non-saccharified particles.

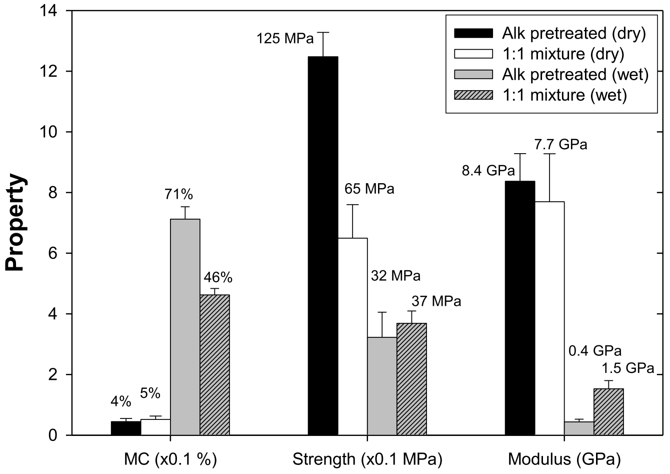


**Fig. 3.** Moisture content and tensile properties of 20-min hotpressed films tested dry (50% RH) and wet (24-h soaking). Note: The 1:1 mixture refers to the film comprising an equal weight mixture of alkali-pretreated biomass and saccharification residue (both fibrillated).

then 50 wt%, albeit the strain at break of the 50-50 blend was still small at around 1.0%. More remarkable is the maximum stress value, which clearly attained a higher value when a higher fraction of fibrillated, non-saccharified samples was added. Judging from the slope of linear regions of the stress-strain curves, the stiffness of films did not seem to be significantly altered by particle blending; this preliminary inference will be verified in the subsequent discussion.

A closer examination using the (1:1 mixture) film comprising 50 wt% each of saccharified and non-saccharified particles shows mutual benefits of blending. Without pre-saccharification, films of fibrillated particles exhibited a tensile strength of 125 MPa by average (measured at 50% RH; Fig. 3). This high value is believed to be a result of large area for fibril-fibril bonding enabled by their high aspect ratio. Such highly favorable film-forming capacity made it possible to include ground particles of the saccharification residue, with a resulting tensile strength of 65 MPa, which is about half of its original value. The stiffness values are similar even with the blend, confirming the observations discussed earlier based on their stress-strain curves. Upon 24-h soaking in water, the tensile strength reduced to similar mean values of 32–37 MPa for film samples with or without the saccharification residue. This signifies less severe weakening of the film containing (50 wt%) ground particles of the lignin-rich residue. Specifically, their wet strength retention was about 50% of its dry value in contrast to 25% for films comprising only fibrillated non-saccharified particulates. More remarkably, the wet modulus of films was enhanced by addition of the pre-ground saccharification residue; its mean value of 1.5 GPa is about 3.5-time that of films without the residue (0.4 GPa).

The beneficial retention of wet strength and stiffness is related to the enhanced water resistance of the films containing blended particles. The moisture content of water-soaked films was reduced by about one-third, with a mean value of 46% compared to 71% for films containing only fibrillated alkali-pretreated particulates (Fig. 3). Biobased materials are known to be weakened by the ingress of water which could disrupt their hydrogen bonding or/and act as a lubricant between the constituting elements. Regarding film constituents, it was explained earlier (Table 2) that ultra-fine ground particulates of saccharified samples retained less water (by half) than those of non-saccharified samples. From the perspective of thermal responsiveness, it could be that lignin and the cell wall polymeric components after enzymatic hydrolysis are more susceptible to thermal degradation/modification when compared to the hotpressing of non-saccharified samples. These (enhanced) alterations result in the (increased) liberation or re-distribution of hydrophobic compounds, thereby improving water resistance of the heat-treated substrates [31,32].

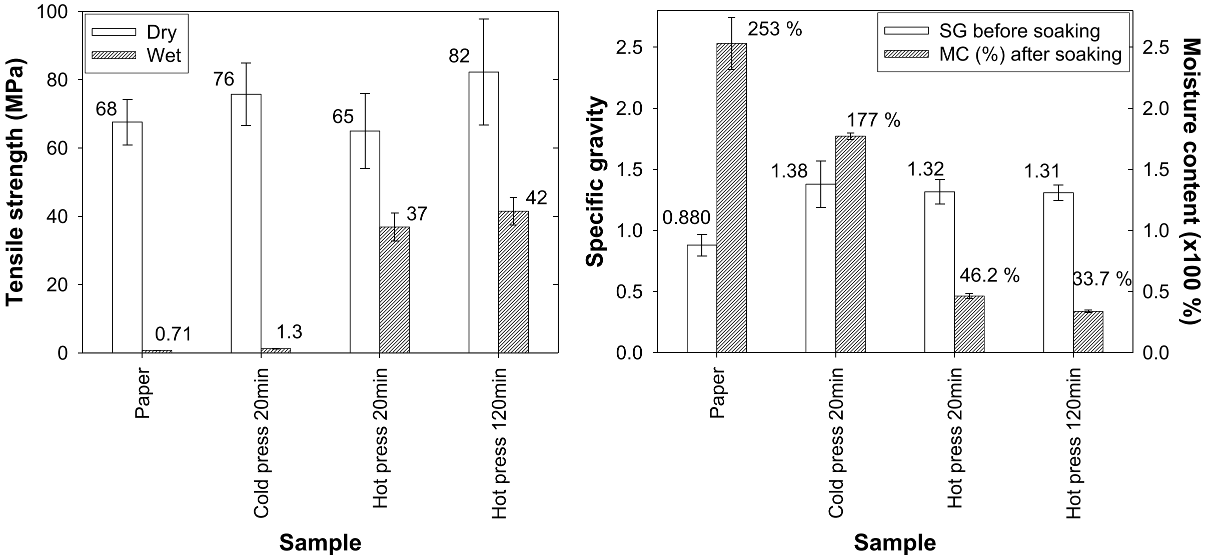
### 3.3. *Manifestations of thermally induced self-bonding*

To further elucidate the wet strength retention of the films made of the 1:1 blend of saccharified and alkali-pretreated particles, two reference samples were evaluated: unpressed and cold-pressed films. Films that were hot-pressed for 2 h were also examined to gauge the extent of such a property enhancement. Results of water-soaking and tensile tests revealed that the wet strength improvement was none-to-subtle following cold-pressing relative to the unpressed (paper) substrate (Fig. 4a). It was upon hotpressing that the wet strength increased remarkably (from about 1.0 to 37 MPa). It follows that heating during the particulate consolidation process plays an important role in developing the wet strength retaining property of the films. A prolonged hotpressing duration (2 h), however, did not lead to a remarkable further increase in wet strength.

The wet strength improvement was not primarily due to densification, judging from the specific gravity (SG) values of both cold- and hotpressed films (before soaking), which were insignificantly different (Fig. 4b). For the unpressed substrates (paper), densification due to pressing (without heating) did impart a certain extent of water resistance. The SG (before soaking) of cold-pressed films was higher than unpressed films (mean value 1.38 versus 0.88), justifying a decrease in water uptake evidenced from the moisture content of the soaked samples (177 versus 253% for unpressed film). For hotpressed films, however, the water resistance was much higher despite having an average SG value (1.32) similar to that of cold-pressed films. Indeed, the MC values of their soaked samples are about 75% lower (average MC value 46 versus 177%) compared to cold-pressed films that were soaked in the same manner. Therefore, the observed water resistance hence wet strength enhancement in hotpressed films is primarily a result of thermally induced modification, not merely densification, of the film substrates.

The heat-induced wet strength enhancement could be due to the combined effects of self-bonding and hydrophobization. In studying self-bonding, Zhang et al. [14] discovered breakage of inter-unit linkages (mostly C-O-C ether bonds) and formation of new C-C bonds between lignin fragments in hotpressed (130–180 °C for 20 min) industrial alkaline lignin of corn cob from bioethanol production. The presence of these C-C bonds was the highest at 160 °C; this was also the pressing temperature for attaining the highest internal bond strength in the same study when alkaline lignin was blended (20 wt%) with milled particles of Poplar wood to make binderless boards. As these C-C bonds, which are hydrolytically stable, can be accounted for inter-particle bonding, they offer the explanation in the present study for the considerably higher wet strength retention of hotpressed films compared to cold pressed samples whose integrity depend largely on hydrogen bonding. Another supplemental explanation for the enhanced water resistance is the heat-induced hydrophobicity of the particulates. Besides self-re-condensation of lignin due to heating, factors contributing to increased hydrophobicity include 1) thermal degradation of the less stable hemicelluloses which are hydrophilic; 2) generation of hydrophobic compounds from wood component degradation [31]; 3) migration of hydrophobic extractives onto wood surfaces [33]; 4) increased crystallinity (reduced water permeability) of cellulose due to its conformation rearrangement when the encrusting lignin became more molecularly mobile at sufficiently high (above glass transition) temperature [34,35].

One other attribute that has been less investigated, as commented by Hubbe et al. [11] in their review of binderless boards, is the spreading (wetting) of lignin during hotpressing which would favor molecular contact with the adherent substrates to facilitate bonding. In this regard, Takada et al. [32] observed increased presence of lignin on surfaces of (Douglas-fir) mechanical pulp fibers as they were steam pretreated (160 °C for 10 min). This signifies lignin migration and relocation to surfaces, which would lead to increased surface hydrophobicity. Furthermore, when lignin was extracted from the wood and coated onto filter paper, they observed melt droplets upon heating (121 °C for 10 min at 10% MC). In the present study, this fluidization of lignin could also take place in the films (initial MC 7 ± 1%) during hotpressing. Building on this anticipation, the films were examined under the scanning electron microscope (Fig. 5). SEM images showed coalesced globules of irregular shape in hotpressed films, in contrast to smaller, distinct round-shaped globules in the cold-pressed samples. This suggests signs of phase-change, presumably of lignin melting, taking place during hotpressing. While re-imaging the structure after lignin staining would more conclusively pinpoint the origin of the globules, this study opts to leave the tedious task for future investigations to not dilute the focus of the present report.



(a) (b)

**Fig. 4.** Properties of films (1:1 saccharification residue/alkali-pretreated) depicting the effects of pressing without and with 190 °C heating: (a) wet and dry tensile strength; (b) densification and water uptake resistance.

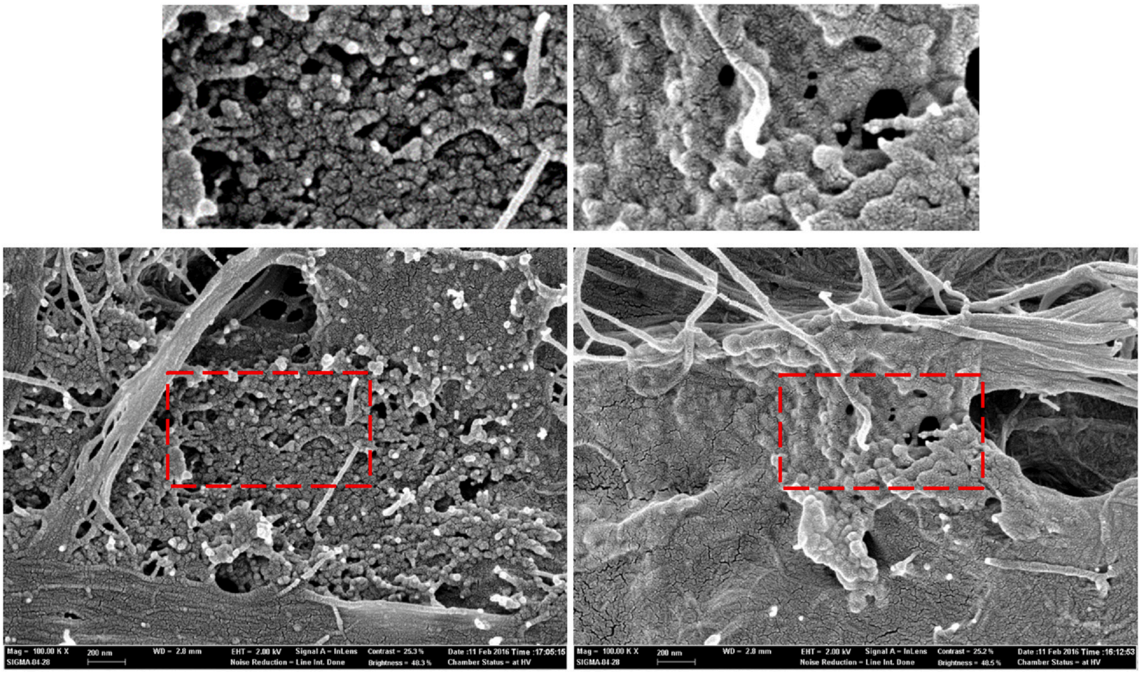


**Fig. 5.** SEM images (HFW = 3 μm) of film samples (1:1 mixture) pressed at room temperature (left) and 190 °C (right), with the smaller images on the top representing digital magnification (4x) of the highlighted areas. HFW: horizontal field width.

**Table 3**
Tensile property comparisons with some lignocellulosic binderless products prepared at similar hotpressing conditions.

| Constituent | Hotpress condition | Tensile strength (MPa) | Tensile modulus (GPa) |
|---|---|---|---|
| Saccharified/non-saccharified wood 1:1 blend; both fibrillated (this study) | 190 °C, 5.4 MPa, 20 min | 65 (dry);<br>37 (wet 24 h) | 7.7 (dry);<br>1.5 (wet 24 h) |
| Chemi-thermomechanical pulp (CTMP); lignin content ~ 0–25%[a] | 170 °C, 8 MPa, 20 min | 38–64 (dry) | – |
| CTMP/enzymatic hydrolysis lignin 1:1 blend[b] | 130–220 °C, 8 MPa, 5 min | 1.2–13 (dry) | – |
| Wood nanofiber(from unbleached groundwood pulp)[c] | 150 °C, 2 MPa (3 min), then 50 MPa (15 min) | 68 (dry);<br>38 (wet 60 s) | 4.3 (dry);<br>3.2 (wet 60 s) |

Note: Data from [a] Wang et al. [36], [b] Zhao et al. [15], and [c] Sethi et al. [37]. Published data for hotpressed films comprising cellulose (micro/nano) fibers were not compared due to the present focus on lignin self-bonding.

### 3.4. *Evaluation of performance*

The binderless films from this study are mechanically competitive when compared to other lignin-rich binderless products. At quite similar hotpressing conditions (Table 3), the tensile strength (averaged at 65 MPa) of the 20-min hotpressed films (1:1 mixture) is close to the upper end of the data range (38–64 MPa) for thermally molded products of variously pre-delignified chemi-thermomechanical pulp [36]. When comparing to the use of enzymatic hydrolysis lignin [15], the binderless film is also stronger than their molded materials (1:1 blend of lignin and chemi-thermomechanical pulp), which were pre-compressed at 10 MPa (2 min at ambient) before hotpressing. Unfortunately, there were no stiffness data or wet tensile test results provided in both mentioned reports. When considering wet strength (Table 3), the film of this present study shows a decline to 37 MPa in a way very similar to that (38 MPa dropped from 68 MPa) of spruce wood nanofiber films that were hotpressed [37]. For stiffness, the films are about two times stiffer than their wood nanofiber films (moduli 7.7 versus 4.3 GPa). When wet, the films at first glance were only half as stiff as theirs (1.5 versus 3.2 GPa), but noteworthy is their wetting period which was only 60 s (versus 24-h soaking in this study). As such, the tensile properties of the hotpressed film are favorably comparable to, if not better than, other products of similar nature and pressing conditions.

The thermally formed materials made of (50 wt%) saccharification residues in this study are also comparable in tensile properties with polystyrene. Polystyrene is one of the most used polymers. Being stiff (glassy) materials, both the product in the present study and polystyrene are brittle, with strain at break averaged at 0.8% and 1.5%, respectively

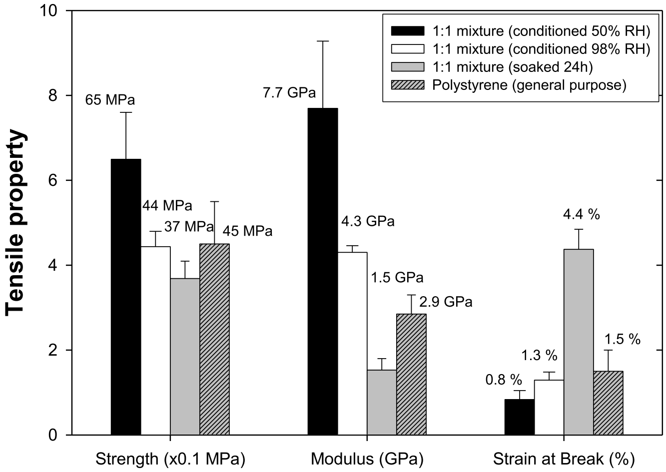


**Fig. 6.** Tensile property comparisons of the film product from this study against polystyrene. Note: Films were 20-min hotpressed, and comprising 1:1 mixture of saccharified and non-saccharified particulates (both fibrillated). Polystyrene data from Rodriguez et al. [38].

[38] (Fig. 6). More remarkable are the dry strength and moduli (50% RH) which exceed those of polystyrene (PS) by 40% and 170%, respectively. However, upon direct contact with liquid water (24-h soaking), these properties respectively reduced to 80% and 50% of the (dry) strength and moduli of polystyrene (assume negligible impacts of water on PS due to its hydrophobicity). As water-soaking is extreme, and likely not a realistic end-use environment in most applications, a high humidity exposure experiment was conducted at 98% RH for 60 days for the 20-min hotpressed films. Favorably, the moist sample exhibited strength and moduli values that are comparable to polystyrene (Fig. 6). These findings show a potentially wide range of end-use humidity conditions in the context of tensile strength and stiffness, while recognizing that the product, like polystyrene, is brittle in nature.

Biologically sourced and compostability are perhaps the biggest advantages of the product in the present study over commonly used fossil-based materials, such as polystyrene. Acknowledging that not all biologically derived materials are biodegradable or compostable, this study conducted compostability tests which also included polystyrene. Results show that films without hotpressing were 98 ± 0.6% (average ± standard deviation) disintegrated after 90 days, suggesting fully compostable, although there are other criteria such as toxicity of the compost that were not tested. The hotpressed films, interestingly, turned out to be partially composted, with 47 ± 5% of their initial mass disintegrated. This suggests hotpressing retards biodegradation, attributable to thermally induced crosslinking, chemical modification/degradation, and/or enhanced water resistance. An increase in biodurability was also reported for heat-treated wood [39]. For the present study, the compostability, though retarded, is still significant when compared to polystyrene which showed negligible (6%) disintegration. Therefore, the product in the present study is not only competitive in tensile properties, but also has the advantage of biodegradability.

### *3.5. Implication of findings to cellulosic sugar platform of herbaceous origin*

Findings from this study, though derived from (hard)wood, could also shed some light on the binderless bonding of enzymatic saccharification residues of herbaceous origin. One supporting evidence is the success with enzymatic hydrolysis lignin from the cellulosic ethanol production of corn stover [40]. The lignin was used as an intrinsic binder for cotton stalk fiber in the formation of binderless fiberboard. In a similar context, the structural function in the present study was provided by non-saccharified wood biomass (fibrillated), while the intrinsic binder was uniquely the lignin-rich saccharification residue (also fibrillated) without pre-purification. Relevantly, in its unrefined form, enzymatic hydrolysis lignin residues of corn stover had been found to be sufficiently reactive as a partial ingredient for thermosetting adhesive ([41] supplemented with [42]). The reactivity of such unrefined residues for binderless bonding could be further enhanced through the proposed fibrillation treatment, which had been proven for flax fiber [43] albeit without pre-saccharification. As such, the proposed concept and strategy for utilizing lignin-rich saccharification residues of wood are likely feasible with those of herbaceous origin, although the structure and molecular weight of their lignin (and also hemicelluloses) are different from those in wood. Additional studies, nevertheless, should be conducted not only to verify this feasibility, but also adjust the processing protocol to cater for any specific characteristics of the biomass and residue concerned.

## 4. Conclusions

This study demonstrated the feasibility of producing strong and moisture-resistant binderless films using the enzymatic saccharification residue (mass fraction 50%) of wood via fibrillation and hotpressing. The simple technology presents a near-term adoption advantage. The non-saccharified (alkaline-pretreated) particles used as a mat-forming enhancer (upon fibrillation) could be obtained either from the saccharification facility or a separate, cheaper source. The high inclusion of residues in the fully biobased product effectively reduces waste while allowing revenue generation. For future studies, blend optimization, technoeconomic and life cycle assessments are recommended. If proven viable, this co-production strategy could improve the economics of the cellulosic sugar platform.

## Author contributions

**Han-Seung Yang:** Methodology, Investigation (fibrillation and film studies), Validation, Formal analysis, Visualization (graphs), Writing - Reviewing and editing. **Feng Jin Liew**: Resources, Investigation (chemical composition). **Justin Kaffenberger**: Investigation (composting). **Nicholas Seaton**: Visualization (fibrillation SEM). **Ohkyung Kwon:** Visualization (film SEM). **Jonathan Schilling:** Funding acquisition, Writing - Reviewing and editing. **William Tze:** Conceptualization, Funding acquisition, Supervision, Writing – Original draft.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgements

This work was supported by the United States Department of Agriculture's National Institute of Food and Agriculture [grant number 2011-67009-20063] for the earlier portion of this study; and its McIntire Stennis project [grant number MIN-12-053; under accession no. 1010000] for the later portion. Part of the work was conducted at the University of Minnesota's Characterization Facility, which receives partial support from the National Science Foundation through the MRSEC (Award Number DMR-2011401) and the NNCI (Award Number ECCS-2025124) programs. The authors also acknowledge the assistance of Dr. Islam Hafez, former member of Tze's lab, in preparing (freeze drying and mounting) SEM specimens of the ultra-fine friction ground particles.

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