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One-Step Activation and Surface Fatty Acylation of Cellulose Fibers in a Solvent-Free Condition

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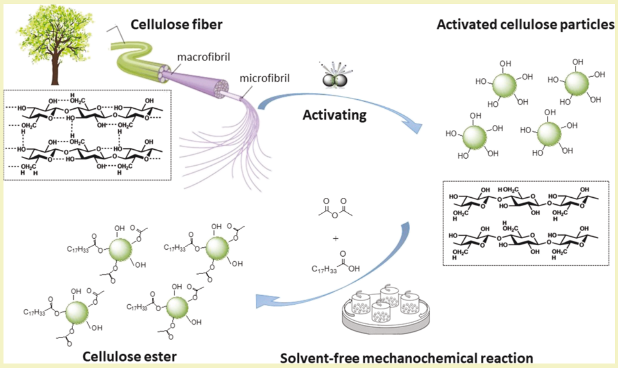
ABSTRACT: Fatty acid cellulose esters with excellent water repellency and improved processability have gained a lot of attention in varied applications. In this study, a "green" synthetic route employing mechanochemical reaction methods was developed to prepare long-chain cellulose esters from cellulose fibers. Specifically, cellulose fibers were ball-milled to prepare activated cellulose particles; asymmetric mixed anhydrides from acetic anhydride and oleic acid were formed for improved esterification reactivity. Cellulose powder and mixed anhydride were mechanochemically reacted during ball-milling. The effects of the catalyst, ball-milling time, and reagent molar ratio were investigated. The results revealed that ball-milling was shown to be an effective approach to modifying the surface of cellulose powder with acetic−oleic mixed chains. The adding of a catalyst accelerated the reaction greatly. Increasing the ball-milling time and raising the mixed anhydride molar fractions promoted the esterification of cellulose and increased the degree of substitution. The modified cellulose esters exhibited higher thermal stability and better water repellency than the untreated cellulose powders.



KEYWORDS: *fatty acid cellulose ester, oleic acid, mixed anhydride, degree of substitution, water repellency*

1. INTRODUCTION

As one of the most abundant natural resources, cellulose has been widely used with varied modifications for a broad number of applications to deal with the increasing consciousness of energy supply and environmental protection. However, the limited processability and high hydrophilicity because of the intra/inter-hydrogen connections and abundant hydroxyl group of cellulose become major obstacles, preventing the widespread utilization of cellulosic materials.[1] Various polymers or functional groups have been grafted onto the cellulose backbone for improved processability and tailored functionalities.[2] Cellulose esterification, substituting the hydroxyl group from cellulose by the ester group, has been demonstrated as one of the most effective cellulose property-modifying approaches. Short-chain cellulose esters such as cellulose acetate and cellulose propionate, which offer promising properties as thermoplastics, have been thoroughly investigated and consequently industrialized in many areas.[3,4] However, the short-chain cellulose derivatives still exhibit higher water sensitivity compared with many other polymeric materials. In addition, the high glass transition temperatures also limit their melt processability, which cannot be fully overcome by adding plasticizers.[5]

In recent years, more focus has been given to modifying cellulose with long-chain fatty acids for their excellent hydrophobicity, easy-processing, and promising applications in wood preservations, thermoplastics, and selective lipophilic filters.[6−8] The best option for producing long-chain fatty cellulose esters is by employing fatty acids directly as the reagent to react with cellulose. However, the inactive chemical nature of both the reagents, the low accessibility of hydroxyl groups from the highly ordered cellulose structure, and the long carbon chain with corresponding steric hindrance of the fatty acid make the reaction extremely hard to conduct. Attempts toward improving both reaction agents have been made to overcome this problem. On one hand, swelling agents were used to disconnect the hydrogen bonds and increase the availability of the hydroxyl groups of cellulose. For example, *p*-

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toluenesolfonyl chloride and *N*,*N*-dimethylacetamide/lithium chloride (DMAc/LiCl) have been utilized as co-reagents to improve reactivity,[9,10] but the environmental issues and cost are always limitations for scale-up applications. On the other hand, acyl chloride, for instance, the pyridine-acyl chloride system, is commonly employed for long-chain cellulose ester preparations, but it also results in hydrochloric acid as a byproduct, which, in turn, leads to cellulose degradation, and the required neutralization and recycling steps are energy-demanding and environmentally harmful.[11,12]

Mechanical methods, which alter the cellulose supramolecular structure by breaking or reducing the interchain hydrogen bonds while preserving the original solid form, present a cost-effective means to improve the accessibility of the cellulose fiber. At the same time, the combination of mechanical and chemical thermodynamics changes on a molecular scale can also promote solid-state chemical reactions, namely, mechanochemistry. Different from the traditional chemical reactions occurring in solution, mechanochemical approaches not only reduce the use of solvent but also eliminate the need for heat. It can promote reactions in the solid state, whereas mechanical energy directly ruptures chemical bonds and forms reactive centers for further reactions, presenting a promising alternative technique to the unsustainable traditional solution-based reaction.[13,14] Cellulose esterification employing mechanochemical methods has been studied previously, but most of them were focused on the short-chain carboxyl acid or anhydride, in the presence of solvent during the reaction because of the low chemical reaction.[15,16]

In this study, solvent-free mechanochemical ball-milling was adopted as a one-step approach to pulverize, activate, and surface-modify cellulose fibers to prepare surface acylated cellulose particles. Specifically, highly crystallized cellulose fibers were subjected to ball-milling to disrupt the interconnected hydrogen bonds, then selected chemicals were added and co-milled with cellulose for surface esterification. Long-chain oleic acid (OA) was used as an esterifying agent for its characteristics of hydrophobicity, low cost, being nontoxic, and being renewable. In addition, acetic anhydride (AA) was employed as a co-reagent to form asymmetric and unstable acetic−oleic mixed anhydride to improve the reactivity of the long-chain fatty acid during the solid-state reaction. The preparation of acetic−oleic mixed anhydrides was explored during the ball-milling condition. The effects of the catalyst, reaction time, and molar ratio on the cellulose esterification during mechanochemical reaction were characterized and analyzed. In addition, the degree of substitution (DS), the thermal stability, and the surface hydrophobicity of the esterified cellulose were also investigated.

2. EXPERIMENTAL SECTION

2.1. Materials. Northern softwood bleached kraft pulp, 99% purify, was purchased from Sigma-Aldrich. AA (≥99%) and OA (technical grade, 90%) were used for mixed anhydride preparation. Methylating reagent trimethylsulfonium hydroxide (TMSH) in *tert*-butyl methyl ether [BME, for high-performance liquid chromatography (HPLC), ≥99%] was used for the cellulose transesterification. Pentadecanoic acid (99%, GC grade) was used as an internal standard. Acetonitrile was of HPLC grade. Sodium hypophosphite (NaH_2PO_2, ≥99%) was used as a catalyst for the esterification. All chemicals were obtained from Sigma-Aldrich and used without further purification.

2.2. Mixed Anhydride Preparation Using AA and OA. The complex reactions of the synthesis of the mixed anhydride from AA and OA have been investigated by other researchers in the solution state,[17] but no examples were found for the mechanochemical preparation. Here, an ultrahigh performance liquid phase chromatography (UPLC) protocol was used to study the constituent of the reaction medium. A planetary ball mill (Across International, PQ-N04), with two 100 mL stainless steel jars and stainless balls was used for mixed anhydride preparation, with a rotational speed of 500 rpm. Different molar ratios of AA and OA (OA/AA = 0.25:1, 0.5:1, 1:1, 2:1, and 4:1) and reaction times (0, 1, 5, 10, 30, and 60 min) were investigated. After the reaction, the samples were quickly removed to 2 mL vials and immediately frozen at −4 °C to stop the reaction. All the samples were quantitatively analyzed by UPLC.

2.3. Liquid Phase Chromatograph Analysis. The mixed anhydride reaction was analyzed with an Accela PDA UPLC (Thermo Fisher Scientific, USA), including a 1250 pump and a hypersil gold column. The column was set at a temperature of 25 °C and samples (10 μL) with a concentration of 10 g/L in acetonitrile were used for the test in accordance with the method described below. The initial flow rate was set at 150 μL/min, with an eluent gradient starting at t = 0 from a ratio of 30%/70% acetonitrile/water to 100% acetonitrile in 6 min and then keeping at 100% acetonitrile. After 12 min, the flow rate was increased to 200 μL/min until the end of the 30 min test. The UV detector was set at 212 nm.

2.4. Mixed Anhydride Cellulose Ester Preparation. Cellulose fibers were ball-milled for 30 min to activate the cellulose powders. The mixed anhydrides and catalyst were added to the milling jar and co-milled with the cellulose powder. The reaction was conducted at ambient temperature and pressure. After milling, the residual was washed with ethanol and deionized (DI) water, then Soxhlet extracted for 5 days to completely remove any unreacted chemicals. The filtered cellulose powder was dried at 80 °C overnight before characterization.

To assess the process parameters governing the mechanochemical reaction, the effects of catalyst, milling time, and the molar ratio of the reagents were investigated. For catalyst evaluation, the dosage of the NaH_2PO_2 catalyst was 10 wt %, the molar ratio of mixed anhydride to cellulose particle was 2:1, and ball-milling time was 120 min. Milling was conducted for of 30, 90, 150, and 240 min, with a 2:1 molar ratio for mixed anhydrides to cellulose particle, and the presence of 10% NaH_2PO_2 acting as the catalyst. At last, the molar ratio of mixed anhydrides to cellulose was varied from 0.25 to 4, with 10% NaH_2PO_2 and ball-milling for 150 min.

2.5. Characterizations. *2.5.1. Fourier Transform Infrared.* A Fourier transform infrared (FT-IR) spectrometer (Nicolet) were employed to conduct the FT-IR test. Sample discs were made using a laboratory pellet press and the pellet mold, mixed with KBr at a mass ratio of cellulose powder/KBr = 1:100. Spectra were collected at a resolution of 4 cm^{-1} and 64 scans, with a range from 500 to 4000 cm^{-1}.

2.5.2. Nuclear Magnetic Resonance Spectroscopy. ^1H nuclear magnetic resonance (NMR) analysis was conducted on a Bruker AVANCE 600 NMR. Cellulose samples (1 mg) were added to 10 mL of dimethyl sulfoxide (DMSO)-d_6 and stirred for 5 min to get a homogeneous solution; then, the solution was removed to a glass NMR tube. The samples' testing temperature was set at 30 °C.

2.5.3. DS Determination. Determining the DS for the cellulose ester is complicated for mixed cellulose substituting with long and short chains at the same time. To our knowledge, it is very difficult to determine the two different DS values simultaneously and accurately, especially with low DS values. Therefore, two different techniques were employed to calculate the fatty acyl DS (DS_f) and the short-chain DS (DS_a) separately.

2.5.3.1. Acetyl Content Determination. The acetyl substitution of the cellulose was determined by the ^1H NMR Spectra using the equation below.[18] The intensity of the methyl-group proton signals ($PA_{acetylgroup}$, δ = 1.85, 1.91, and 2.05 ppm) was compared with the cellulose backbone protons signals ($PA_{cellulosebackbone}$, δ = 0.8−1.1 ppm).

$$\mathrm{DS_a} = \frac{\mathrm{PA_{acetyl\ group}}/3}{\mathrm{PA_{cellulose\ backbone}}/7} \tag{1}$$

2.5.3.2. Fatty Acyl Content Determination. $\mathrm{DS_f}$ was determined by transesterification of cellulose esters with TMSH, and then analyzed by gas chromatography.[19] Specifically, 10 mg of modified cellulose powder was placed in a 2 mL vial, and then 500 μL of 0.5 mmol/L pentadecanoic acid in TBME was added as an internal standard. Finally, 400 μL of TMSH was introduced into the vial and hot-stirred in an incubator at 75 °C and 200 rpm for 5 h. After the reaction, the vial was cooled and the supernatant was collected and analyzed by gas chromatography.

Gas chromatography (GC) analysis was conducted via a GC equipped with a flame ionization detector and DB-WAX capillary column. Nitrogen was used as a carrier gas. The testing procedure was programmed as follows: the oven temperature was set at 60 °C for 2 min and was then ramped to 260 °C at a rate of 10 °C/min. $\mathrm{DS_f}$ was calculated based on the equation shown below.

$$\mathrm{DS_f} = \frac{C_\mathrm{f} \times V_\mathrm{f}}{\left(m - C_\mathrm{f} \times V_\mathrm{f} \times 264 - \frac{m}{162} \times \mathrm{DS_a} \times 42\right)/162} \tag{2}$$

where C_f is the concentration of fatty acyl determined by GC (mol/L). V_f is the volume of internal standard (mL) and m represents the mass of the sample analyzed (g).

2.5.4. Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was carried out with a TA SDT-Q600 instrument, under nitrogen atmosphere with a flow rate of 100 μL/min. An alumina crucible was used to encapsulate a10 mg sample and the temperature was ramped from 25 to 600 °C with a 10 °C/min rate.

2.5.5. Water Contact Angles. Modified cellulose powder (100 mg) was pressed (3500 psi) into 10 mm diameter pellets, using a laboratory press and the pellet mold. The metal surfaces were carefully cleaned to avoid any contamination. Contact angles were measured using DI water with a goniometer with an automatic camera. The water contact angles were calculated by the traditional three-point method.

3. RESULTS AND DISCUSSION

3.1. Mixed Anhydride Reaction. There are two consecutive reactions taking place when AA and OA were mixed during ball-milling: one forms the acetic−oleic mixed anhydride and the other is the continuous reaction of mixed anhydride with OA to produce oleic anhydride. Therefore, five reaction products, acetic acid, AA, acetic−oleic anhydride, OA, and oleic anhydride, exist as a mixture at equilibrium. Usually, mixed anhydrides are not explicitly quantified in industrial applications for their complexity of reaction medium and analytical process. With the UPLC characterization in our study, different reaction mediums could be separated and quantified in a single run. As the amounts of the acetic−oleic anhydride and oleic anhydride are important for the long-chain cellulose ester preparation, the concentrations of both anhydrides were monitored and analyzed.

The reaction time of mixed anhydrides in ball-milling was studied with an initial equal molar ratio of AA and OA. As presented in Figure 1a, the contents of the mixed anhydride and oleic anhydride were monitored at different milling durations. The concentration of the acetic−oleic anhydride increased immediately after mixing the two initial reagents in the ball mill, then reached its maximum after approximately 30 min, and then displayed a plateau. The concentration of oleic anhydride also exhibited a similar trend, initially increasing and then reaching an equilibrium. In the solution reaction, it takes approximately 5 days to reach the equilibrium as reported previously.[20] During ball-milling, the mechanical energy input accelerates the reaction process and the mixed anhydride attained the equilibrium state in less than 1 h, indicating that the ball-milling, with a large energy input from the mechanical collision, is an effective approach for increasing chemical reaction at room temperature and pressure.

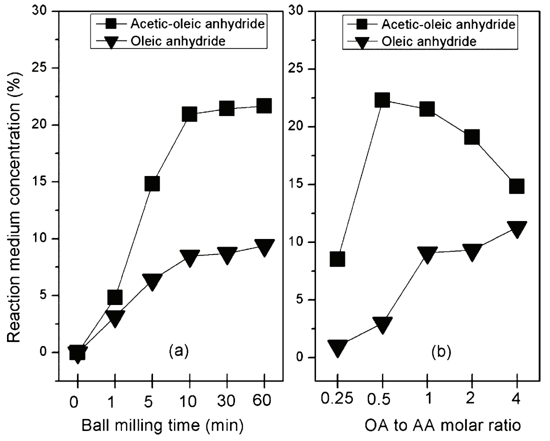

Figure 1. Mixed anhydride and oleic anhydride concentration for (a) different ball milling times and (b) different molar ratios.

Figure 1b presents the effect of the molar ratio of the two initial reagents on the resulting anhydrides' molar fractions. The OA to AA molar ratios of 0.25:1, 0.5:1, 1:1, 2:1, and 4:1 were investigated for 30 min of ball-milling. The acetic−oleic anhydride concentration increased on raising the OA−AA ratio, reached its highest value at 0.5:1, and then showed a decrease when further increasing the OA fraction. The low AA or low OA fractions both reduced the mixed anhydride yield because the lack of either initial reagent limited the propagation of the reaction. For oleic anhydride content, apparently, it raised on increasing the OA fraction. Considering both yields of the mixed anhydride and oleic anhydride, equal molar of the reagent was the optimized condition for preparation of the long-chain fatty acid cellulose esters in this study.

3.2. Preparation of Mixed Cellulose Ester. With the mixed anhydride successfully synthesized, we were able to investigate the mechanochemical modification of cellulose grafted with long-chain fatty acids in a solvent-free condition. As discussed above, the reaction of AA−OA yielded a complex composition with five chemicals, among which the two carboxylic acids are with extremely low reactivity, so only the three anhydrides are expected to react with the hydroxyl groups of the cellulose. Figure 2 illustrates the possible chemical reaction of the esterification in this study to form a mixed cellulose ester.

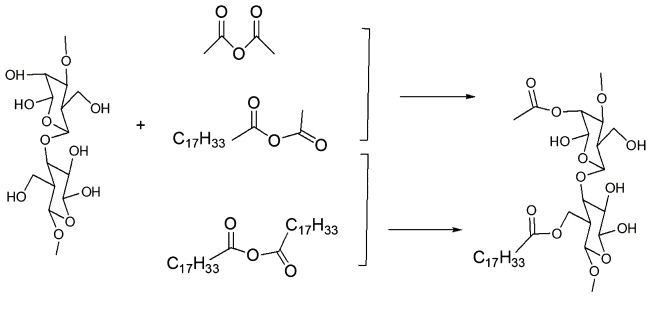

Figure 2. Esterification of mixed anhydrides and cellulose.

Although both the cellulose particles and the anhydrides have been pretreated to improve reactivity, the solvent-free mechanochemical reaction at room temperature is still challenging. Using a catalyst is a simple and fast approach to promote esterification. Strong acids such as sulfuric acid and perchloric acid are among the widely used and most effective catalysts for increasing the yield in cellulose ester preparation, but a liquid state and high temperature are typically required for the conversion.[21] Because of the unique solid-state condition of this mechanochemical process, strong acid catalysts would be highly corrosive to the milling device and can also cause cellulose dehydration. The metal salts are also effective in promoting esterification and NaH_2PO_2 has been identified as a cost-effective catalyst for solid-state esterification.[22,23] Here, 10 wt % NaH_2PO_2 was employed as a mild catalyst for the mechanochemical reaction and the catalytic effect was characterized. Figure 3 shows the FT-IR spectra of the modified cellulose particles conducted with and without the catalyst. The ester bond, as shown at 1740 cm^{-1}, appeared after the mechanochemical reaction both with and without the presence of the catalyst, indicating the occurrence of esterification. However, the C═O bonding peak signal for the reaction without the catalyst was extremely small and weak, because of the insufficient contact with the reagent and limited energy input during solid-state reactions. After adding the catalyst, the C═O peak intensity increased noticeably, which implied that the catalyst was effective for accelerating the mechanochemical modification process.

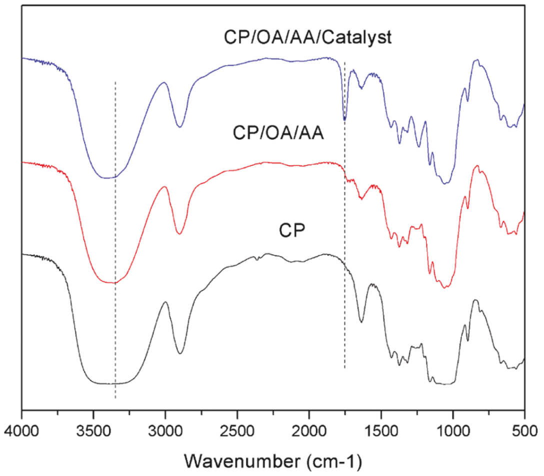

Figure 3. FT-IR spectra of mixed anhydride with cellulose.

A potential reaction scheme has been proposed by others;[22,23] the NaH_2PO_2 can attack the carbonyl group from the mixed anhydride to form an active intermediate, which then can react with active hydroxyl groups from cellulose to produce cellulose esters by the nucleophilic substitution reaction. The reformed NaH_2PO_2 is then available to continue the catalytic esterification. It promoted the mechanochemical reaction in low reaction temperature and low pressure and resulted in a high reaction yield.

However, the occurrence of the ester bond in FT-IR spectra cannot effectively distinguish the long-chain ester from the short-chain grafted cellulose derivates in this study. Proton NMR was employed for further determination of the cellulose ester structure. Here, samples of cellulose, cellulose ball-milled only with AA (CP/AA), and cellulose reacted with mixed anhydride (CP/mixed anhydride) were studied by ^1H NMR. As illustrated in Figure 4, for all the tested samples, the two large peaks, located at δ = 2.49 ppm and δ = 3.45 ppm, were attributed to the protons from the solvent DMSO and absorbed H_2O. The results from the neat cellulose displayed multiple peaks at δ = 3−5 ppm, which are diagnostic for the protons from glucose.[24] When cellulose is ball-milled only with AA, new peaks attributed to methyl protons from the grafted acetyl group appeared at δ = 1.7−2 ppm, with three sharp peaks, at 2.05, 1.91, and 1.85 ppm, representing the methyl protons from C6, C2, and C3 positions from the glucose, respectively,[25,26] showing the successful formation of cellulose acetate. After reacting with the mixed acetic−oleic anhydride, the modified cellulose also showed the peaks at δ = 1.7−2 ppm, confirming the successful substitution of short chains. In addition, small peaks at δ = 0.8−1.5 ppm, attributed to the protons from the long fatty chains as assigned in Figure 4,[27] were observed, which clearly demonstrated the long fatty chain cellulose esters were successfully synthesized during the ball-milling mechanochemical process.

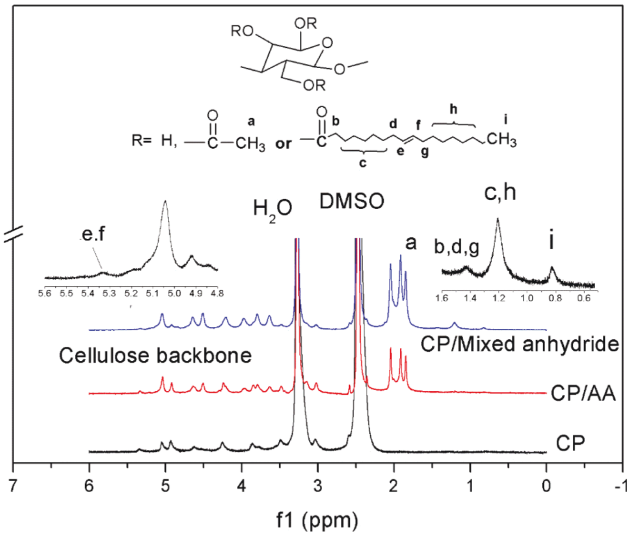

Figure 4. ^1H NMR spectra of mixed anhydride cellulose esters.

The above cellulose esterification method showed the following advantages compared with the traditional ones. (1) Process economy: for cellulose ester preparation, the cellulose crystal structure activation is a prerequisite and it is usually accomplished by employing some organic swelling agents, which are proton acceptors with low molecular weight, such as toluene and pyridine,[28] LiCl/DMAc,[29,30] and ionic liquids.[31] In addition, corrosive catalysts (e.g., sulfuric acid, perchloric acid,[21] *N*,*N*-dimethyl-4-aminopyridine[32]) and high reaction temperatures (e.g., 50,[33] 80,[29,30] 130 °C[19]) are often required to promote the reaction. In the present study, a simple ball-milling approach was proposed, and the acetic−oleic mixed anhydride preparation and cellulose esterification were conducted in a solvent-free condition at room temperature and pressure, which effectively reduced the numerous reaction steps and complex reagents involved, representing a much superior method compared with the solution reactions. (2) Atom economy: most previous studies regarding acylating cellulose with fatty substituents are usually prepared with fatty acyl chlorides,[29,30] fatty acid/*p*-toluenesolfonyl chloride,[34] or vinyl ester of fatty acid,[35] as esterification agents, which produces toxic and harmful byproducts such as hydrochloride acid, leading to a low atom economy. In comparation, here, crude fatty acids with AA were used for the grafting reaction. As depicted in Figure 2, the short and long chain could be both grafted onto the cellulose. By incorporating all reagents used in the final product, it presents a higher atom economy than the conventional methods mentioned above. (3) Environmental compatibility: as discussed above, most of the existing cellulose surface functionalization methods are using a toxic swelling agent and organic solvent such as pyridine, DMSO, and tetrabutylammonium fluoride. The toxicity of such organic compounds is a big challenge for scale-up production, and the consequent drying, purification, and recycling are high energy demanding and unsustainable. In this study, by employing amechanical method, the utilization of such toxic organic solvent was fully eliminated and esterification agents from renewable sources were employed, developing a cleaner, more sustainable process for cellulose esterification.

3.3. Thermal Stability. The thermal stabilities of cellulose particles and different chains grafted cellulose esters were studied by TGA and derivative thermal gravimetric (DTG) results. As presented in Figure 5, cellulose started its decomposition at approximately 250 °C, and then followed by a rapid pyrolysis of its main structure, whereas for the synthesized cellulose acetate, it exhibited a higher degradation temperature compared with neat cellulose particles. This increase can be attributed to the acetyl groups, which require more energy to degrade.[36,37] When the cellulose is modified with the mixed anhydrides, the initial degraded temperature shifted to a higher point compared to that of pure cellulose, but somewhat lower than that of cellulose acetate. The functional groups grafted onto the cellulose backbone have important influences on the thermal degradation behavior of the cellulose derivates. As summarized in other studies, the increase of the carbon chain length corresponded with the decrease of the thermal stability.[38] Cellulose oleate, although imparting promising properties like hydrophobicity, is limited in polymer processing because of its low thermal stability. In this study, the mixed acetic−oleic cellulose ester, that is the relatively high substituted short chain with better thermal stability, balanced the decrease caused by fatty acid chain esters. This result is shown by an overall higher and broader decomposition zone in the TGA curves than the untreated cellulose. Therefore, the mixed acetic−oleic cellulose ester could provide a wide processing temperature window in varied applications.

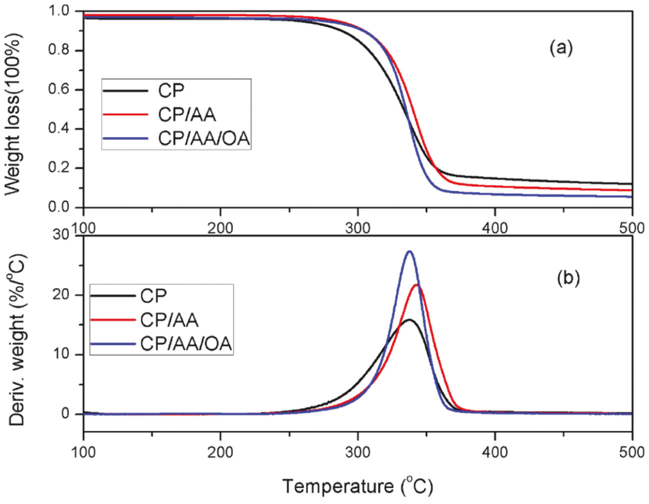

Figure 5. (a) TGA & (b) DTG curves for cellulose acetate and the mixed cellulose ester.

3.4. Ball-Milling Time. During most mechanochemical reactions, the milling duration is generally considered as the most important variable, representing the mechanical energy input. Different milling time durations of 30, 90, 150, and 240 min were investigated.

The ^{1}H NMR spectra reveal the detailed reaction information at different milling times. As can be seen in Figure 6, for the short-chain grafting process, the emergence of signals from 1.7 to 2.0 ppm is attributed to the occurrence of the acetyl group. As the milling time increased from 30 to 150 min, the acetyl peak intensity increased correspondingly. However, after 150 min, further ball-milling barely increased the intensity of the acetyl peaks, for this reaction had reached its maximum yield and continued energy input resulted in no change. As calculated in Table 1, the DS$_a$ values for ball-milling times of 30, 90, 150, and 240 min are 0.43, 0.61, 0.99 and 1.01, respectively. The acetyl protons appeared with three different sharp shoulders, meaning that hydroxyl groups from different positions participated in the esterification, regardless of the milling time variation. The DS$_f$ values for the ball-milling times of 30, 90, 150, and 240 min are 0.011, 0.020, 0.024, and 0.026, respectively. The fatty acetyl followed the same trend as the acetyl group; however, the long chain substitution increased slightly with prolonged ball-milling time after 150 min of milling.

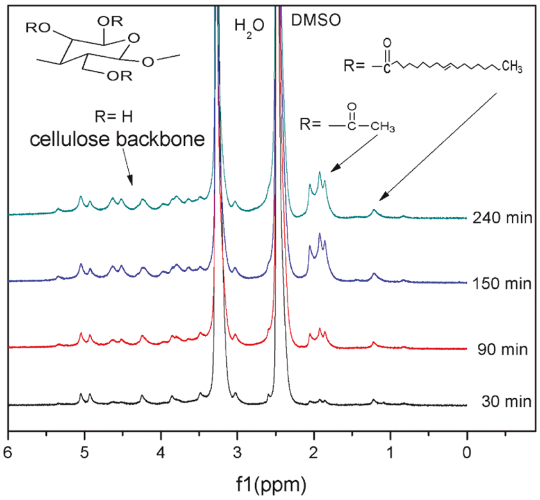

Figure 6. ^{1}H NMR curves for different ball-milling durations.

3.5. Molar Ratio. The molar ratios of the initial reagents also have a critical influence on the mechanochemical esterification. The ratio reactions of the mixed anhydride to cellulose powder was varied from 0.25 to 4 and analyzed with proton NMR (Figure 7). As discussed above, the peaks representing the protons from the acetyl group appeared for all the ratios ranging from 0.25 to 4, demonstrating the occurrence of short-chain grafting. However, for low ratio of 0.25 and 1, only one single peak, located at 2.05 ppm, appeared. This peak is responsible for the methyl proton from the C6 position. As the ratio was raised to 2:1 and 4:1, this single peak developed into three sharp shoulders, at 2.05, 1.91,

Table 1. DS Values of the Cellulose Esters Obtained by Mechanochemical Reaction

	ball-mill time (min)				molar ratio of mixed anhydrides and cellulose			
DS values	30	90	150	240	0.25:1	1:1	2:1	4:1
DS_a	0.43	0.61	0.99	1.01	0.22	0.46	0.99	1.67
DS_f	0.011	0.020	0.024	0.026	0.009	0.015	0.024	0.041

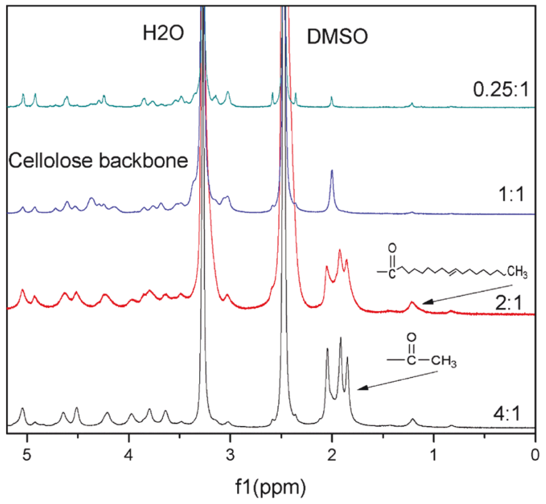

Figure 7. ^{1}H NMR for different initial ratios of mixed anhydride to cellulose.

and 1.85 ppm, which were attributed to the three different hydroxyl positions, C6, C2, and C3, respectively. This difference indicated that for a low mixed anhydride−cellulose ratio, the anhydrides are preferential to react with the primary C6−OH group, whereas for high ratios, all the three hydroxyl positions on the glucose were equally substituted during the esterification. For the heterogeneous cellulose reactions, the three hydroxyl groups have different reactivities because of steric hindrance. C6−OH is a primary hydroxyl group, whereas those at C2 and C3 are secondary hydroxyl groups. It is reported that C6−OH reacts 10 times faster than the other two in cellulose esterification.[2] In this study, when the mixed anhydride fractions were low, the regent's contact reaction was insufficient and limited; only the more reactive C6−OH were substituted during the reaction. By adding more mixed anhydride, all the hydroxyl groups were involved in the mechanochemical reaction and resulted in esterification for C6−OH, C2−OH, and C3−OH.

The DS value (Table 1) was calculated for the mixed anhydride to CP ratio of 0.25, 1, 2, and 4; the DS_a values were 0.22, 0.46, 0.99, and 1.67 respectively, whereas DS_f were 0.009, 0.015, 0.024, and 0.041. The DS_a and DS_f both exhibited an increase upon improving the anhydrides' molar fractions. When the amount of the mixed anhydrides is insufficient, the effective contact frequency between those initial reagents was limited and only a small part of the hydroxyl groups was able to react, resulting in low total substitutions. After increasing the dosage of the acetic−oleic anhydride, all the cellulose particles were surrounded by the anhydrides, improving the effective collision chances and led to the increased DS values.

High DS-value cellulose esters are favorable when working with soluble or thermoplastics, but their synthesis depends highly on reactive reagents and complex procedures.[39] Even though previous solution approaches could obtain high DS values (>0.5) for long aliphatic cellulose esters,[40,41] their industrial utilization is still limited because of the complexity and high cost. On the contrary, when surface hydrophobic characteristic is the only characteristic considered, a low DS value is enough to attain this property.[42,43] In addition, low DS cellulose esters could be achieved by using less reactive and cheap reagents, and at the same time, it could maintain the fibrous morphology and mechanical performance of cellulose. Attempts at preparing fatty chain grafted cellulose esters in solvent-free condition have been made but a high reaction temperature was required, and the obtained DS value was extremely low (<0.002).[44] In this study, to the best of our knowledge, the presented mechanochemical technique is the first study to prepare the fatty acylated cellulose employing fatty acids directly in the solvent-free condition at room temperature, and the obtained acylation DS value (>0.5) is also higher than that from similar conditions,[44] demonstrating the effectiveness of the mechanochemical approach.

3.6. Water Contact Angle. The water repellency of the cellulose modified with the mixed anhydrides was charac-

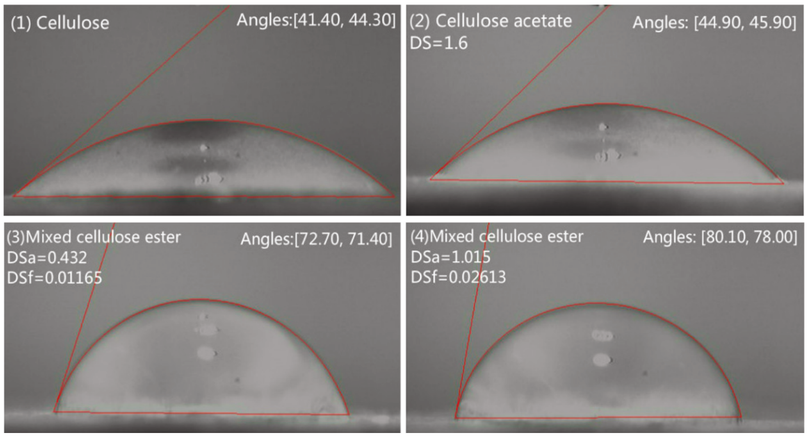

Figure 8. Water contact angles for different DS cellulose samples.

terized by evaluating the water contact angle performance. As shown in Figure 8(1), the neat cellulose exhibited a high wettability as the water droplet was observed to spread and form a low contact angle of 42.7° with the cellulose surface. The polar behavior of the neat cellulose is due to the large number of hydroxyl groups on the surface. In Figure 8(2), the cellulose acetate with a DS value of 1.6 displayed an increased water contact angle of 45.4°, which indicated that the short chains almost had little contribution on decreasing the wettability of the cellulose powder. After clarifying this point, the influence of grafting long fatty chains on the water contact angle performance of cellulose was investigated. Samples with different DS_f values, Figures 8(3,4), displayed high water contact angles and corresponded with higher water repellency. The initial contact angles for $DS_f = 0.01165$ and $DS_f = 0.02613$ samples were 72 and 79°, respectively. This result demonstrated that the grafting of a long carbon chain decreased the surface energy and wettability of the cellulose powder with water. In addition, a correlation between the DS_f and contact angles could be observed in Figures 8(3,4). The cellulose with a higher DS_f value exhibited higher water contact angles. Apparently, the surface energy of cellulose esters depends more on grafted carbon chains rather than the substitution of the hydroxyl groups with ester bonds. Short-chain cellulose esters possessed high surface energy and wettability, whereas the substitution of a lipophilic oleate chain decreased the surface energy. The fatty chains grafted on the cellulose particles may take on a posture that is perpendicular to the fiber surface, thereby forming a sort of "nanopin" structure.[45] This surface morphology would emphasize their nonpolar property antagonist with the highly polar cellulose molecules, increasing the free volume and consequently decreasing the surface energy and wettability.

4. CONCLUSIONS

A mechanochemical process to synthesize cellulose esters with long fatty chains and short chains was developed in this study. Asymmetric anhydride formation from mixing AA and OA during ball-milling was studied by UPLC. The results showed that 30 min of ball-milling with an equal molar ratio of the initial reagent led to the most efficient result. Cellulose-mixed anhydride esters were prepared using mechanochemical reaction in ball millings with activated cellulose particles and mixed anhydrides. Adding NaH_2PO_2 increased the reaction rate and yield. Increasing the milling time and the mixed anhydride molar fraction of the reaction led to increased DS value of the mixed cellulose ester. The mixed anhydride cellulose esters displayed higher thermal stability than that of the unreacted one. The grafting of the long fatty chains increased the water repellency of cellulose particles, presenting promising properties for applications such as reinforcing agents, which will be explored in our following work. The mechanochemical reaction in this study is an entirely solvent-free modification with a simplified synthesis procedure, and the successful conducting of the solid-state milling esterification will shed light on the utilization of mechanochemistry in cellulose modifications.

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