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Biobased and Sustainable Alternative Route to Long-Chain Cellulose Esters

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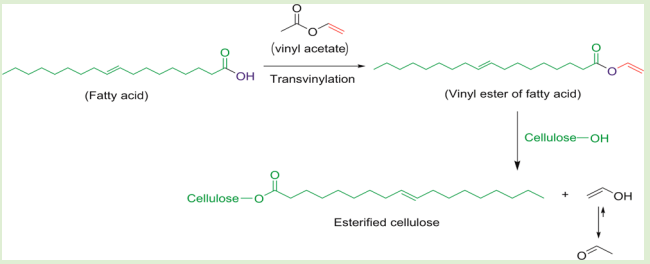
ABSTRACT: Fatty acid cellulose esters (FACEs), which have been identified recently as sustainable film materials, are conventionally synthesized by the use of the reaction with acyl chloride/anhydride pyridine in the presence of LiCl/*N*,*N*-dimethylacetamide. In this study, we have developed a new synthetic route to FACEs using a vinyl ester of long chain fatty acid, which is an excellent biobased and highly reactive reagent, for the functionalization of cellulose. The developed method involves the synthesis of the long aliphatic fatty acid vinyl ester via a transition-metal-catalyzed transvinylation reaction between vinyl acetate and the fatty acid, followed by its subsequent reaction with cellulose to yield FACEs. In this work, we have used vinyl oleate as a model precursor to introduce the fatty acid chain to cellulose. The covalent grafting of the fatty acid chain to the free hydroxyl groups of cellulose was achieved through potassium carbonate (K_2CO_3)-catalyzed transesterification of vinyl oleate in the presence of *N*-methyl pyrrolidone as solvent with low toxicity. Successful functionalization of cellulose was confirmed by FTIR, ^{13}C CP-MAS NMR, X-ray diffraction, and the thermogravimetric analysis. The results obtained showed that the functionalization efficiency of the cellulose increased with higher temperature and prolonged reaction times. The strategy proposed in the present work is an important step onward in terms of sustainability because the long-chain vinyl ester can be synthesized from a renewable and biobased source, and the toxic and corrosive chemicals commonly employed for cellulose esterification are avoided.



INTRODUCTION

Polysaccharides are increasingly recognized as promising materials in biotransformation processes for achieving a biobased economy. In particular, much attention has been given to cellulose and its derivatives for their potential application in numerous areas of modern life, as a result of the environmental benefits, high versatility, renewability, nontoxicity and abundance of this natural polymer.[1] In addition, there has been a growing interest in developing new biobased materials, which can compete with fossil-based materials in performance, and thus developing new technologies or modifying the existing ones by using environmentally friendly chemical processes.

Notwithstanding cellulose acetate and other short-chain cellulose derivatives, recently, long fatty acid cellulose esters (FACEs) have drawn much attention and have been identified as sustainable and biodegradable plastics.[2−7] Traditionally, FACEs are synthesized mainly by the pyridine−acyl chloride or anhydride reactions.[2,3,6−12] These reaction systems produce aggressive hydrochloric acid as a byproduct, resulting in cellulose degradation. To limit acid degradation of cellulose, bases such as pyridine, its derivative DMAP,[4,13,14] or trimethylamine,[9] are usually used to neutralize the acid generated. Nitrogen stream[16] or vacuum[2] are also applied to remove gaseous HCl as it is formed.

The use of crude fatty acids as esterifying agents is the best option for synthesis of FACEs, but their extremely low reactivity toward cellulose's hydroxyl groups and the steric effect prevent the grafting reaction. Attempts to convert in situ the fatty carboxylic acids into more reactive entities have been made by using *p*-toluenesolfonyl chloride,[17,18] or acetic anhydride[19−21] as coreactant. For an homogeneous modification, the mixed solvent *N*,*N*-dimethylacetamide with lithium chloride (DMAc/LiCl) systems is widely used.[4−6,8−10,13−15] However, the ecological impact and the price of such compounds limit their utilization to a laboratory scale.

In this study, we present a new acylation process based on the transesterification reaction between cellulose hydroxyl groups and vinyl ester of fatty acid. Compared with the traditional esterification methods using either acyl chlorides or anhydrides, the novel proposed transesterification method using vinyl ester of fatty acid obtained from innocuous acyl donor is indeed a mild acylation method. This new approach generates acetaldehyde as a byproduct that is not acidic and can be easily removed from the reaction medium because of its low boiling point. It has been reported that polysaccharides including cellulose can be successfully esterified by this

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method.[22−26] Recently, it has been shown that cellulose nanowhiskers can be easily esterified by vinyl acetate and vinyl cinnamate under microwave activation.[27,28] To our knowledge, the use of vinyl ester of long-chain fatty acids as a reagent to esterify cellulose has not yet been exploited. Accordingly, in this study, we explored the sustainable and nontoxic functionalization of microcrystalline cellulose (MCC) using vinyl ester of fatty acid under mild conditions. This method first called upon the synthesis of vinyl ester of fatty acid by the transvinylation of oleic acid (OA) with vinyl acetate. The synthesized vinyl oleate (VO) was then used to functionalize cellulose through a transesterification reaction between a synthesized precursor and the hydroxyl groups of cellulose, using K_2CO_3 as mild catalyst and NMP as low toxic solvent. The supramolecular/crystal structure and thermal properties of functionalized MCC were characterized using FTIR, ^{13}C CP-MAS nuclear magnetic resonance (NMR) spectroscopy, X-ray diffraction (XRD), and thermogravimetry.

EXPERIMENTAL SECTION

Materials. Microcrystalline cellulose (powder, 20 μm) prepared from cotton linters, sulfuric acid (95%), chloro(1,5-cyclooctadiene) iridium-(I) dimer (Ir 57.2%) ($[Ir(cod)Cl]_2$), OA (97%), vinyl acetate (VAc), *N*-methyl-2-pyrrolidone (NMP), potassium carbonate (K_2CO_3), sodium acetate, and sodium sulfate were purchased from Sigma-Aldrich. All other solvents were ACS-grade and used as received.

Instrumentation. *IR-ATR Instrument.* Spectrum Two FTIR (Perkin-Elmer) was equipped with an UATR Diamond accessory, which allows collection of FTIR spectra directly on a sample without any special preparation. The "pressure arm" of the instrument was used to apply a constant pressure (monitored by software) to the sample positioned on top of the Diamond crystal to ensure a good contact between the sample and the incident IR beam. All FTIR spectra were collected at a spectrum resolution of 4 cm^{-1}, with 32 scans over the range from 4000 to 450 cm^{-1}.

Nuclear Magnetic Resonance. ^1H and ^{13}C NMR spectra in $CDCl_3$ were recorded in Bruker BioSpin 700 MHz using TMS as reference. Multiplicities are abbreviated as follows: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, and m = multiplet.

Solid-state ^{13}C CP MAS NMR spectra of modified and unmodified cellulose were obtained at room temperature on a Bruker Avance-II spectrometer operating at 150.9 MHz using a custom-built MAS NMR probe. The samples were packed into 4 mm zirconia rotors. The sample spinning speed was regulated to 12.0 Hz, the contact time was 1 ms, and the relaxation delay between the acquisitions was 5 s. Chemical shifts were relative to TMS used as an external standard. For each sample, a total of 20 000 scans were accumulated.

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) plots were carried out using a Mettler-Toledo TGA/SDTA 851e, under nitrogen with a flow rate of 40 mL min^{-1}, using alumina pans. The samples were ramparted from room temperature to 600 °C at a scanning rate of 10 °C min^{-1}.

X-Ray Diffraction Analysis. XRD patterns were recorded on PANanalytical B.V. X'Pert3 powder diffractometer (Netherland) with Cu Kα radiation in the angular range of 2θ = 5−70° at 25 °C.

Synthetic Strategies. *Synthesis of Vinyl Oleate.* Vinyl ester of OA was synthesized by mixing 10.56 g (37.40 mmol) OA with a 10 equiv excess of vinyl acetate in a three-necked round-bottomed glass flask equipped with a reflux condenser and thermometer and thereafter degassed with argon. The catalyst $[Ir(cod)Cl]_2$ (0.01 equiv), along with sodium acetate (0.03 equiv), was then added, and the reaction mixture was kept under magnetic stirring in a dry argon atmosphere at 100 °C for 16 h. After reaction, the mixture was poured in water and extracted with dichloromethane, and the organic fraction was dried over anhydrous sodium sulfate before removing the solvent in a rotary evaporator. Silica-gel column chromatography was used to purify the obtained residue using a mixture of petroleum ether/dichloromethane (4:1; v/v), and the reaction yielded 98% VO.

The obtained VO was characterized by FTIR-ATR and NMR spectroscopy. IR-ATR (Figure 1) (ν, cm^{-1}): 3091 (vinyl C−H stretching), 3006 (chain unsaturation C−H stretching), 2923 and 2854 (saturated CH_2 stretching modes), 1758 (C=O stretching of vinyl ester), 1646 (nonconjugated C=C stretching), 1464 (H bending of CH_2 and CH_3 groups), 1141 (ester C−O stretching), 949 (CH out-of-plane deformation of $CH=CH_2$), 868 (CH_2 out-of-plane deformation of $-CH=CH_2$), and 722 (skeletal vibration of $-(CH_2)_n-$). ^1H NMR (700 MHz, $CDCl_3$, δ) (Figure 2): 0.89 (t, 3H, $-C\underline{H}_3$), 1.28−1.32 (m, 20H, aliphatic $-C\underline{H}_2-$), 1.65 (m, 2H, $-CH_2-C\underline{H}_2-C(=O)-$), 2.02 (m, 4H, $-C\underline{H}_2-CH=CH-C\underline{H}_2-$), 2.35−2.40 (t, 2H, $-C\underline{H}_2-C(=O)-$), 4.57 and 4.88 (dd, 2H, $COO-CH=C\underline{H}_2$), 5.35 (m, 2H, $-C\underline{H}=C\underline{H}-$), and 7.27−7.30 (dd, 1H, $COO-C\underline{H}=CH_2$). ^{13}C NMR (700 MHz, $CDCl_3$, δ) (Figure 3): 14.2 (C_v, $-\underline{C}H_3$), 22.8 (C_q, $CH_3-\underline{C}H_2-$), 24.7 (C_c, $-O-C(=O)-CH_2-\underline{C}H_2-$), 27.3 ($C_b$, $-O-C(=O)-\underline{C}H_2-$), 29.2 ($C_h$ and C_k, $-\underline{C}H_2-CH=CH-\underline{C}H_2-$), 29.4−29.6 ($C_{d,e}$ and C_o, $-O-(C=O)-(CH_2)_2-\underline{C}H_2-\underline{C}H_2-$, $CH_3-(CH_2)_2-\underline{C}H_2-$), 29.8−29.9 ($C_{f,g}$ and C_{l-n}, $-\underline{C}H_2-\underline{C}H_2-CH_2-CH=CH-CH_2-\underline{C}H_2-\underline{C}H_2-\underline{C}H_2-$), 32.0 ($C_p$, $CH_3-CH_2-\underline{C}H_2-$), 97.0 ($C_v$, $-(C=O)-O-CH=\underline{C}H_2$), 130 ($C_{i,j}$, $-CH_2-\underline{C}H=\underline{C}H-CH_2-$), 141.4 ($C_s$, $-(C=O)-O-\underline{C}H=CH_2$), 170.9 ($C_a$, $-O-\underline{C}(=O)-$).

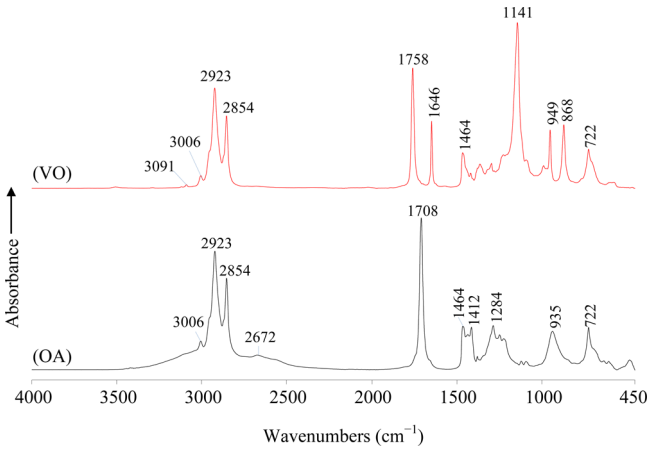

Figure 1. FTIR absorbance spectra of oleic acid (OA) and vinyl oleate (VO).

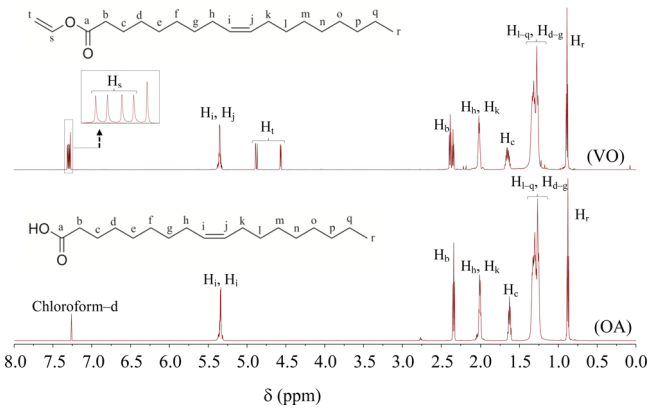

Figure 2. ^1H NMR spectra of oleic acid (OA) and vinyl oleate (VO) in $CDCl_3$ and peak assignments.

General Procedure for the Chemical Functionalization of Microcrystalline Cellulose. Cellulose Activation. Microcrystalline cellulose (MCC) was first activated by mercerisation to make its

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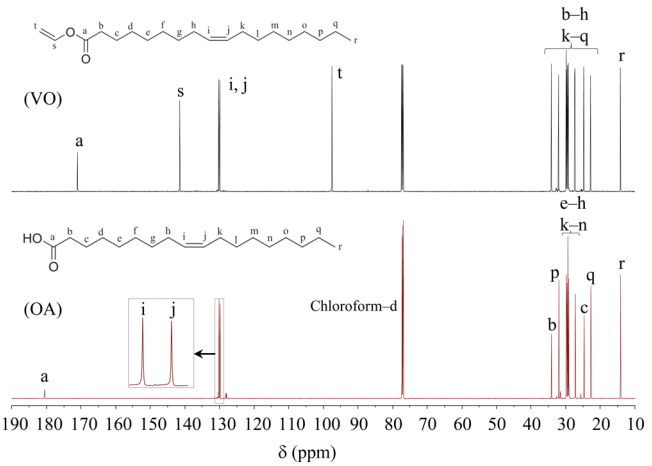


Figure 3. ^{13}C NMR spectra of oleic acid (OA) and vinyl oleate (VO) in $CDCl_3$ and peak assignments.

hydroxyl groups accessible for reaction. A 20 g MCC was mercerised in 1 L of sodium hydroxide solution (4 M) and then filtered and washed by a series of dehydrating solvents, methanol, acetone. and hexane.[2] The sample was then oven-dried at 80 °C for 24 h and was stored under vacuum in a desiccator.

Synthesis of FACEs. Several experiments were carried out, varying the reaction time and temperatures. Activated MCC (1 g) was placed in a 100 mL round-bottomed flask, containing a solution of 7 mmol of VO per 1 g of MCC, 0.15 g K_2CO_3 (catalyst), and 20 mL of NMP. The mixture was then heated under reflux with vigorous magnetic agitation for different reaction times ranged from 1 to 24 h and temperatures from 90 to 125 °C. At the end of reaction, the flask content was filtered and excessively washed with water and ethanol. To remove any residual traces of unreacted VO and solvent, the modified MCC was Soxhlet-extracted with ethanol for 6 h and then dried at 80 °C for 24 h.

Kinetics of the Reaction and the Effect of Reaction Temperature. To evaluate the synthesis efficiency to afford FACEs, the esterification reaction was conducted for 3 h at either series stepwise temperature increases (90−125 °C) or at 90 °C at varying reaction times. After reaction, the modified MCC was analyzed by FTIR spectroscopy, and the characteristic vibrations of the grafted acyl groups were used to estimate the extent of grafting over reaction times and temperatures. The influence of increasing reaction time or temperature was quantified by calculating the peak height ratio of $I_{C=O/C-O}$ and plotting this ratio as a function of reaction time and reaction temperature (Figure 6). This method was adopted as a valid means of quantifying the extent of esterification and investigating reaction kinetics of cellulose modification.[29] The method consists of comparing the intensity of the C=O vibration of the grafted acyl moieties with the vibration at 1060 cm^{-1} associated with C−O stretching of the cellulose backbone, which is used as an internal standard.

RESULTS AND DISCUSSION

Chemical Synthesis and Spectroscopic Characterization of Cellulose Precursor. For comparison with the classical acylation of cellulose with fatty acids by means of acyl chloride, the corresponding long-chain vinyl ester was synthesized. The commercially available OA was functionalized by transesterification with vinyl acetate to obtain VO according to the procedure presented in Scheme 1A. The structure of the new biobased long-chain vinyl ester was confirmed by the combined spectroscopic analyses reported above.

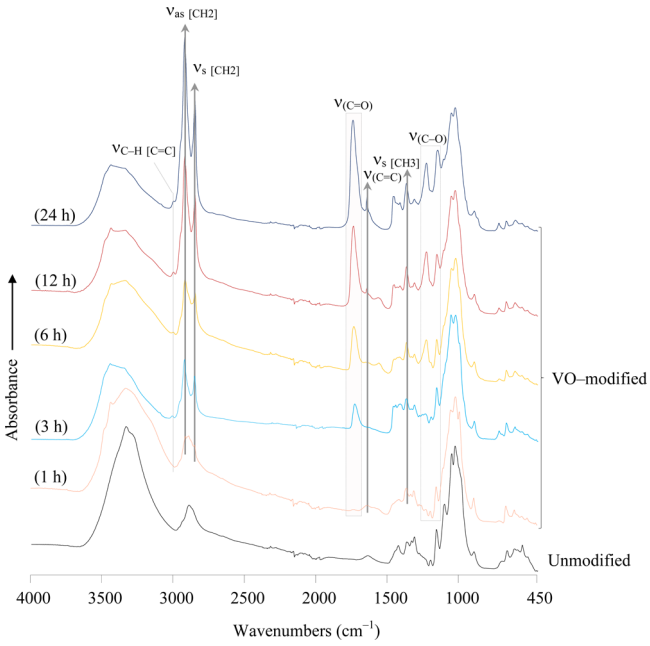
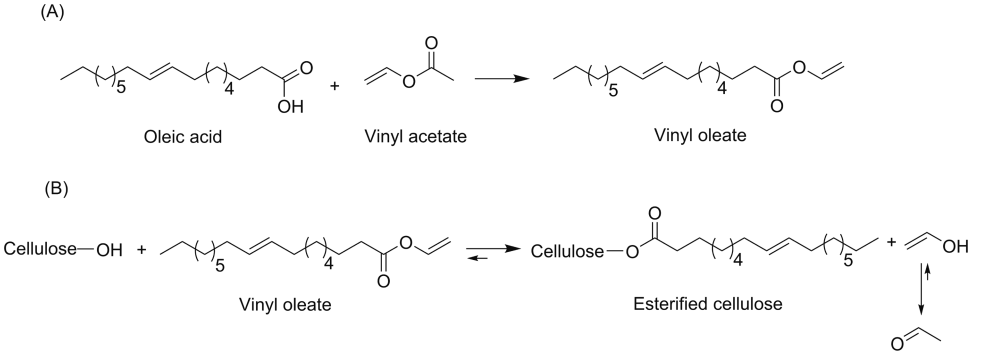


Figure 4. FTIR absorbance spectra of unmodified and modified MCC with vinyl oleate (VO-modified) for 3, 6, 12, and 24 h at 90 °C.

Compared with the FTIR spectra of the starting OA, the spectra of the synthesized VO showed the emergence of new characteristic absorption bands (Figure 1). These new absorption bands were observed around 3091 cm^{-1} (vinyl C−H stretching), 3006 cm^{-1} (chain unsaturation C−H stretching), 2923 and 2854 cm^{-1} (saturated CH_2 stretching modes), 1758 cm^{-1} (C=O stretching of vinyl ester), 1646 cm^{-1} (non−conjugated C=C stretching), 1464 cm^{-1} (H

Scheme 1. Synthesis of Vinyl Ester of Oleic Acid (A) Followed by the Cellulose Functionalization Procedure (B)



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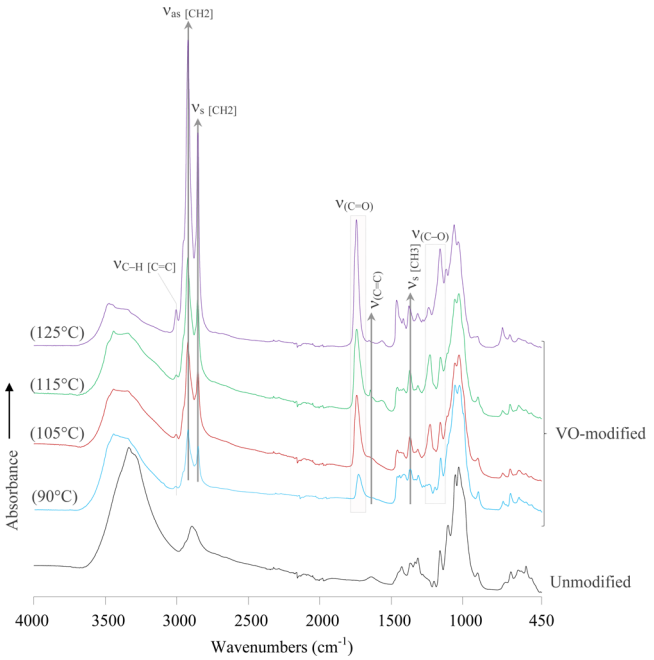

Figure 5. FTIR absorbance spectra of unmodified− and modified MCC with vinyl oleate (VO-modified) at 90, 105, 115, and 125 °C for 3 h.

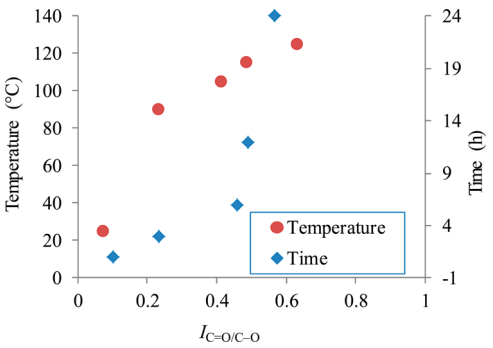

Figure 6. Peak heights ratio ($I_{C=O/C-O}$) as a function of reaction time and temperature for MCC modified with vinyl oleate.

bending of CH_2 and CH_3 groups), 1141 cm^{-1} (ester C−O stretching), 949 cm^{-1} (CH out-of-plane deformation of CH═CH_2), 868 cm^{-1} (CH_2 out-of-plane deformation of −CH═CH_2), and 722 cm^{-1} (skeletal vibration of $-(CH_2)_n-$).[30,31] In addition to the appearance of new characteristic bands, a disappearance of carboxyl groups at ∼2672 cm^{-1} (OH stretching) and at 1708 cm^{-1} (C═O stretching) was observed, confirming the complete transformation of OA into VO.

The transvinylation reaction was further confirmed by ^{1}H NMR and ^{13}C NMR. The ^{1}H NMR spectra of the synthesized VO showed the emergence of new resonances typical for the vinyl ester protons (δ 4.7, 5.1, and 7.5), in addition to those of the starting fatty acid precursor (Figure 2).

The ^{13}C NMR analysis of the synthesized VO (Figure 3) was in agreement with the evidence shown by ^{1}H NMR (Figure 2). In addition to the unchanged resonances related to the fatty acid, spectra of the synthesized VO showed a new group of signals resonating at δ 97.0 and 141.4, which were identified as methylenic and methinic carbons of the vinyl ester group (Figure 3).

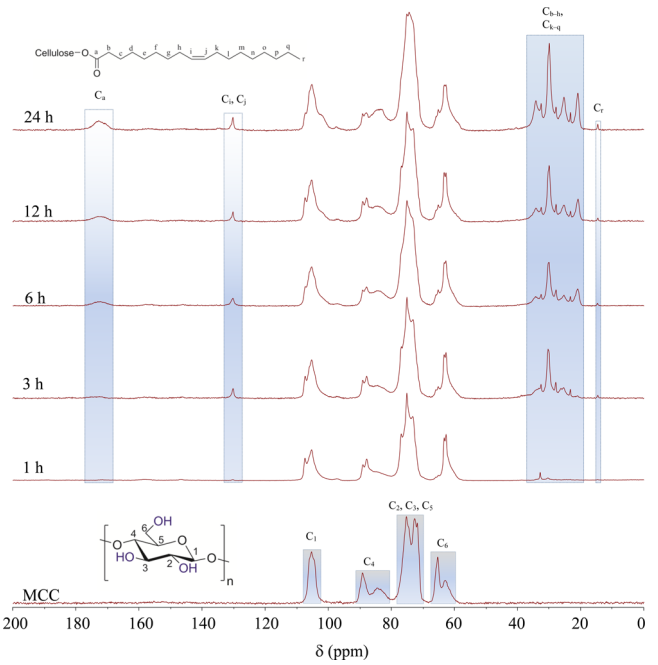

Figure 7. ^{13}C CP-MAS NMR spectra of unmodified and modified MCC with vinyl oleate for 1, 3, 6, 12, and 24 h at 90 °C.

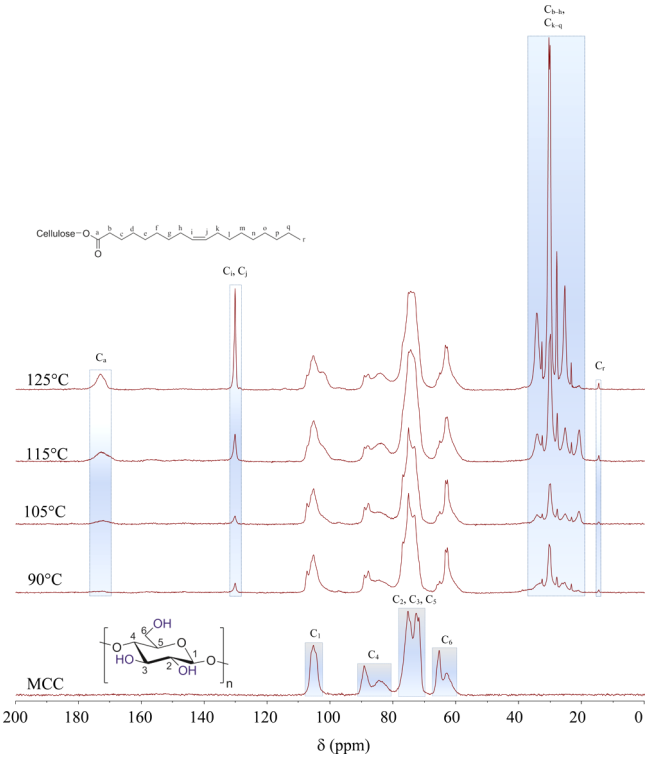

Figure 8. ^{13}C CP-MAS NMR spectra of unmodified and modified MCC with vinyl oleate at 90, 105, 115, and 125 °C for 3 h.

Esterification of Cellulose by Vinyl Oleate and Spectroscopic Characterization. A biobased and more sustainable route to FACEs was investigated by using a transesterification process under heterogeneous conditions. The VO was chosen as long acyl chain donor for its known capacity to increase the hydrophobicity of polar biomolecules.[32] Reactions were performed according to Scheme 1B, with potassium carbonate as a mild catalyst and NMP as low toxic

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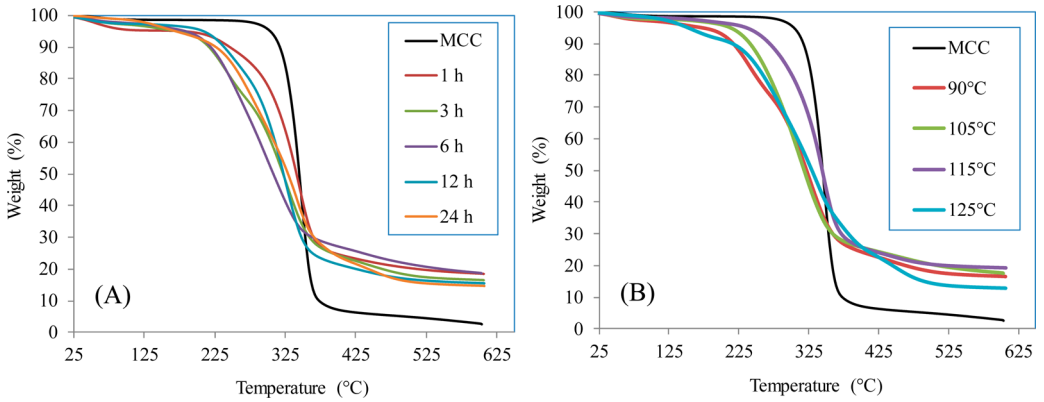

Figure 9. TGA thermograms of unmodified (MCC) and modified MCC with vinyl oleate for 1, 3, 6, 12, and 24 h at 90 °C (A) and for 3 h at 90, 105, 115, and 125 °C (B).

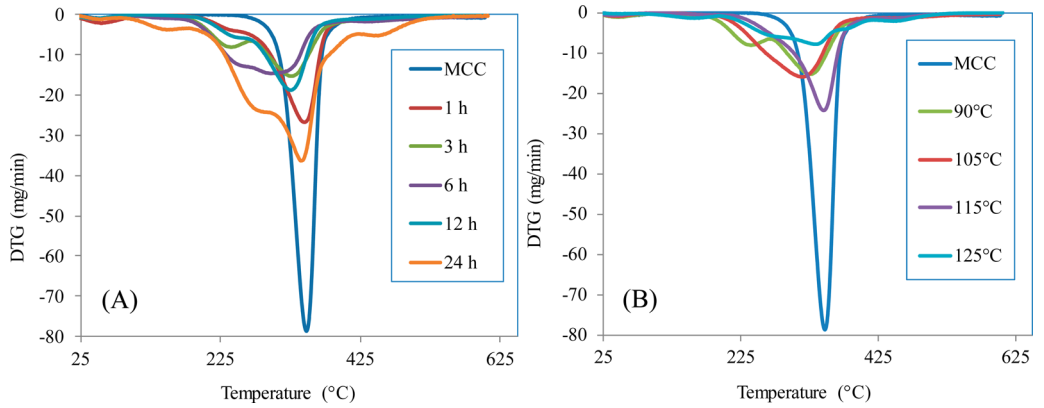

Figure 10. DTG thermograms of unmodified (MCC) and modified MCC with vinyl oleate for 1, 3, 6, 12, and 24 h at 90 °C (A) and for 3 h at 90, 105, 115, and 125 °C (B).

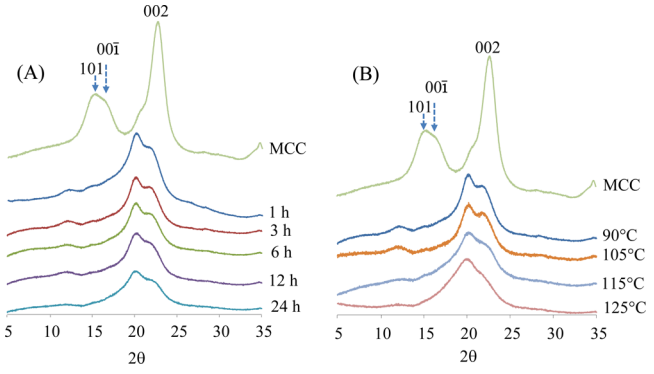

Figure 11. X-ray diffraction patterns of unmodified (MCC) and modified MCC with vinyl oleate for 1, 3, 6, 12, and 24 h at 90 °C (A) and for 3 h at 90, 105, 115, and 125 °C (B).

solvent. Various reaction times (1, 3, 6, 12, or 24 h) and temperatures (90, 105, 115, or 125 °C) were investigated. The selected esterification method offers the possibility to graft a large variety of biobased saturated and unsaturated long-chain moieties into lignocellulosic materials. Unlike classical methods involving acyl chlorides, the current method generates vinyl alcohol as a nonacidic byproduct, which tautomerizes to the highly volatile acetaldehyde, and thus the equilibrium is naturally shifted toward the ester formation (Scheme 1B). The modified cellulose samples were first characterized by FTIR and ^{13}C CP-MAS spectroscopy. Figures 4 and 5 depict the FTIR spectra of unmodified MCC (unmodified) and functionalized MCC with vinyl oleate (VO-modified). In addition to the prominent carbonyl stretching vibration at 1735−1743 cm^{-1} ($\nu_{C=O}$) and the C−O stretching vibrations at 1157−1230 cm^{-1} (ν_{C-O}), some new characteristic vibrations of the grafted aliphatic acyl chain moieties were identified, namely, the strong skeletal bands of long-chain moieties at 2922 and 2853 cm^{-1} (ν_{C-H}), 1370 cm^{-1} (γ_{C-H}), and 720 cm^{-1} (CH_2 rocking). Additionally, a new vibration arose at 3010 cm^{-1}, which is a characteristic band of unsaturated function (H−C═C) of oleic chain.[5,31,33] These bands confirm the esterification reaction in VO-modified MCC. Similar FTIR features were observed when fatty acid moieties were introduced into the cellulose using acyl chlorides as a precursor.[5−18,21]

The extent of grafting of fatty chain into cellulose's hydroxyl groups over reaction time and temperature was quantified through the calculation of the $I_{C=O/C-O}$ peak heights ratio (Figure 6). By increasing both reaction time and temperature, the $I_{C=O/C-O}$ ratio gradually increased, indicating that the MCCs were increasingly esterified. However, the effect of reaction temperature was more prominent than that of reaction time; that is, the diffusion of the VO into the cellulose hydroxyl groups is more favorable by increasing reaction temperature. This difference may result from the diffusion mechanism that governs the accessibility of hydroxyl groups as well as the size effect of the reagent. This is possible as the three hydroxyls on an anhydroglucose unit of cellulose are not equally accessible. The primary hydroxyl is more reactive than the two secondary hydroxyls due to the stereochemical hindrance.

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VO-modified MCC samples were further characterized by ^{13}C CP-MAS NMR spectroscopy (Figures 7 and 8). In addition to the dominant pattern corresponding to the carbons of cellulose, signals for carbons of the newly introduced long chain oleic moieties appeared clearly in the VO-modified MCC spectra. These signals were assigned directly on the spectra of VO-modified MCC according to the nomenclature given on the associated structure.

Thermal Properties of the Synthesized Fatty Acid Cellulose Esters. The TGAs of native MCC and VO-modified MCC at different reaction times and temperatures were performed under continuous nitrogen to study the decomposition properties of the FACEs. The reported weight loss was normalized against the initial weight of the analyzed samples (Figure 9). The analyses showed that thermal degradation of native MCC starts at 348 °C following a single weight-loss step. The VO-modified MCCs were, however, less stable becaue they started to decompose at temperatures substantially lower than that of unmodified MCC. These results were expected because the grafting of long-chain acyl groups into cellulose's hydroxyl groups resulted in significant decrease in crystallinity.

In addition to the lower degradation temperatures, modified MCC showed two main separate degradation steps, attributed to degradation of grafted fatty acid chain and cellulose backbone (Figure 10). Similar results were reported in the literature when cellulose is functionalized with fatty acid chlorides.[12,17,18,34]

Crystal Structure by XRD. The XRD patterns of native MCC before and after esterification under various conditions were presented in Figure 11. The native MCC exhibited three main planes of the crystalline cellulose I structure with the characteristic peaks at around 2θ = 14.7, 16.3, and 22.5°, attributed, respectively, to the 101, $10\bar{1}$, and 002 diffraction planes.[8,21,35] After reaction with VO, the cellulose's main characteristic planes were substantially weakened or completely disappeared, while a new broad diffraction peak between 2θ = 18 and 22° was clearly observed. These new diffractions were, in general, attributed to the amorphous regions of cellulosic backbone.[8,36] Similar results were reported in the literature when cellulose was modified with acyl chlorides.[8,9,12] The intensity of changes in XRD patterns was not proportional to the extent of grafting. This may be attributed to the loss of crystallinity of the starting substrate following the mercerization process prior to the grafting reaction. Nonetheless, the extent of the changes tends to increase with the reaction temperature.

CONCLUSIONS

Functionalization of cellulose with VO in the presence of low toxic solvent (NMP) and mild catalyst (K_2CO_3) was found to be highly effective, avoiding the problems of cellulose degradation and complex methods. Esterification of cellulose via the vinyl ester of fatty acid means appeared to be an efficient method for grafting a variety of biobased long chain moieties into the cellulose, resulting in FACEs with relatively high grafting rates. The concept comprises a synthesis of vinyl ester of fatty acid from cheaply available vinyl acetate and a long-chain fatty acid, followed by a covalent incorporation of the fatty chain onto the cellulose via transesterification reaction between cellulose's hydroxyl groups and the synthesized vinyl ester. The efficiency of the reaction was found to increase with increasing reaction time and temperature. However, the effect of increasing reaction temperature was found to have a significant effect on the grafting rates. Using this new approach, a variety of plant polyunsaturated fatty acids can be functionalized and utilized to produce multifunctional cellulose-based materials for optical, electronic, and selective separation applications.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Olaru, N.; Olaru, L.; Vasile, C.; Ander, P. *Polimery* **2011**, *56*, 834−840.
(2) Kwatra, H. S.; Caruthers, J. M.; Tao, B. Y. *Ind. Eng. Chem. Res.* **1992**, *31*, 2647−2651.
(3) Wang, P.; Tao, B. T. *J. Environ. Polym. Degrad.* **1995**, *3*, 115−119.
(4) Joly, N.; Granet, R.; Branland, P.; Verneuil, B.; Krausz, P. *J. Appl. Polym. Sci.* **2005**, *97*, 1266−1278.
(5) Crépy, L.; Chaveriat, L.; Banoub, J.; Martin, P.; Joly, N. *ChemSusChem* **2009**, *2*, 165−170.
(6) Zhou, Y.; Min, D.; Wang, Z.; Yang, Y.; Kuga, S. *BioResources* **2014**, *9*, 3901−3908.
(7) Kulomaa, T.; Matikainen, J.; Karhunen, P.; Heikkilä, M.; Fiskari, J.; Kilpeläinen, I. *RSC Adv.* **2015**, *5*, 80702−80708.
(8) Guo, Y.; Wang, X.; Li, D.; Du, H.; Wang, X.; Sun, R. *Polym. Bull.* **2012**, *69*, 389−403.
(9) Wei, Y.; Cheng, F.; Hou, G. *J. Sci. Ind. Res.* **2007**, *66*, 1019−1024.
(10) Samaranayake, G.; Glasser, W. G. *Carbohydr. Polym.* **1993**, *22*, 1−7.
(11) Freire, C. S. R.; Silvestre, A. J. D.; Pascoal Neto, C.; Rocha, R. M. A. *Cellulose* **2005**, *12*, 449−458.
(12) Freire, C. S. R.; Silvestre, A. J. D.; Neto, C. P.; Belgacem, M. N.; Gandini, A. *J. Appl. Polym. Sci.* **2006**, *100*, 1093−1102.
(13) Memmi, A.; Granet, R.; Gahbiche, M. A.; Fekih, A.; Bakhrouf, A.; Krausz, P. *J. Appl. Polym. Sci.* **2006**, *101*, 751−755.
(14) Crépy, L.; Miri, V.; Joly, N.; Martin, P.; Lefebvre, J.−M. *Carbohydr. Polym.* **2011**, *83*, 1812−1820.
(15) Vaca-Garcia, C.; Thiebaud, S.; Borredon, M. E.; Gozzelino, G. *J. Am. Oil Chem. Soc.* **1998**, *75*, 315−319.
(16) Thiebaud, S.; Borredon, M. E. *Bioresour. Technol.* **1995**, *52*, 169−173.
(17) Uschanov, P.; Johansson, L.−S.; Maunu, S. L.; Laine, J. *Cellulose* **2011**, *18*, 393−404.
(18) Almasi, H.; Ghanbarzadeh, B.; Dehghannia, J.; Pirsa, S.; Zandi, M. *Fibers Polym.* **2015**, *16*, 1715−1722.
(19) Miao, J.; Yu, Y.; Jiang, Z.; Zhang, L. *Cellulose* **2016**, *23*, 1209−1219.
(20) Sealey, J. E.; Samaranayake, G.; Todd, J. G.; Glasser, W. G. *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 1613−1620.
(21) Hu, H.; Li, H.; Zhang, Y.; Chen, Y.; Huang, Z.; Huang, A.; Zhu, Y.; Qin, X.; Lin, B. *RSC Adv.* **2015**, *5*, 20656−20662.
(22) Jebrane, M.; Sèbe, G. *Holzforschung* **2007**, *61*, 143−147.

DOI: 10.1021/acs.biomac.6b01584
Biomacromolecules XXXX, XXX, XXX−XXX

(23) Jebrane, M.; Sèbe, G. *Carbohydr. Polym.* **2008**, *72*, 657−663.
(24) Jebrane, M.; Pichavant, F.; Sèbe, G. *Carbohydr. Polym.* **2011**, *83*, 339−345.
(25) Jebrane, M.; Sèbe, G.; Cullis, L.; Evans, P. *Polym. Degrad. Stab.* **2009**, *94*, 151−157.
(26) Jebrane, M.; Harper, D.; Labbe, N.; Sèbe, G. *Carbohydr. Polym.* **2011**, *84*, 1314−1320.
(27) Çetin, N.−S.; Tingaut, P.; Özmen, N.; Henry, N.; Harper, D.; Dadmun, M.; Sèbe, G. *Macromol. Biosci.* **2009**, *9*, 997−1003.
(28) Sèbe, G.; Ham-Pichavant, F.; Pecastaings, G. *Biomacromolecules* **2013**, *14*, 2937−2944.
(29) Zini, E.; Scandola, M.; Gatenholm, P. *Biomacromolecules* **2003**, *4*, 821−827.
(30) Bellamy, L. J. In *The Infra−Red Spectra Of Complex Molecules*, 3rd ed.; Chapman and Hall: New York, 1975.
(31) Vilela, C.; Rua, R.; Silvestre, A. J. D.; Gandini, A. *Ind. Crops Prod.* **2010**, *32*, 97−104.
(32) Husson, E.; Humeau, C.; Paris, C.; Vanderesse, R.; Framboisier, X.; Marc, I.; Chevalot, I. *Process Biochem.* **2009**, *44*, 428−434.
(33) Song, L.; Gao, J.; Song, R. *J. Lumin.* **2010**, *130*, 1179−1182.
(34) Jandura, P.; Riedl, B.; Kokta, B. V. *Polym. Degrad. Stab.* **2000**, *70*, 387−394.
(35) Liao, Z.; Huang, Z.; Hu, H.; Zhang, Y.; Tan, Y. *Bioresour. Technol.* **2011**, *102*, 7953−7958.
(36) Jandura, P.; Kokta, B. V.; Riedl, B. *J. Appl. Polym. Sci.* **2000**, *78*, 1354−1365.

DOI: 10.1021/acs.biomac.6b01584
Biomacromolecules XXXX, XXX, XXX−XXX