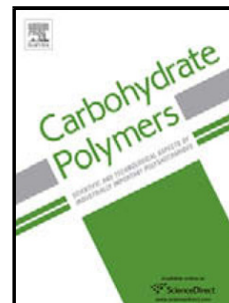


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Cellulose Modified by Citric Acid Reinforced Polypropylene Resin as Fillers

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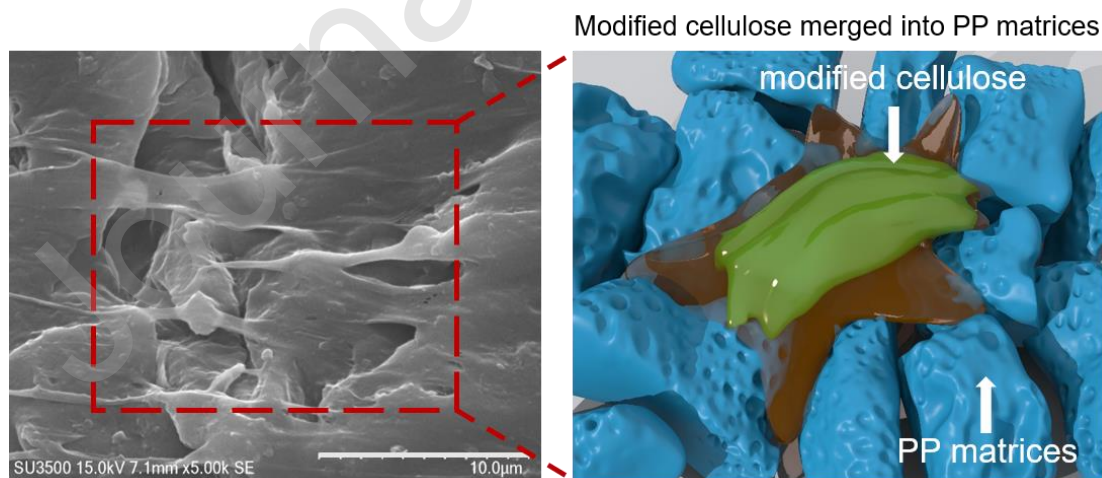
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Graphical abstract



Highlights

- Cellulose is rendered with high carboxyl content in the solid-state reaction.
- Modified cellulose merges into the hydrophobic PP matrices with good compatibility.
- Modified cellulose reinforced the composite by improving the flexural property.

Abstract

The greatest challenge hindering the use of cellulose as a reinforcing filler in polymeric composites is its poor compatibility due to the inherent hydrophilicity of cellulose and the hydrophobic nature of polymeric matrices. To solve this issue, we demonstrate an effective water-based method to render the cellulose surface with high carboxyl content through the esterification of hydroxyl groups with citric acid in a solid phase reaction without the use of noxious solvents. The modified cellulose was then further hydrophobized by grafting magnesium stearate to the surface. Consequently, the flexural properties of PP composites reinforced by the hydrophobized cellulose fillers were greatly improved compared to those of composites containing hydrophilic cellulose and pure PP resin. The surface modification conditions and filler proportions in composites were optimized. Because of the innocuity and cost-efficiency of citric acid, we believe that citric acid-modified cellulose has immense potential as a sustainable and cost-effective reinforcing filler.

Keywords: citric acid, cellulose modification, solid phase reaction, resin reinforcement, composite fillers

Abbreviations

CA, citric acid

TEMPO, 2,2,6,6-tetramethylpiperidine-1-oxyl

PP, Polypropylene

Raw C, raw cellulose

CAC, citric acid-modified cellulose

Na-CAC, CA-modified cellulose neutralized by NaOH

H-CAC, Na-CAC hydrophilized by magnesium stearate

F-CAC, fibrillated form of CAC

1. Introduction

Besides its natural abundance, cellulose has gained immense interest in both academic and industrial fields because of its low density, hydrophilicity, chirality, degradability, and broad chemical variability (Klemm, Heublein, Fink, & Bohn, 2005). Given the increasing demand for sustainable products and environmentally friendly production methods, cellulose and its derivatives have been widely used in fields such as textiles, biofuels (Mascal & Nikitin, 2008), and pharmaceutical industries (Shokri & Adibkia, 2013). Cellulose is particularly attractive as a biomass filler for conventional polymeric materials, allowing the construction of high-performance and sustainable composite materials. However, cellulose is inherently incompatible with hydrophobic thermoplastics, resulting in poor interfacial adhesion between the fillers and polymeric matrices. This greatly limits the utilization of cellulose fillers for reinforcement.

Until now, cellulose has undergone various chemical modifications and treatments to enhance the interactions between the cellulose surface and polymers, thereby improving its dispersibility and thus the subsequent composite properties. Given the abundance of hydroxyl groups on the surface of cellulose, chemical modifications such as acidification, esterification, etherification, urethanization, silane coupling, and polymer grafting through surface-initiated radical polymerization and ring-opening polymerization have been performed (Chakrabarty & Teramoto, 2018; Isik, Sardon, & Mecerreyes, 2014). Meanwhile, hydrogen bonding, electrostatic interactions, and physisorption have also been used to produce composites with the desired performance and functional properties (Chakrabarty & Teramoto, 2018).

Polypropylene (PP), one of the typical commodity thermoplastics, has been mostly used as a polymeric matrix in the manufacture of natural fiber-reinforced plastic composites. However, the modification methods described for cellulose as fillers have been rarely applied to the fabrication of cellulose/PP composites, while conventional approaches focus on use of maleic anhydride (MA). MA-functionalized PP is directly

used as a resin matrix to improve the interfacial adhesion between the polymer and biomass filler (Niwa et al., 2017; Qiu, Endo, & Hirotsu, 2004; Sunaga, Ogoe, Aoki, Ito, & Teramoto, 2018). Alternatively, the filler is modified by MA or acrylic acid-functionalized PP coupling agents via esterification of the hydroxyl groups of cellulose to improve the compatibility with polymeric matrices (Q. Li & Matuana, 2003; Peng, Gallegos, Gardner, Han, & Cai, 2016).

To enhance the functionality, cellulose has been modified by the strong acids including oxalic acid (Chen, Zhu, Baez, Kitin, & Elder, 2016), nitroxyl radicals (Coseri et al., 2015), cyclic anhydrides (Sehaqui, Kulasinski, Pfenninger, Zimmermann, & Tingaut, 2017), hydrochloric acid and a nitric acid mixture (Cheng, Qin, Chen, Liu, & Ren, 2017) to render the surface with carboxylic acid groups, which can serve as reactive sites. A procedure using ammonium persulfate can produce carboxylated cellulose nanocrystals directly from the raw starting materials (Leung et al., 2011). As a representative of the acidification method, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation effectively converts the primary hydroxyls on C6 position to carboxyl groups under aqueous condition for micro- and nano-fibrillations (Isogai, Saito, & Fukuzumi, 2011), which prevents hydrolysis by strong acids but still incurs problems related to the toxicity of the oxidants. In contrast, citric acid (CA) produced commercially by fermentation has been reported to modify the OH-functional polyester by reacting hydroxyl groups with primary and tertiary carboxylic acid groups of CA (Noordover, Duchateau, Benthem, Ming, & Koning, 2007). Thus, through the esterification reaction, at least one carboxylic acid group of CA can be released from the cellulose after one-step of preparation (Ji et al., 2019; Wu, Xu, Wang, & Wang, 2018) leading to comparable carboxylic acid group content to the TEMPO-mediated oxidation method. The new carboxylic acid groups then act as new functional sites where the hydrophobic moiety like cetyltrimethylammonium bromide (Nagalakshmaiah, El Kissi, & Dufresne, 2016) can easily be grafted to enhance the compatibility between cellulose and the PP polymer matrix. The branched carboxylic acid groups of CA multiply the functionality of cellulose, while the preparation method shows merits compared to the conventional approach that open the prospect of application in various resins.

In this study, we prepared CA-modified cellulose to achieve a high carboxylic acid group content on the cellulose surface. The modification reaction proceeded in the solid

state, which allowed the manufacture of modified cellulose in large quantities without the use of organic solvents. Magnesium stearate was then added to the acid-enriched cellulose to render the surface hydrophobic. The modified and fibrillated cellulose was kneaded with PP resin as a filler. The resulting composite exhibited desirable filler-polymer compatibility that led to an increase in the flexural modulus and maximum stress during a 3-point bending test. This study reports a feasible procedure to develop a cellulose-reinforced PP composite, providing a fabrication method capable of producing large quantities of material consistently and reproducibly, with minimal cost and impact on the environment.

2. Materials and Methods

2.1 Materials

Cellulose powder was purchased from Nacalai Tesque, Inc., Kyoto, Japan. CA (hydrate, Wako Pure Chemical Industries Ltd., Osaka, Japan) was used for the esterification reaction on cellulose. In the experiment, 1 mol/L sodium hydroxide solution (Wako Pure Chemical Industries) was used for the pH adjustment. Magnesium stearate purchased from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan was used for the hydrophobization of CA-modified cellulose. Isopropyl alcohol, methanol, and acetone (Nacalai Tesque) were used as solvents. PP, Prime Polypro™, was supplied from Prime Polymer Co., Ltd., Tokyo, Japan and kneaded with the modified cellulose to fabricate the cellulose/PP composites.

2.2 Modification of cellulose

30 g of cellulose was dispersed in 300 mL of distilled water and stirred for 10 min at room temperature. 90 g of CA was added to the dispersion, followed by 30 min of further stirring. The mixture was incubated in oven for 15 h and the reaction began with the evaporation of water under high temperature. To investigate the effect of temperature on the esterification between CA and hydroxyls of cellulose, the mixture was incubated at 110 °C, 120 °C, 130 °C, and 145 °C, separately. Additionally, different weight ratios of CA to cellulose (1:1, 2:1, 3:1, and 4:1, respectively) were mixed and

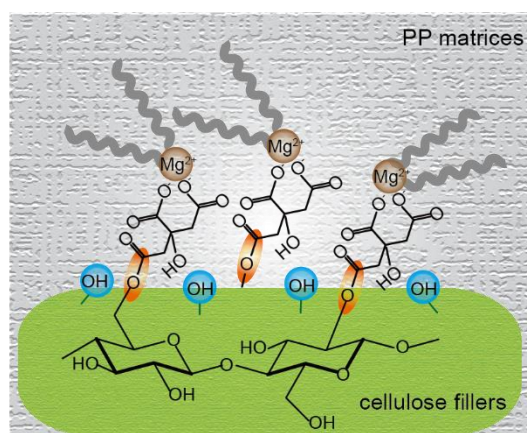
heated at 130 °C to optimize the feed ratio of CA. After the reaction, the residual CA was removed by washing thoroughly with water until the pH of filtrate was approximately pH 7. After CA was removed, the modified cellulose was washed with 300 mL methanol, 300 mL acetone, and then dried under vacuum. The introduced carboxylic acid groups were confirmed by Fourier transform-infrared spectroscopy (FT-IR; Spectrum One, PerkinElmer Co., Ltd., Japan) and the carboxylic acid group content of the cellulose was evaluated via conductometric titration (LAQUA F-74, HORIBA, Ltd., Kyoto, Japan).

20 g of CA-modified cellulose was dispersed in 400 mL of distilled water and the pH of dispersion was adjusted by 1 mol/L NaOH solution. Centrifugation with distilled water was carried out until the pH of supernatants became neutral. 400 mL of water was then added to the recovered material and fibrillation of the cellulose was conducted using Vitamix (TNC5200; EntreX Incorporated, Tokyo, Japan) for 15 sec, 50 times. Due to the viscosity of the fibrillated cellulose suspension, the flow resistance of suspension during centrifugation would be too high to separate the cellulose efficiently. Thus, fibrillation proceeded after deprotonation in order to avoid the difficulties in gathering cellulose by centrifugation. The raw cellulose was also fibrillated under the same conditions. The cellulose suspension was concentrated by evaporating the water and the fibrillated cellulose powder was obtained after freeze-drying.

5 g of the fibrillated CA-modified cellulose was added to isopropyl alcohol in which 0.2 g of magnesium stearate had been totally dissolved in advance. After continuously stirring for 30 min, the solvent was evaporated until a powdered product was obtained. The fibrillated cellulose contained unreacted magnesium stearate which acted as a lubricant to improve the flowability and reduce the friction reduction of raw materials during the kneading. Scheme 1 illustrated the chemical modification of cellulose and the combination with PP matrices as fillers.

The processed cellulose was characterized using X-ray photoelectron spectroscopy (XPS; JPS-9010MC, JEOL Ltd., Japan). The hydrophobized Na-CAC was purified by washing thoroughly with *n*-butanol and dried under vacuum to prepare the test specimen for XPS. The processed cellulose was observed through scanning electron microscopy (SEM; SU8000, Hitachi High-Technologies Co., Tokyo, Japan). Thermogravimetric and differential thermal analysis (TG/DTA) was performed using a

simultaneous thermogravimetric analyzer (STA7200RV; Hitachi) and the samples were scanned from room temperature to 600 °C at a heating rate of 10 °C min⁻¹.



Scheme 1. Schematic diagram of modification on cellulose and combination with PP matrices.

2.3 Fabrication and characterization of cellulose/PP composites

The composites were fabricated using a Labo Plastomill (4C150-01; Toyo Seiki Seisakusho, Ltd., Japan). For this, the PP primer was melted at 180 °C and 50 rpm in 2 min and the cellulose filler containing lubricant was added at 175 °C, 50 rpm for 2 min. This was followed by kneading at 160 °C and 80 rpm for 4 min to produce the cellulose/PP composite. The total amount of fillers and PP resin was 50 g for composite fabrication and the weight ratio of fillers was changed as 2, 5, 10, 30 % to optimize the content in composite.

A composite specimen for further mechanical testing was molded using a HAAKE MiniJet Pro (Thermo Fisher Scientific K.K., Japan). The kneaded product was melted at 195 °C over 15 min and injected at 860 bar in 8 s into a dumbbell mold at 65 °C. The dumbbell-shaped pieces were used in the 3-point bending test via a table-top material tester (EZ Graph; Shimadzu Corporation, Kyoto, Japan) and the test was performed following JIS K 7171(ISO 178) regulations.

3. Results and Discussion

3.1 Modification of cellulose

Surface analysis

The surface modification of cellulose was confirmed by IR and XPS measurements. The IR spectra of raw cellulose (raw C), CA-modified cellulose (CAC), CAC neutralized by NaOH (Na-CAC), and Na-CAC hydrophilized by magnesium stearate (H-CAC) are presented in Figure 1. Compared with the characteristic spectrum of cellulose, the esterification by CA was confirmed by the emergence of new carboxylic acid and ester carbonyl peaks at approximately 1730 cm^{-1} and an increase in C-H stretching ($2800\text{-}2950\text{ cm}^{-1}$) assigned to the CA chain. After deprotonation with NaOH, the overlapping ester-carbonyl band formed in the esterification process was exposed. New adsorption was also found to occur at 1590 cm^{-1} arising from the sodium carboxylate of the grafted CA. Magnesium stearate was added to render the Na-CAC hydrophobic through ion exchange of Na ions with divalent cations (Kim & Yun, 2005), leading to an increase in intensities of the carboxylate and C-H band signals that were attributed to the aliphatic acid chain.

XPS measurements were also carried out to evaluate the surface modification process. The C(1s) spectra of raw cellulose, CAC, and refined H-CAC are shown in Figure 2. A weak peak assigned to O-C-O at $\sim 288.0\text{ eV}$ (Figure 2(A)) was observed on the raw cellulose surface derived from the virgin material. The intensity of the peak at $\sim 288.0\text{ eV}$ (Figure 2(B)) was increased and broadened compared with that of the raw C surface, suggesting C=O in grafted carboxyl groups and the newly formed ester after the CA modification of the surface. After magnesium stearate grafting, the peak corresponding to the C-C bond at $\sim 248.8\text{ eV}$ (Figure 2(C)) was much more intense than the C-C peak for the CAC surface, confirming the grafting of long fatty chains on the cellulose surface.

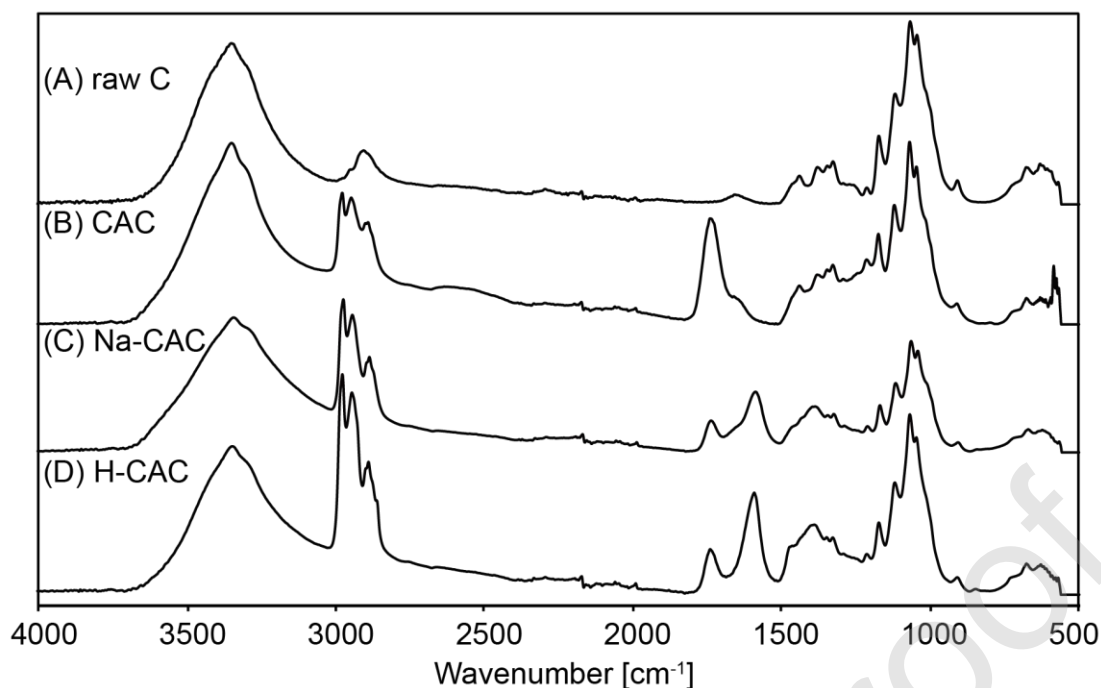


Figure 1. IR spectra of (A) raw cellulose (raw C), (B) citric acid (CA)-modified cellulose (CAC), (C) CA-modified cellulose neutralized by NaOH (Na-CAC), and (D) Na-CAC hydrophilized by magnesium stearate (H-CAC).

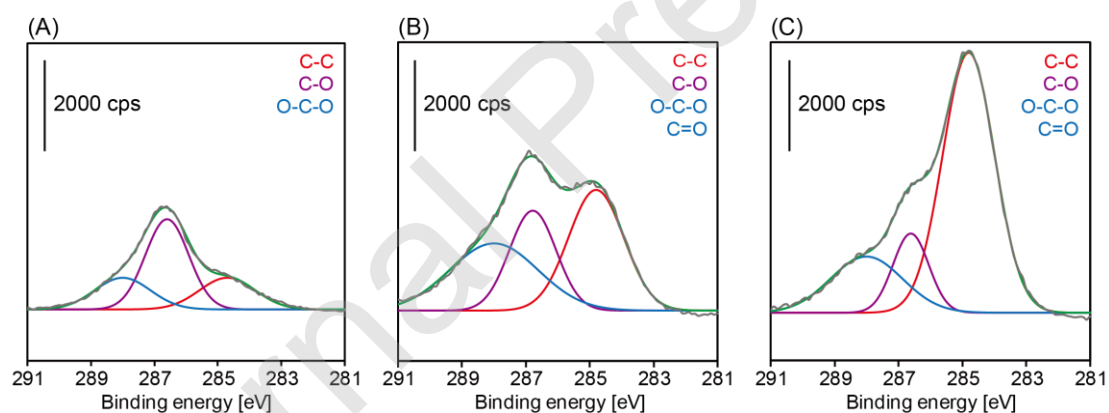


Figure 2. XPS C(1s) profiles of (A) raw C, (B) CAC, and (C) H-CAC.

Feed ratio and temperature

The carboxylic acid group content of CAC was determined by conductometric titration under different incubation temperature and feed ratio (CA/cellulose) conditions, as summarized in Table 1. When the feed ratio (CA/cellulose) was fixed at 3:1, the reaction began with the evaporation of water and the carboxylic acid content of the cellulose increased from 1.7 mmol/g at 110 °C to a maximum of 2.4 mmol/g as the temperature was elevated to 130 °C. The saturation of the carboxyl content indicates

the optimal thermal conditions (130 °C) for evaporating the water to promote the esterification reaction in this case. When the temperature was set at 130 °C, the carboxylic acid group content increased with the addition of increasing quantities of CA, reaching a maximum of 2.4 mmol/g (feed ratio 3:1). This carboxyl content was higher than that of the conventional TEMPO-mediated oxidation method (Okita, Saito, & Isogai, 2010; Saito, Kimura, Nishiyama, & Isogai, 2007). The modification of cellulose by citric acid is carried out thorough the esterification between the hydroxyl groups of cellulose and carboxyl groups of citric acid. To disperse uniformly, cellulose and citric acid were added in the water and fully stirred. However, the modification of cellulose with citric acid, the ester bonding formation, was unlikely to proceed with the present of water. Since the reaction is considered to start with the evaporation of water in environment, we set the reaction temperature at 110 °C and over to ensure the reaction in solid phase. The carboxyl content showed a distinct decrease when the feed ratio was increased to 4:1 (CA to cellulose), suggesting the possible decomposition of cellulose under acidic conditions (Long, Yu, Chua, & Wu, 2017) due to the excessive addition of CA. Moreover, the acidified cellulose powder was prone to yellowing due to CA byproducts from the dehydration process (Noordover et al., 2007). SEM showed that the surface morphology of the cellulose was unchanged following the esterification reaction (Figure S1). Thus, the optimal conditions for cellulose acidification by CA were found to be a feed ratio of 3:1 (CA to cellulose) at a temperature of 130 °C.

Admittedly, the TEMPO-mediated oxidation is categorized as an effective method for the preparation of position-selective oxidized cellulose nanomaterials under moderate aqueous conditions. However, the cellulose nanofiber tends to intertwine with each other resulting in large intrinsic viscosity values. Limited by the viscosity, the nanofiber dispersion of preparation is highly diluted (approaching approximately 1 wt%) to ensure the continuous output. The removal of extra water in yield nanofiber dispersion is also clearly cost and energy-consumptive. In contrast, powdered CA-modified cellulose with comparable carboxyl content can be produced in substantial quantities in the solid state and can be further modified and fibrillated to satisfy specific requirements. These merits demonstrate that this method is an industrially applicable approach for acid-introduced cellulose manufacture, serving a variety of applications.

pH of carboxylic acid deprotonation

To effectively render the surface with hydrophobic moieties, magnesium stearate was grafted to the deprotonated CAC. NaOH aqueous solution was added into the CAC dispersion (in water) to adjust the pH value to 3, 5, 7, 9, and 11, respectively. The IR spectra of CAC deprotonated under different pH condition is shown in Figure S2. The signal assigned to carboxylic acid carbonyl stretch at approximately 1730 cm^{-1} was gradually converted to a new signal for sodium carboxylate that appeared at 1590 cm^{-1} in samples up to pH 5. The conversion was completed at pH 9 and the ester carbonyl band formed in esterification was detected at 1735 cm^{-1} . Since the pK_a 's of monomeric CA are 3.1, 4.7, and 6.4 (Ferdousi, Islam, Okajima, & Ohsaka, 2016), respectively, the protons in the carboxylic acid groups are theoretically no longer present when the pH is higher than 7.

The pH of deprotonation affected the further fibrillation of Na-CAC. The SEM images of fibrillated Na-CAC and raw cellulose under same conditions are presented in Figure 3. The cellulose fiber before fibrillation was typical length $1\text{ mm} \times$ width $10\sim 13\text{ }\mu\text{m}$ according to the SEM observation. Compared with the fibrillation after deprotonation at pH 3 and 5, the clavate cellulose raw fiber was spread out and crushed up becoming fragmented at pH 7. Meanwhile the rod-shape of the cellulose was rarely observed at pH 9. The deprotonation of carboxyl groups by NaOH produced stronger electrostatic repulsion (Sun, Wu, Ren, & Lei, 2015) and promoted the disruption of hydrogen bonding (X. Li, Tabil, & Panigrahi, 2007) which led to the disintegration of the cellulose during mechanical fibrillation in water. However, without surface modification, the fibrillation of raw cellulose under the same conditions showed that insufficient rod-shape cellulose remained over the full pH range. This fact indicates that the fibrillation of raw cellulose could be a challenge and require more harsh treatments. For the fibrillated CAC, the exposed surface played a crucial role in the interlocking with the polymer matrix in the composite, while the structural damage caused by excess alkali (Bali, Meng, Deneff, Sun, & Ragauskas, 2015) may weaken the mechanical properties. Accordingly, the pH of the carboxylic acid deprotonation was adjusted to pH 9 to completely deprotonate the carboxyl and avoid the excess damage to the cellulose.

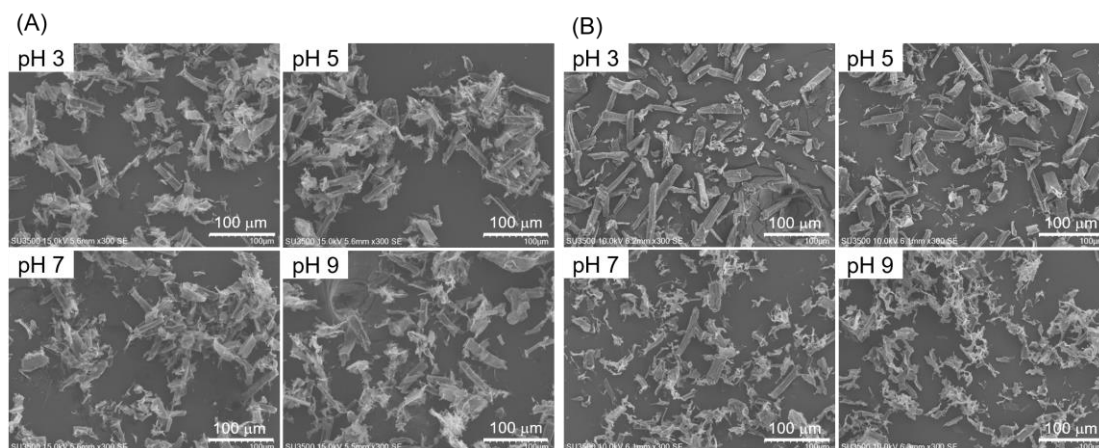


Figure 3. SEM images of fibrillated (A) raw cellulose, and (B) Na-CAC after deprotonation by NaOH under different pH condition.

3.2 Mechanical properties of cellulose/PP composites

Addition of hydrophobic moieties

Magnesium stearate, known as an effective lubricant, was used as the hydrophobic moiety to graft hydrophobic chains onto the Na-CAC. This means that magnesium stearate functions to render the cellulose surface with hydrophobicity, as well as aiding the kneading process for composites given its anti-adherent properties. The amount of the hydrophobic moiety added was of great importance to composite performance. The flexural modulus and maximum stress tests for the cellulose/PP composites (cellulose 5 wt%) were performed by 3-point bending test with varying addition amounts of magnesium stearate, as listed in Table 2. The stress-strain curves of bending test are shown in Figure S3. Consequently, the mechanical strength was enhanced as the addition amount of magnesium stearate was increased from 2 wt% to 4 wt% of the feeding cellulose mass. These results suggested that magnesium stearate hydrophobized the Na-CAC thoroughly and balanced with an appropriate amount of residue remaining to act as the lubricant. The flexural modulus and maximum stress achieved a maximum at 2.0 GPa and 49.4 MPa, respectively, when the addition amount was 4 wt% of cellulose. The maximum stress decreased when more magnesium stearate was added, which suggests an adverse impact of excessive lubricant on the samples' flexural properties through interference with the bonding between components required for composite formation (Huang et al., 2008). Consequently, the optimal addition amount of magnesium stearate was determined as 4 wt% of cellulose. SEM images of

hydrophobized CAC (H-CAC) are shown in Figure S1, and no change in the surface morphology of cellulose grafted by the hydrophobic long chains was observed. Moreover, the contact angle of the highly hydrophilic CAC was altered to approximately 63° on the H-CAC (images shown in Figure S4), which proved the change in the surface physicochemical properties.

Fillers' content and performance in composites

The proportion of H-CAC within the composites was varied to determine the optimal content for composite fabrication. The curves of neat PP and its composite reinforced with varying amounts of H-CAC are shown in Figure 4. The flexural modulus and maximum stress of the composites are summarized in Table 3. Consequently, compared with the neat PP resin, the flexural property of the composites was enhanced by the incorporation of H-CAC. A continuous increase of flexural properties was measured through the addition of the H-CAC fillers up to 10 wt% of the total sample mass. The flexural modulus reached 2.3 GPa while the maximum stress reached 54.0 MPa. These represented an improved performance compared to the neat PP resin of 2 and 1.5 times, respectively. In contrast, the composite containing 30 wt% filler behaved stiffly, which is attributed to the accentuated brittle fractions caused by aggregates or unmodified cellulose in the composite. The filler content was optimized at 10 wt% of total sample mass. The thermal stability of processed cellulose was evaluated via TG measurements to ensure that no thermal decomposition occurred during the kneading process (curves shown in Figure S5).

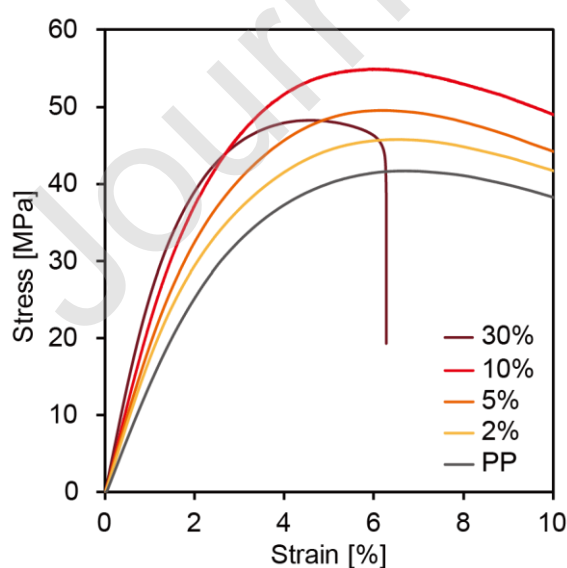


Figure 4. Stress-strain curves of neat PP and cellulose/PP composites reinforced with varying amounts of H-CAC.

The reinforcing effect of H-CAC on the PP matrix was further investigated by comparing with the CAC, and F-CAC as fillers (Figure S6 and Table 4). By comparing the performance of cellulose with its fibrillated forms (CAC and F-CAC), the flexural modulus and stress were strengthened from 1.8 GPa to 2.0 GPa and 45.5 MPa to 48.1 MPa with reduced variation. The best flexural properties were achieved by replacing the F-CAC with H-CAC, which saw the flexural modulus and stress increase to 2.3 GPa and 54.0 MPa, respectively. In a further experiment, magnesium stearate (4 wt% of CAC) was added directly during kneading to act as lubricant for the composite (PP+F-CAC+H) and verify the necessity of hydrophobization on cellulose surface. This experiment showed no increase in either the flexural modulus or the maximum stress compared to a composite with only CAC added. These samples were markedly weakened compared with the results of composite reinforced by hydrophobized cellulose (H-CAC) fillers.

After fibrillation, the flexural modulus and stress were improved with less deviation suggesting that the appropriate increase in the surface area of the fillers extended by fibrillation contributes to the uniform dispersion, and potential network formation of the fillers within the polymer matrices. Noticeably, the growth in value of the flexural modulus and stress was amplified when using H-CAC compared to F-CAC. It can be explained that instead of adding the hydrophobized moiety as an additive, the compatibility with hydrophobic polymer matrix may have developed by introducing the long fatty chains on the fillers surface, increasing filler-polymer interfacial adhesion which benefits the stress transfer at the interface during flexion. This fact demonstrates that the material compatibility is improved by surface hydrophobization and is a decisive factor on the improvement of composite mechanical properties. The synergy of both fibrillation and hydrophobization meant that H-CAC was capable of embedding multidirectionally into the PP matrices. H-CAC was therefore serving as the most effective reinforcing filler in terms of flexural properties in the cellulose/PP composite.

The surface morphology of the fracture surface of cellulose reinforced PP composites was investigated by SEM (images shown in Figure 5). By comparing the surfaces of the CAC/PP and F-CAC/PP composites, the rod-shape cellulose fillers could not be observed and were completely embedded in the surrounding PP matrices after fibrillation. The additional hydrophobized moiety did not have any impact on the construction of F-CAC/PP composite. Impressively, the lacerated and continuous surface morphology observed on the fracture surface of the H-CAC/PP composite indicates the thorough mixing of the cellulose fillers with the surrounding polymer matrices. As shown in Scheme 1, after modification the isolated and aggregated cellulose fillers were adapted to the PP matrices with good compatibility, interfacial adhesion between components, and then consequently enhanced the mechanical properties of the composites.

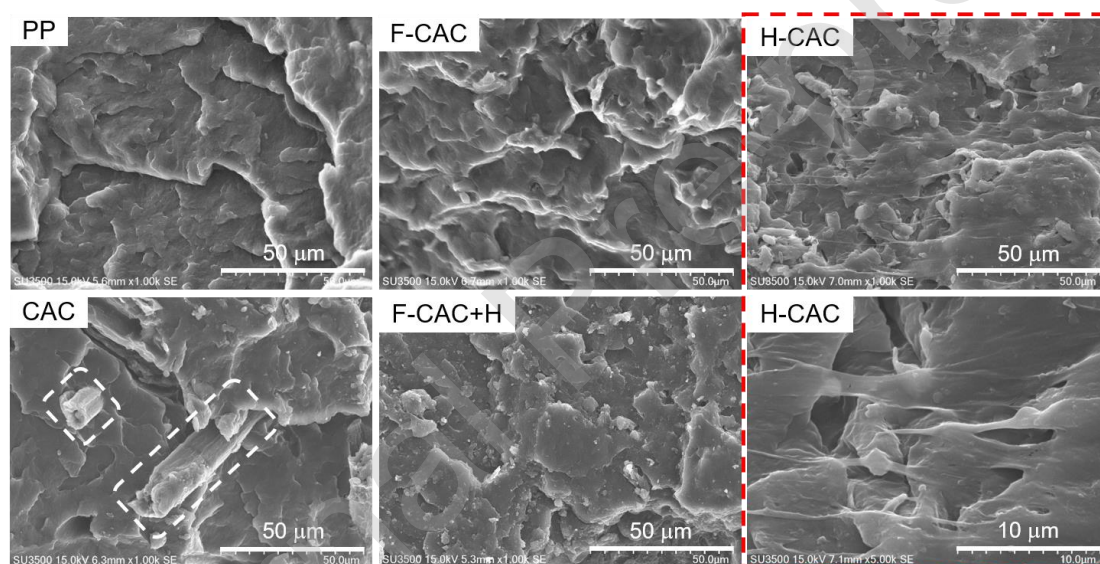


Figure 5. SEM images of the fracture surfaces of neat PP, CAC/PP, F-CAC/PP, F-CAC/PP with additional magnesium stearate, and the H-CAC/PP composite. The white dashed line highlighted the existence of rod-shape cellulose fillers.

Conclusions

In this study, cellulose was modified via esterification with CA under optimal reaction conditions of mass ratio 3:1 CA to cellulose and a temperature of 130 °C. The CA-modified cellulose obtained exhibits a high carboxylic acid content comparable to

cellulose nanofibers produced by the TEMPO method without the requirement for harmful solvents or oxidants to be applied. After deprotonation of carboxylic acid groups with NaOH and further fibrillation, hydrophobization was achieved by grafting magnesium stearate onto the modified cellulose surface. The amounts of magnesium stearate and modified cellulose filler were optimized through testing the fabricated composites in a 3-point bending test. Finally, it can be concluded that the hydrophobized cellulose reinforced composites showed superior flexural properties, which suggested good compatibility between the fillers and polymer matrices. Distinguished from conventional methods, such as sole mechanical or chemical treatments applied to cellulose for composite preparation, this study provides an operational and systematic reference combining efficient chemical modification with mechanical fibrillation by water-based methods. The procedure and results herein provide experimental evidence for the promise of cellulose as a reinforcing filler for industrial production with minimal cost and environmental impact.

Acknowledgments

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Reference

- Bali, G., Meng, X., Deneff, J. I., Sun, Q., & Ragauskas, A. J. (2015). The effect of alkaline pretreatment methods on cellulose structure and accessibility. *ChemSusChem*, 8(2), 275-279.
- Chakrabarty, A., & Teramoto, Y. (2018). Recent Advances in Nanocellulose Composites with Polymers: A Guide for Choosing Partners and How to Incorporate Them. *Polymers (Basel)*, 10(5), 517.
- Chen, L., Zhu, J. Y., Baez, C., Kitin, P., & Elder, T. (2016). Highly thermal-stable and functional cellulose nanocrystals and nanofibrils produced using fully recyclable organic acids. *Green Chemistry*, 18(13), 3835-3843.

- Cheng, M., Qin, Z., Chen, Y., Liu, J., & Ren, Z. (2017). Facile one-step extraction and oxidative carboxylation of cellulose nanocrystals through hydrothermal reaction by using mixed inorganic acids. *Cellulose*, 24(8), 3243-3254.
- Coseri, S., Biliuta, G., Zemljic, L. F., Srndovic, J. S., Larsson, P. T., Strnad, S., . . . Lindström, T. (2015). One-shot carboxylation of microcrystalline cellulose in the presence of nitroxyl radicals and sodium periodate. *RSC Advances*, 5(104), 85889-85897.
- Ferdousi, B. N., Islam, M. M., Okajima, T., & Ohsaka, T. (2016). Exploring pKa of Peroxycitric Acid Coexisting with Citric Acid in Aqueous Solution with Voltmmetric, Potentiometric and Chromatographic Approaches. *International Journal of Electrochemical Science*, 11, 6215-6228.
- Huang, H., Tian, M., Yang, J., Li, H., Liang, W., Zhang, L., & Li, X. (2008). Stearic acid surface modifying Mg(OH)₂: Mechanism and its effect on properties of ethylene vinyl acetate/Mg(OH)₂ composites. *Journal of Applied Polymer Science*, 107(5), 3325-3331.
- Isik, M., Sardon, H., & Mecerreyes, D. (2014). Ionic liquids and cellulose: dissolution, chemical modification and preparation of new cellulosic materials. *Int J Mol Sci*, 15(7), 11922-11940.
- Isogai, A., Saito, T., & Fukuzumi, H. (2011). TEMPO-oxidized cellulose nanofibers. *Nanoscale*, 3(1), 71-85.
- Ji, H., Xiang, Z., Qi, H., Han, T., Pranovich, A., & Song, T. (2019). Strategy towards one-step preparation of carboxylic cellulose nanocrystals and nanofibrils with high yield, carboxylation and highly stable dispersibility using innocuous citric acid. *Green Chemistry*, 21(8), 1956-1964.
- Kim, K., & Yun, S.-T. (2005). Buffering of sodium concentration by cation exchange in the groundwater system of a sandy aquifer. *Geochemical Journal*, 39(3), 273-284.
- Klemm, D., Heublein, B., Fink, H. P., & Bohn, A. (2005). Cellulose: fascinating biopolymer and sustainable raw material. *Angew Chem Int Ed Engl*, 44(22), 3358-3393.
- Leung, A. C., Hrapovic, S., Lam, E., Liu, Y., Male, K. B., Mahmoud, K. A., & Luong, J. H. (2011). Characteristics and properties of carboxylated cellulose nanocrystals prepared from a novel one-step procedure. *Small*, 7(3), 302-305.
- Li, Q., & Matuana, L. M. (2003). Surface of Cellulosic Materials Modified with Functionalized Polyethylene Coupling Agents. *Journal of Applied Polymer Science*, 88(2), 278-286.
- Li, X., Tabil, L. G., & Panigrahi, S. (2007). Chemical Treatments of Natural Fiber for Use in Natural Fiber-Reinforced Composites: A Review. *Journal of Polymers and the Environment*, 15(1), 25-33.
- Long, Y., Yu, Y., Chua, Y. W., & Wu, H. (2017). Acid-catalysed cellulose pyrolysis at low temperatures. *Fuel*, 193(1), 460-466.
- Mascal, M., & Nikitin, E. B. (2008). Direct, high-yield conversion of cellulose into biofuel. *Angew Chem Int Ed Engl*, 47(41), 7924-7926.
- Nagalakshmaiah, M., El Kissi, N., & Dufresne, A. (2016). Ionic Compatibilization of Cellulose Nanocrystals with Quaternary Ammonium Salt and Their Melt Extrusion with Polypropylene. *ACS Appl Mater Interfaces*, 8(13), 8755-8764.
- Niwa, S., Saito, Y., Ito, M., Ogoe, S., Ito, H., Sunaga, Y., . . . Teramoto, Y. (2017). Direct spectroscopic detection of binding formation by kneading of biomass filler and acid-modified resin. *Polymer*, 125, 161-171.

- Noordover, B. A. J., Duchateau, R., Benthem, R. A. T. M. v., Ming, W., & Koning, C. E. (2007). Enhancing the Functionality of Biobased Polyester Coating Resins through Modification with Citric Acid. *Biomacromolecules*, 8(12), 3860-3870.
- Okita, Y., Saito, T., & Isogai, A. (2010). Entire surface oxidation of various cellulose microfibrils by TEMPO-mediated oxidation. *Biomacromolecules*, 11(6), 1696-1700.
- Peng, Y., Gallegos, S. A., Gardner, D. J., Han, Y., & Cai, Z. (2016). Maleic anhydride polypropylene modified cellulose nanofibril polypropylene nanocomposites with enhanced impact strength. *Polymer Composites*, 37(3), 782-793.
- Qiu, W., Endo, T., & Hirotsu, T. (2004). Interfacial interactions of a novel mechanochemical composite of cellulose with maleated polypropylene. *Journal of Applied Polymer Science*, 94(3), 1326-1335.
- Saito, T., Kimura, S., Nishiyama, Y., & Isogai, A. (2007). Cellulose Nanofibers Prepared by TEMPO-Mediated Oxidation of Native Cellulose. *Biomacromolecules*, 8(8), 2485-2491.
- Sehaqui, H., Kulasinski, K., Pfenninger, N., Zimmermann, T., & Tingaut, P. (2017). Highly Carboxylated Cellulose Nanofibers via Succinic Anhydride Esterification of Wheat Fibers and Facile Mechanical Disintegration. *Biomacromolecules*, 18(1), 242-248.
- Shokri, J., & Adibkia, K. (2013). *Application of Cellulose and Cellulose Derivatives in Pharmaceutical Industries*. In *Cellulose - Medical, Pharmaceutical and Electronic Applications* (pp. 47-66)
- Sun, X., Wu, Q., Ren, S., & Lei, T. (2015). Comparison of highly transparent all-cellulose nanopaper prepared using sulfuric acid and TEMPO-mediated oxidation methods. *Cellulose*, 22(2), 1123-1133.
- Sunaga, Y., Ogoe, S., Aoki, K., Ito, H., & Teramoto, Y. (2018). Profitable Mass-Production of Acid-Modified Recovered Resins for Value-Added Mechanical Recycling as a Compatibilizer for Composites. *ACS Sustainable Chemistry & Engineering*, 6(9), 12110-12118.
- Wu, Y. L., Xu, S., Wang, T., & Wang, C. F. (2018). Enhanced Metal Ion Rejection by a Low-Pressure Microfiltration System Using Cellulose Filter Papers Modified with Citric Acid. *ACS Appl Mater Interfaces*, 10(38), 32736-32746.

Table 1. Carboxylic acid group contents of CAC under different temperature and feed ratio conditions.

(A) CA: cellulose = 3: 1

Temperature (°C)	carboxylic groups content (mmol/g)
110	1.7
120	1.9
130	2.4
145	2.3

(B) temperature: 130 °C

CA/cellulose (mass ratio)	carboxylic groups content (mmol/g)
1	1.6
2	2.1
3	2.4
4	1.7

Table 2. Flexural modulus and maximum stress of cellulose/PP composites with the addition of different amounts of magnesium stearate in 3-point bending test.

Magnesium stearate addition (wt%)	Flexural modulus (GPa)	Maximum stress (MPa)
2	1.9 ± 0.1	48.0 ± 3.0
4	2.0 ± 0.1	49.4 ± 0.8
6	1.8 ± 0.1	47.6 ± 1.0
8	1.8 ± 0.1	45.8 ± 1.1
10	1.8 ± 0.1	45.4 ± 1.3

Table 3. Flexural modulus and maximum stress of neat PP and cellulose/PP composites containing different H-CAC contents.

H-CAC content (wt%)	Flexural modulus (GPa)	Maximum stress (MPa)
0	1.0 ± 0.1	34.9 ± 3.0
2	1.7 ± 0.1	46.1 ± 0.6
5	2.0 ± 0.1	49.4 ± 0.8
10	2.3 ± 0.1	54.0 ± 0.6
30	2.8 ± 0.1	45.4 ± 2.0

Table 4. Flexural modulus and maximum stress of neat PP and cellulose/PP composites containing different components.

Sample	Flexural modulus (GPa)	Maximum stress (MPa)
PP	1.0 ± 0.1	34.9 ± 3.0
PP+CAC	1.8 ± 0.2	45.5 ± 4.7
PP+F-CAC	2.0 ± 0.1	48.1 ± 1.2
PP+F-CAC+H	1.9 ± 0.1	49.1 ± 1.1
PP+H-CAC	2.3 ± 0.1	54.0 ± 0.6

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