

Esterification of Nanofibrillated Cellulose using Lauroyl Chloride and its Composite Films with Polybutylene Succinate

Jeong-Ki Kim,^a Rajkumar Bandi,^b Ramakrishna Dadigala,^b Le Van Hai,^b Song-Yi Han,^b Gu-Joong Kwon,^{b,c} Seung-Woo Cho,^a Seo-Young Ma,^a and Seung-Hwan Lee^{a,b,c,*}

Esterified nanofibrillated cellulose (eNFC) with varying degrees of substitution was prepared using fatty acid chloride. Furthermore, the effect of esterification on properties of pure NFC and its composites with polybutylene succinate (PBS) was investigated. Lauroyl chloride (LC) with 12 carbon atoms was used for esterification. An increase in the amount of LC increased the degree of substitution (DS), which significantly decreased the water contact angle and improved the hydrophobicity of NFC. The addition of fatty acid to NFCs lowered their crystallinity. However, the fatty acid increased the hydrophobicity of NFCs, thereby improving their dispersibility in nonpolar solvents. Compared with pure NFCs, eNFC exhibited enhanced compatibility with PBS, and the addition of eNFC with an appropriate DS increased the tensile strength and elastic modulus of PBS. These findings suggest the potential of NFC esterification for improving the performance of NFC-based composite materials.

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Contact information: a: Department of Forest Biomaterials Engineering, College of Forest and Environmental Sciences, Kangwon National University, Chuncheon, 24341, Republic of Korea; b: Institute of Forest Science, Kangwon National University, Chuncheon, 24341, Republic of Korea; c: Kangwon Institute of Inclusion Technology, Kangwon National University, Chuncheon, 24341, Republic of Korea; *Corresponding author: lshyhk@kangwon.ac.kr

INTRODUCTION

Nanofibrillated cellulose (NFC) has significant potential as an alternative to petroleum-based materials. NFC consists of nanoscale fiber made from the defibrillation of wood pulp through mechanical treatments such as wet disk milling, high-pressure homogenization, and ball milling (Park *et al.* 2017). NFC generally has a fibrous morphology with diameters ranging from 5 to 30 nm, a length distribution of several micrometers, and it contains both amorphous and crystalline regions (Carter *et al.* 2021). In particular, NFC has several advantages relative to its use in various polymer composites, such as biodegradability, low density, non-abrasiveness, and combustibility (Sharma *et al.* 2019). Owing to these advantages, many studies have been conducted to combine polymers such as poly(lactic acid) (Jonoobi *et al.* 2010; Qu *et al.* 2012; Clarkson *et al.* 2018), poly(vinyl alcohol) (Danni *et al.* 2016; Rowe *et al.* 2016), and starch (Fazeli *et al.* 2018; Almeida *et al.* 2020; Granda *et al.* 2020) with NFCs. However, the high hydrophilicity of NFC, owing to its hydroxyl groups, is a major obstacle to its molecular contact with hydrophobic polymers. The interfacial adhesion between the NFC and polymer plays an important role in the mechanical properties of the composite (Wang *et al.* 2007). Therefore, it is important to uniformly disperse NFC in a polymer matrix, which can be achieved through chemical modification of NFC.

Polybutylene succinate (PBS) is a biodegradable polyester synthesized via polycondensation of succinic acid and butanediol (Jiang and Zhang 2017). PBS decomposes naturally into water and carbon dioxide and has excellent biodegradability, thermal properties, melt processability, and chemical resistance (Rafiqah *et al.* 2021). Owing to these properties, PBS has various applications, such as in PBS mulching films, compostable bags, nonwoven sheets and garments, catering goods, and foams (Rafiqah *et al.* 2021). However, compared with synthetic plastics, PBS has inferior mechanical properties. Hence, it is difficult to use it as a replacement for synthetic plastics. The mechanical properties of PBS can be enhanced using fillers or reinforcements; however, the use of non-biodegradable materials defeats the objective of using biodegradable PBS. An effective strategy improves mechanical properties while maintaining biodegradability. The use of NFC can address this situation. The use of NFC reinforcement in polymers is becoming an alternative route to developing sustainable bio-nanocomposites. The use of biodegradable composites in packaging, furniture, and disposable product industries is expected to significantly reduce the amount of synthetic plastic waste.

In this study, for effective utilization of NFC and to improve its affinity for PBS, NFC was esterified with three different amounts of lauroyl chloride. Furthermore, the characteristics of esterified NFCs were analyzed. In addition, esterified NFCs were combined with PBS and composite films were fabricated by the solvent casting method. The characteristics of the PBS/esterified NFC composite films were analyzed.

EXPERIMENTAL

Materials

The NFC aqueous dispersion was obtained from Cellulose Lab Co., Ltd. (QC, Canada). Lauroyl chloride (LC) (TCI Co., Japan; >98.0%) was used for to esterify the NFC. Pyridine (>99.5%), *N,N*-dimethylformamide (DMF, >99.5%), and chloroform (>99.5%) were obtained from Daejung Chemical & Metals Co., Ltd. (Republic of Korea). Polybutylene succinate (PBS, SOLPOL 5000) was purchased from SOLTECH (Republic of Korea).

Esterification of NFC

First, NFC aqueous dispersion was solvent exchanged with DMF, and 100 g of 1 wt% DMF dispersion (NFC dry weight: 1 g and total hydroxyl groups :18.51 mmol/g) was prepared. Next, under nitrogen gas, lauroyl chloride (0.5, 1.0, 2.0 eq/cellulose OH) and pyridine (2.0 eq/cellulose OH) were added. The reaction was performed at 80 °C for 6 h and was terminated by adding excess ethanol to the hot reaction mixture. The NFCs were washed with ethanol via vacuum filtration. Esterified NFCs (eNFC) were maintained in two ways. First, for the Fourier transform infrared (FTIR), X-ray diffraction (XRD), and contact angle analyses, the esterified NFC was freeze dried at -55 °C. Second, the esterified NFC was dispersed and kept in DMF or chloroform for the preparation of the PBS/eNFC composite.

Preparation of PBS/eNFC Composite Film

First, 0.25 g of PBS and eNFC were mixed in a weight ratio of 90:10, 70:30, and 50:50 and dissolved in 5 mL of chloroform at 50 °C for 3 h. Pure NFC and eNFC obtained by 0.5 equivalents of LC treatment were unable to be dispersed in chloroform. Hence, they were first dispersed in DMF and mixed with PBS chloroform solution. The dispersions were poured into polytetrafluoroethylene (PTFE) dishes and dried at 100 °C for 30 min, and the obtained films were stored in a vacuum oven at 40 °C.

Degree of Substitution of eNFC

The degree of substitution (DS) of eNFC was determined by elemental analysis (EA3000 Eurovector, Italy). It was calculated according to a previously reported method (Vaca-Garcia *et al.* 2001) using the following equation,

$$\text{Degree of substitution (DS)} = \frac{5.13766 - 11.5592 \times C}{0.996863 \times C - 0.856277 \times n + n \times C}$$

where C is the carbon content obtained from elemental analysis, and n is the number of carbon atoms present in fatty acid chloride.

FTIR Spectroscopy

The FTIR spectra of pure NFC and eNFC were recorded using an FTIR instrument (Nicolet Summit Thermo Fisher Scientific, USA). The attenuated total reflection (ATR) mode was used for recording the spectra. A total of 32 scans were performed for each sample in the range of 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1} .

XRD Analysis

The XRD patterns of pure NFC and eNFC were recorded using an X-ray diffractometer (X'Pert PRO MPD PANalytical, Netherlands) with Cu $K\alpha$ radiation. The samples were scanned in the 2θ range of 10 to 35° at a scan speed of 1°/min. The crystallinity index (CrI) was calculated using the following equation:

$$\text{Crystallinity index (CrI, \%)} = \frac{I_{002} - I_{am}}{I_{002}} \times 100$$

where I_{002} and I_{am} are the intensities at $2\theta = 22.7^\circ$ and 18° , which represent crystalline and amorphous states, respectively.

Contact Angle Analysis

The static sessile drop method was used to determine the water contact angles on eNFC using a contact angle analyzer (Theta Lite, Biolin Scientific, UK). The measurements were performed at room temperature (22 to 25 °C). The contact angle was measured for two types of NFCs, namely, freeze-dried powder- and hot-pressed film-type samples (hot pressing conditions: Time: 1 min; Temperature: 105 °C; Pressure: 15 MPa). A 5 μL drop was placed on the sample, and contact angle was measured after 10 s by processing the drop image using an image analysis system. At least five measurements were performed for each sample and the average value is presented.

Morphological Characteristics

The morphologies of eNFC were studied by scanning electron microscopy (S-4800, Hitachi, Ltd., Japan). Pure NFC and eNFC were added at 0.001 wt.% to water and ethanol, respectively, and dispersed by sonication for 3 min using an ultrasonicator (VCX130PBS; Sonics & Materials, Inc., USA). The suspensions were vacuum filtered using a PTFE membrane filter. The filters were solvent exchanged with tert-butanol and freeze dried using a freeze dryer (FDB-5502, Operon Co. Ltd., Republic of Korea) at -55°C . The samples were then placed on an aluminum stub and coated with iridium using a sputter coater (EMACE600, Leica Microsystems, Ltd., Wetzlar, Germany). Morphologies were observed using a scanning electron microscope (Hitachi S-4800, Japan) at an accelerating voltage of 1 kV.

Dispersibility Appearance of eNFC

The visual dispersibility of eNFC was confirmed by dispersing them in various organic solvents. For this, 10 mg of eNFC was added to 10 mL of an organic solvent and sonicated using an ultrasonicator for 5 min. Then the suspensions were kept undisturbed for 1 h and digital photographs were collected using a smartphone.

Tensile Properties of Neat PBS and PBS/eNFC Composite Film

The tensile properties of neat PBS and PBS/eNFC films were measured using a universal testing machine (TO-102D, Test One, Republic of Korea) at a crosshead speed of 10 mm/min with a specimen span length of 30 mm. The samples were cut according to the ASTM D638 standard. At least five specimens were tested for each sample, and the results were averaged. Before the measurement, samples were maintained in a thermohygrostat at 25 °C and a relative humidity of 40% to standardize the effect of relative humidity on their tensile properties.

RESULTS AND DISCUSSION

Degree of Substitution and Contact Angle Analysis

Table 1 lists values of the DS and water contact angles of eNFC. The DS was 0.04 to 1.30, depending on the amount of added fatty acid chloride. The change in the polarity of the eNFC was evaluated using water contact angle measurements (Fig. 1).

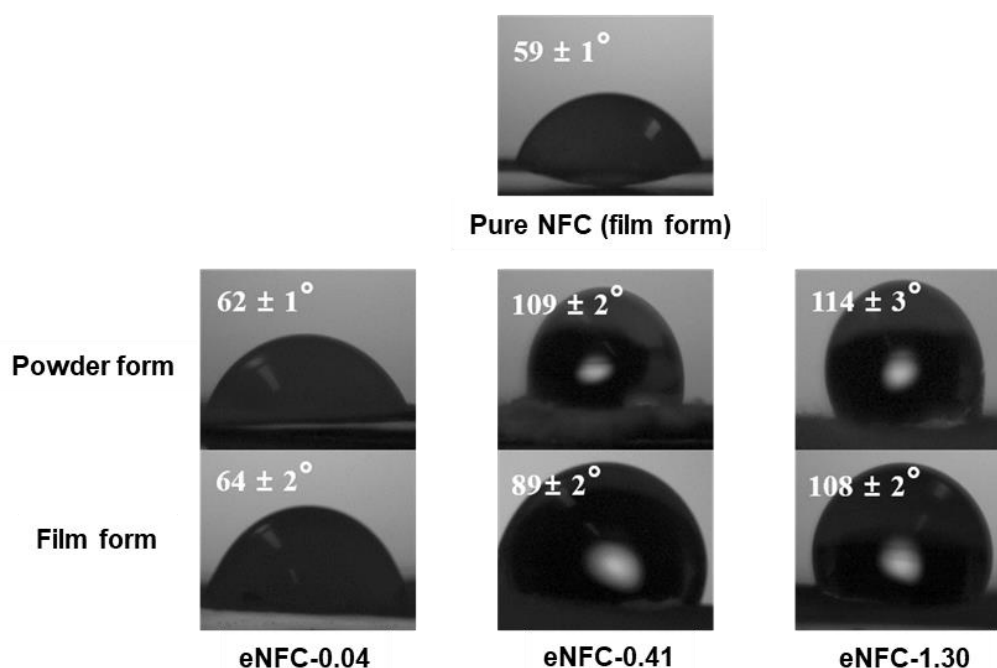


Fig. 1. Water contact angles of eNFC powder and film samples with various DS

Table 1. Degrees of Substitution and Contact Angles of eNFC

Sample	Amount of Fatty Acid Chloride (eq/cellulose OH)	Degree of Substitution (DS)	Powder Form Contact Angle (degree)	Film Form Contact Angle (degree)
Pure NFC				59 ± 1
eNFC-0.04	0.5	0.04	62 ± 1	64 ± 2
eNFC-0.41	1.0	0.41	109 ± 2	89 ± 2
eNFC-1.30	2.0	1.30	114 ± 3	108 ± 2

Pure NFC with hydroxyl groups is highly polar and hydrophilic. The measurement of the water contact angle of the pure NFC powder was not possible owing to its high hydrophilicity and the presence of empty spaces, which facilitate water penetration. As the value of DS increased, the polarity decreased because of the introduction of hydrophobic fatty acid chains, and the water contact angle increased. Further the water contact angles of powder and film forms were compared. As shown in table 1, at higher DS, the powder form exhibited higher contact angles than that of film form. This can be explained based on the Wenzel model. According to the Wenzel model, roughness increases the surface area of the solid, which geometrically enhances hydrophobicity (Wenzel 1936; Wenzel 1949). Here, the eNFC powder had a rougher surface than that of the film; hence, the powder form exhibited a higher water contact angle than that of the film.

FT-IR Spectroscopy

The chemical modification of NFCs was verified by FTIR spectroscopy. As shown in Fig. 2, the FTIR spectrum of the pure NFC exhibited characteristic peaks corresponding to the cellulose structure. As indicated by dotted rectangles in the figure, two new bands were observed after esterification. The first peak at 1740 cm^{-1} corresponds to the vibration of carbonyl groups (C=O). This confirms the esterification reaction between the hydroxyl groups of cellulose and acid chloride groups of LC. The second peak was recorded in the range $2800\text{ to }2920\text{ cm}^{-1}$ corresponding to the methylene groups (CH₂) of side chains of fatty acid and confirms the grafting of the fatty acid to NFC. As the added amount of the fatty acid increased, the intensities of the methylene and carbonyl signals increased. In addition, a decrease in the intensity of the broad band at approximately $3200\text{ to }3500\text{ cm}^{-1}$, assigned to the O–H vibration in cellulose, suggested the consumption of hydroxyl groups in the esterification. These results are in well accordance with the previous report (Trinh and Mekonnen 2018). Consequently, a successful introduction of fatty acids into the NFC was confirmed.

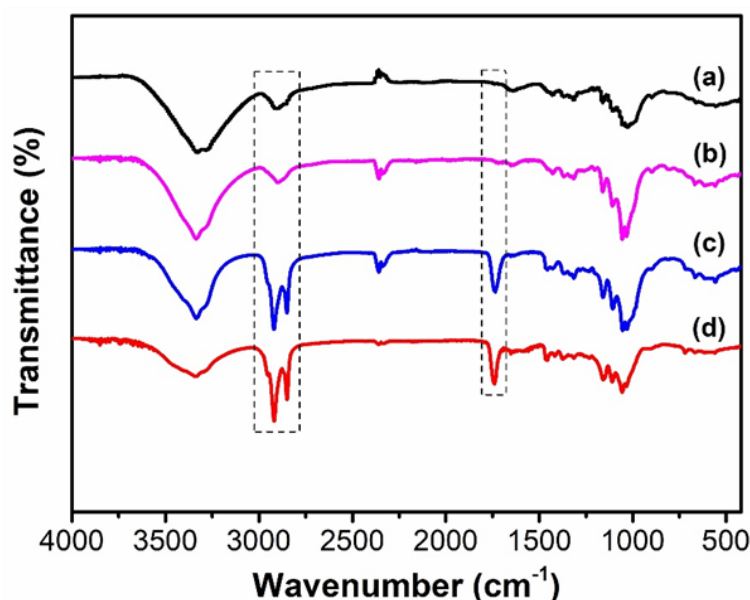


Fig. 2. FT-IR spectra of NFCs: (a) pure NFC, (b) eNFC-0.04, (c) eNFC-0.41, and (d) eNFC-1.30

XRD Analysis

The XRD pattern depicted in Fig. 3 reveals the changes in the NFC crystal structure after esterification. The XRD pattern of pure NFC exhibited peaks corresponding to 2θ values of 14.9° , 16.7° , and 22° , which is consistent with a typical XRD pattern of cellulose I, and the CrI was 67.0%. Similar peaks were observed for the eNFC-0.04 and eNFC-0.41. However, in eNFC-1.30, the characteristic cellulose I peaks at 14.9° and 16.7° disappeared

and a new broad peak appeared at 19.8° , characteristic of cellulose with low crystallinity (Xie *et al.* 2014). Similar XRD patterns were reported by Wen *et al.* (2017) and Onwukamike *et al.* (2018). These results suggest that the esterification of NFC affected its crystal structure. The substitution of hydroxyl groups with fatty acid chains destroys the intermolecular and intramolecular hydrogen bonds in cellulose, which in turn decreases the crystallinity of cellulose.

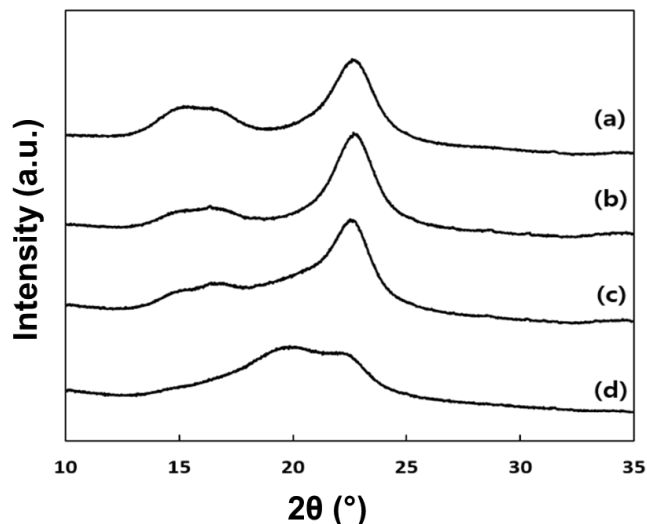


Fig. 3. XRD patterns of NFCs: (a) pure NFC, (b) eNFC-0.04, (c) eNFC-0.41, and (d) eNFC-1.30

Morphological Characteristics of NFC and eNFC

The morphologies of the pure NFC and eNFC were observed from their SEM micrographs (Fig. 4).

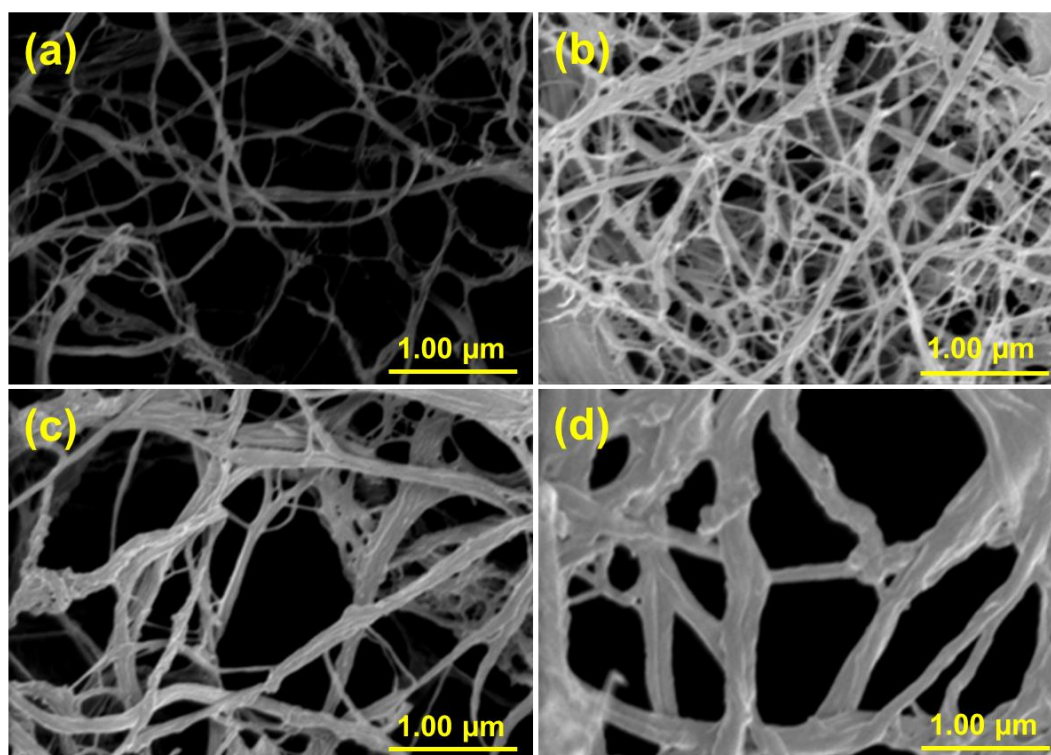


Fig. 4. SEM images NFCs: (a) pure NFC, (b) eNFC-0.04, (c) eNFC-0.41, and (d) eNFC-1.30

The eNFC exhibited a fibrous structure similar to that of pure NFC; however, the fibers were considerably thicker than those of pure NFC. This increased thickness can be

ascribed to the fatty acid coating on the fiber surface and solvent-induced swelling. The solvent (DMF) used in esterification reaction has the property causing the swelling of cellulose, thereby decreasing its crystallinity, and increasing its reactivity (Zhang *et al.* 2018). In addition, while esterified fibers with a low DS essentially preserve the characteristics of unmodified fibers, such as crystallinity and fiber length, an increase in DS generally results in a significant reduction in fiber length (Freire *et al.* 2008).

Dispersibility Visual Appearance of Esterified NFC

To evaluate the hydrophobicity and wettability of eNFC in organic solvents, they were dispersed in solvents such as distilled water, ethanol, dimethyl sulfoxide, N-Methyl-2-pyrrolidone, N,N-DMF, acetone, tetrahydrofuran (THF), and chloroform (in order of polarity). As shown in Fig. 5(a), pure NFC displayed excellent dispersibility in water.

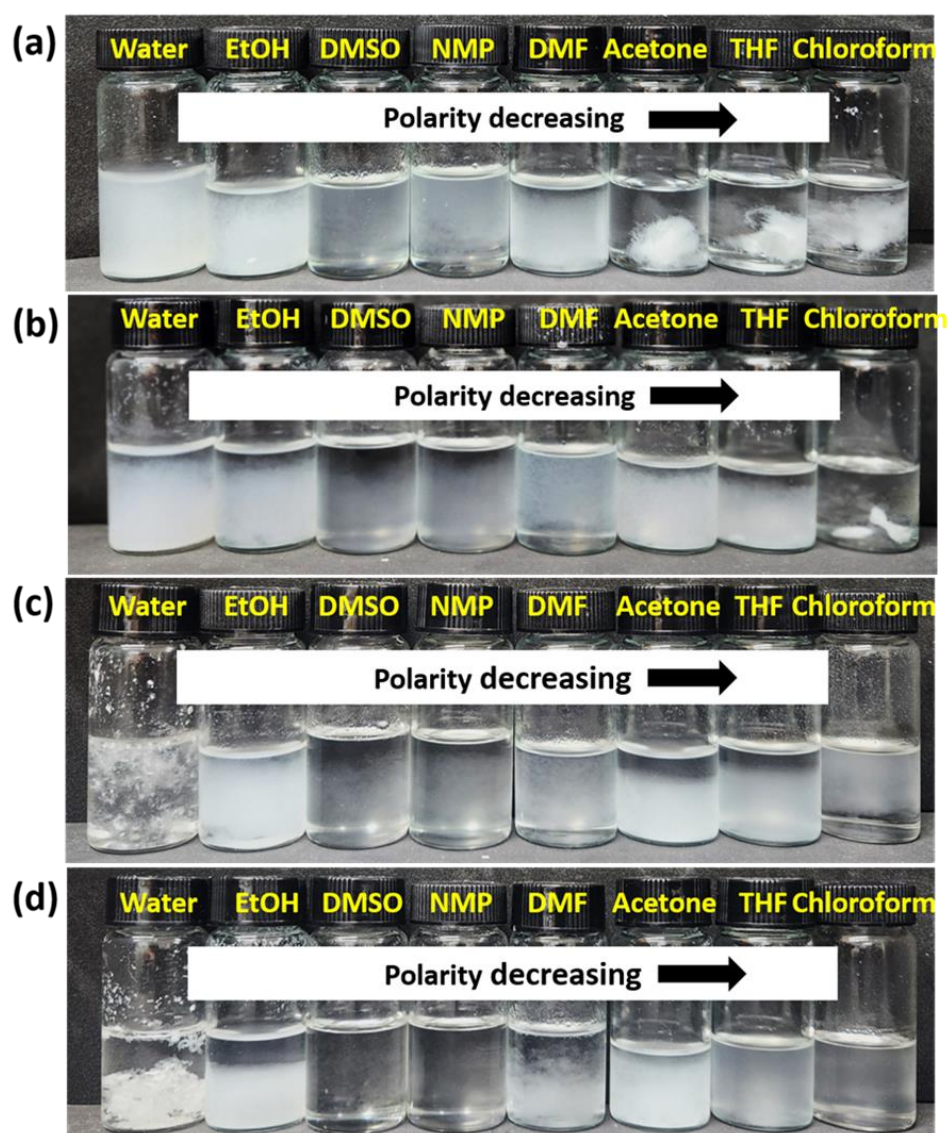


Fig. 5. Photographs showing the dispersibilities of NFCs in various solvents: (a) pure NFC, (b) eNFC-0.04, (c) eNFC-0.41, and (d) eNFC-1.30

The abundant hydroxyl groups of the NFC can form strong hydrogen bonding with water and enable its stable dispersion in water. Pure NFC was relatively well-dispersed in ethanol; however, its dispersibility decreased as the polarity of the solvent decreased. After esterification, the dispersibility of eNFC in water decreased drastically with an increase in the DS. When the DS of the eNFC increased, the polar hydroxyl groups were replaced by nonpolar fatty acid side chains. Hence, the dispersibilities in polar and non-polar solvents

decreased and increased, respectively. The eNFC-0.04 sample showed a dispersibility similar to that of pure NFC; however, its dispersibility improved in acetone and THF compared with that of pure NFC. The eNFC-0.41 and eNFC-1.30 samples displayed poor dispersibility in water but excellent dispersibility in nonpolar solvents. The improvement in the dispersibility of NFC in nonpolar solvents is advantageous for making NFCs and polymer composites (Trinh and Mekonnen 2018).

Tensile Properties of PBS/eNFC Composite Film

The tensile characteristics of the PBS/eNFC composite films based on the eNFC content and DS were investigated using a universal tester (Fig. 6). The highest tensile strength was observed in the PBS/eNFC-0.41 composite, which slightly increased as the content of eNFC-0.41 increased. In the other samples, the tensile strength was lower than that of the pure PBS film. Among the various factors that determine the performance of a composite, interfacial interaction between the polymer matrix and reinforcement is the most important one (Lee *et al.* 2019).

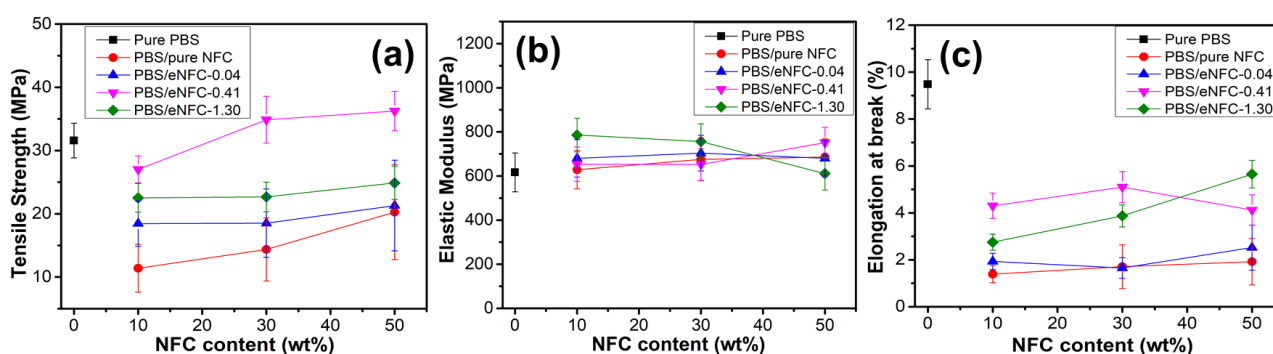


Fig. 6. (a) Tensile strength, (b) Elastic modulus, and (c) Elongation at break of PBS/eNFC composite films with different NFC contents

The lowest tensile strength was observed for the PBS/pure NFC composite, followed by PBS/eNFC-0.04. This is because pure NFC and eNFC-0.04, have low hydrophobicity, and the interfacial interaction between the PBS matrix and NFC filler is poor. This leads to poor stress transfer from the PBS matrix to the NFC filler. Under all the conditions, the tensile strength of the PBS/eNFC sample was higher than that of the pure PBS/NFC sample. Furthermore, with an increase in the DS of eNFC from 0.04 to 0.41, the tensile strength increased. This indicates that esterification improved the interfacial interaction between cellulose and PBS. Similarly, eNFC-1.30, which exhibited the highest DS, was expected to have a high TS. However, in eNFC-1.30, the crystal structure of NFC, which plays an important role in strength, was destroyed by the excessive modification of NFC. This prevented the NFC from acting as a filler in the PBS matrix.

Excessive modification of NFC can degrade the mechanical performance of NFC and its polymer composites (Freire *et al.* 2008). Although NFC-0.41 partially lost its crystallinity owing to modification, the core of the crystal structure was maintained, and the hydrophobicity owing to the modification improved the interfacial interaction with the PBS matrix, displaying a reinforcing effect. The modulus of PBS increased slightly after the addition of NFCs. However, all the samples remained almost constant within the limits of the standard deviation. Elongation was significantly decreased owing to poor interfacial interaction between the PBS matrix with pure NFC and eNFC-0.04. The eNFC-1.30, was plasticized owing to excessive modification, and elongation increased as the content of eNFC-1.30 increased. Finally, the composite films comprising pure NFC and eNFC-0.04 exhibited a greater standard deviation among all the samples, indicating poor interfacial interaction and challenges in achieving uniform dispersion within the PBS matrix.

CONCLUSIONS

1. Nanofibrillated cellulose (NFC) was successfully esterified using lauroyl chloride, and esterified NFC with varying degrees of substitution (0.04 to 1.30 DS) was prepared.
2. Increased DS resulted in increased hydrophobicity (increased water contact angle from $59\pm 1^\circ$ to $108\pm 2^\circ$), but excessive modification led to the disruption of the crystal structure of the NFC.
3. The attachment of fatty acid to the NFC reduced the polarity of NFC and facilitated its uniform dispersion in nonpolar solvents.
4. The addition of esterified NFC to a poly(butylsuccinate) (PBS) matrix improved the tensile strength and elastic modulus compared with that of unmodified NFC.
5. NFC esterification with fatty acid not only enabled stable dispersion in non-polar solvents but also enhanced compatibility with hydrophobic polymers, thereby offering potential for the development of NFC-based polymer composites.

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