

## Water based esterification of cellulose nanofibrils for compounding with PLA

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### Abstract

The incorporation of cellulose nanofibrils (CNFs) into bio-based polymeric systems has been investigated as a method of improving the properties of the bio-based polymers while maintaining bio-based nature of the resulting composite. However, the hydrophobic polymer and hydrophilic CNFs are often incompatible. In this study a water-based catalyzed esterification of CNFs was attempted using lactic acid. The unmodified and modified CNFs were both used to make cast films without a polymer matrix to evaluate the effectiveness of the modification, and to compound with poly(lactic acid) (PLA) to produce injection molded composites. Films were made from lactic acid (LA)-grafted CNFs and ungrafted CNFs by vacuum filtration and were characterized for functional, thermal and mechanical properties. FTIR spectra of the modified samples revealed the presence of carbonyl peaks at  $1720\text{ cm}^{-1}$ , an indication that the esterification reaction was successful. Comparable dynamic mechanical properties were observed in the LA-grafted and ungrafted CNF, but a decrease in tensile strength was observed. In addition, both samples displayed similar levels of thermal stability. PLA composites containing modified CNFs appeared to exhibit better dispersion and improved transparency compared with PLA composites containing unmodified CNFs. Therefore, esterification of CNFs in aqueous medium may provide an environmentally benign way of modifying the surface chemistry of CNFs resulting in enhanced compatibility with PLA, potentially leading to improvement in the properties of PLA as a packaging material.

**Key words:** Cellulose nanofibrils; Esterification; Lactic acid grafted CNFs; Surface modification; Tensile modulus; Thermal Stability; Storage Modulus

### Introduction

Research in cellulose nanofibrils (CNFs) has attracted considerable interest because of its excellent properties such as abundance, high mechanical properties, biodegradability and low density, among others<sup>1</sup>. However, the surface chemistry of CNF predisposes it to poor thermal stability, hygroscopicity and incompatibility with non-polar polymer matrices<sup>2</sup>. Therefore, the need to modify the surface of CNF for better performance become necessary. Among the chemical modification methods, esterification of the surface of CNF is a promising technique, but most esterification reactions are carried out in an organic solvent medium<sup>3</sup>. This is expensive, harmful, and undermines the need for green/sustainable chemistry in CNF modification. Sethi et.

al.<sup>4</sup> prepared nanopapers from lactic acid modified cellulose nanofibers that were modified with lactic acid monomers in an aqueous solution. They reported that the modified nanopapers displayed improved performance under humid conditions. Tensile modulus was also said to improve with modification, but there was a loss in tensile strength. In the investigation, ultrasonication and hot pressing at elevated temperatures (100°C and 150°C) was believed to have aided the success of the esterification procedure. In this work, a water-based catalyzed esterification of CNFs was carried out to graft lactic acid on to the surface of CNF without hot pressing the samples at elevated temperatures. In addition, PLA composites were produced containing both unmodified and modified CNFs.

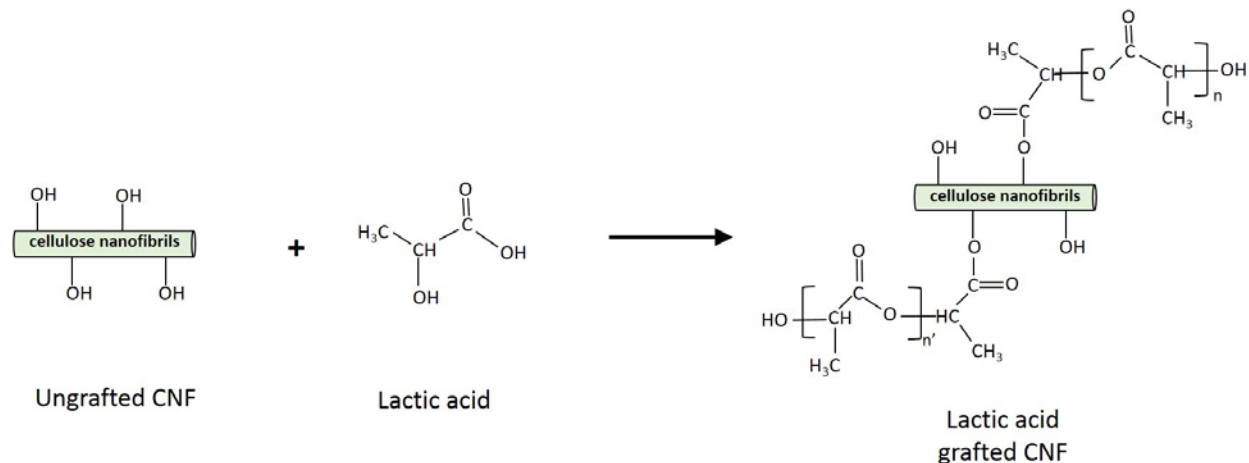
## **Materials and methods**

CNF was produced by grinding 10 L of a 2% bleached Eucalyptus Kraft pulp suspension in a super mass colloidier MKZA6-2 SuperMassColloidier (Masuko Sangyo Co. Ltd, Saitama, Japan) at 1500 rpm for six hours. Reagent grade lactic acid (90%) and Tin II Chloride (98%), supplied by Sigma Aldrich, was added to CNF in a LA to CNF ratio of 20:1. Tin II Chloride was added in trace amount as catalyst. The suspension was mixed thoroughly at 5000 rpm for 10 minutes and sonicated with a probe sonicator (Fischer Scientific, USA) for 1 hr. It was then placed in the oven at 100°C for approximately 40 hours. Lactic acid grafted (LA grafted) and ungrafted nanopapers were produced by vacuum filtration on a 142 mm diameter Millipore vacuum filtration set up, using a 0.45 µm Omnipore membrane filter. The wet films were dried in a stack of blotting and wax paper at room temperature for 24 hours, then in an oven at 60°C for 8 hours before being characterized for functional groups (FTIR), thermal (TGA), dynamic mechanical (DMA) and tensile properties.

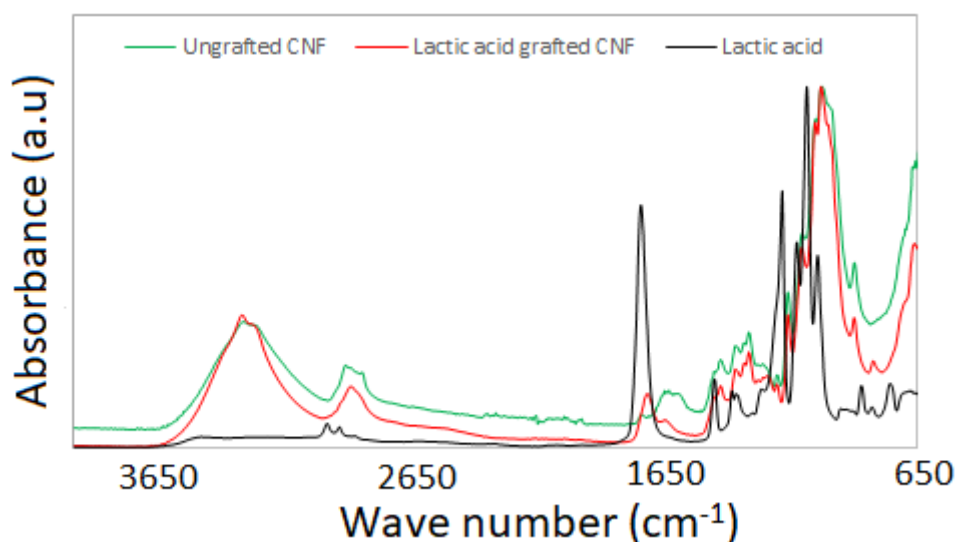
The CNF samples were compounded with PLA at 2% by weight and injection molded into tensile specimens for further characterization. PLA pellets (Ingeo 4044D, NatureWorks, LLC, Minnetonka, MN, US) were cooled with liquid nitrogen and ground in a Wiley Mill, then compounded with CNF suspensions in a thermokinetic mixer set with a discharge temperature of 140 °C. The resulting compound was again ground and injection molded into tensile bars using a 15 mL co-rotating twin screw extruder and 12 mL microinjection molding machine (DSM Xplore, The Netherlands) at barrel temperature of 180°C, screw speed of 100 rpm and an injection pressure of 15 bar. The mold temperature was kept at 60°C.

## **Results and discussion**

The proposed reaction is schematically shown in Figure 1, and Figure 2 presents the FTIR spectra of ungrafted CNF, lactic acid, and LA grafted CNF.



**Figure 1. Reaction scheme for the lactic acid esterification of CNF**



**Figure 2. Normalized FTIR spectra of lactic acid, ungrafted and lactic acid grafted CNF**

From the FTIR spectra, lactic acid esterification of CNF imparts some chemical changes to the sample. Carbonyl band assigned to the aliphatic ester appears at  $1750 \text{ cm}^{-1}$  in the LA. This band shifted to  $1720 \text{ cm}^{-1}$  in the grafted CNF, an indication that an esterification reaction was successful<sup>5,6</sup>. However, further work is needed to determine if a portion of the ester formation was also due lactic acid polymerization.

The Dynamic mechanical analysis presents samples with storage modulus, ( $E'$ ) between 9,000 MPa and 10,000 MPa, and tan delta ( $\text{Tan}\delta$ ) values of 0.06 and 0.07 for the ungrafted and the LA-grafted samples, respectively (Table 1). This has been attributed to the stiff chain conformation

and interaction through hydrogen bonding within the cellulose chains<sup>7</sup>. However, there is no observable difference in the dynamic mechanical properties of ungrafted and LA-grated CNF as the values obtained for storage modulus, maximum loss modulus,  $E_{\max}$  and  $\text{Tan}\delta$  did not change appreciably with esterification (Table 1).

**Table 1. DMA data of CNF films and LA-grafted CNF films.**

	DMA				
	$E'_{50^\circ\text{C}}$ (GPa)	$E''_{\max}$ (MPa)	Temperature at $E''_{\max}$ ( $^\circ\text{C}$ )	$\text{Tan}\delta_{\max}$	Temperature at $\text{Tan}\delta_{\max}$ ( $^\circ\text{C}$ )
Ungrafted CNF	9.4	410.0	120.3	0.06	135.9
LA-grafted CNF	10.6	528.4	113.2	0.07	137.6

In the same manner, the LA-grafted and ungrafted CNF exhibit similar levels of thermal stabilities (Table 2). Thermal degradation of CNF has been said to result from a thermally induced scission of cellulose glycosyl units<sup>8</sup>. The result indicates that LA grafting has no pronounced effect on the thermal stability of CNF films. Agustin et. al.,<sup>5</sup> investigated the effect of the structure of the ester group on the thermal stability of esterified nanocellulose and suggested that temperature at 5% degradation,  $T_{5\%}$ , could help determine suitable processing temperatures for CNF. Based on this criterion, the CNF samples can be compounded with a polymer matrix up to 200 $^\circ\text{C}$  temperature (Table 2).

**Table 2. TGA data of data of CNF films and LA-grafted CNF films.**

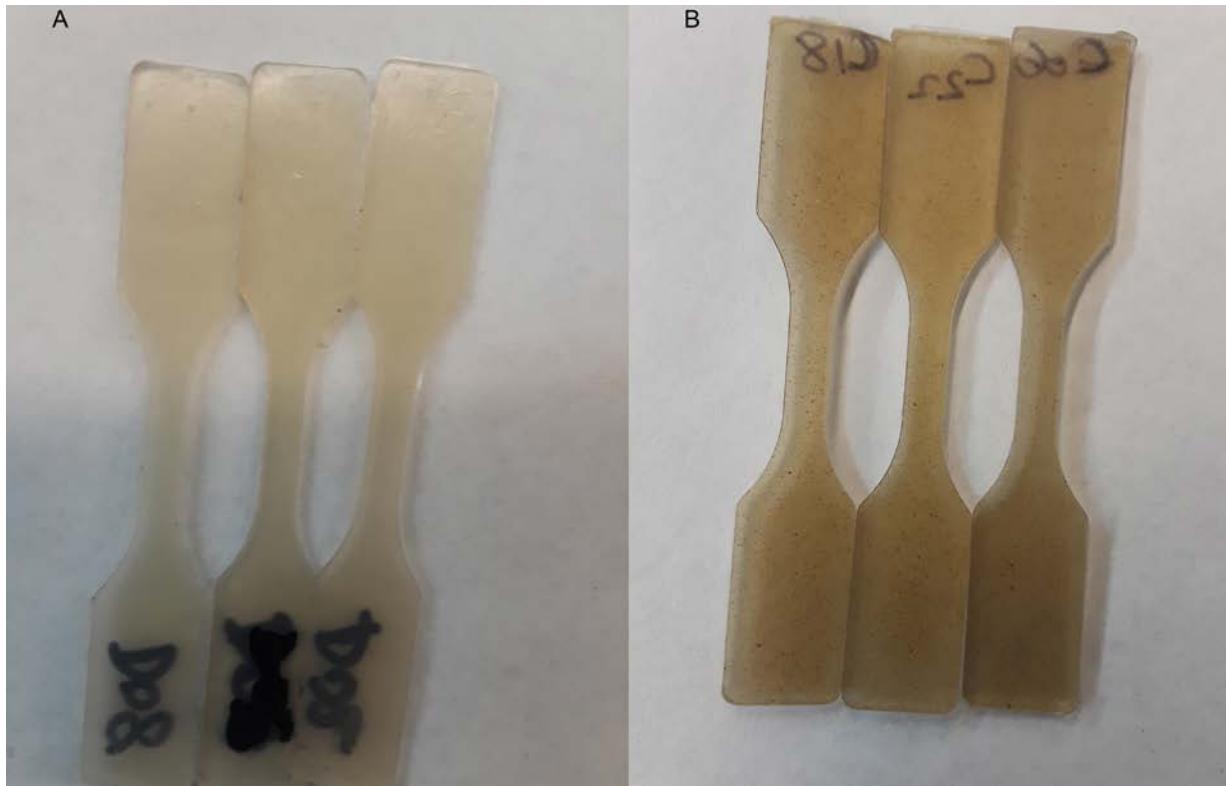
	TGA		
	$T_{\text{onset}}$ ( $^\circ\text{C}$ )	$T_{5\%}$ ( $^\circ\text{C}$ )	$T_p$ ( $^\circ\text{C}$ )
Ungrafted CNF	338.39	214.54	381.06
LA-grafted CNF	334.79	213.65	383.08

The tensile properties of CNF films were evaluated, and the ungrafted and LA-grafted CNF films exhibited tensile modulus values of about 19 GPa (Table 3). Contrarily, the tensile strength of the ungrafted CNF (125 MPa) was found to be higher than the LA-grafted sample (66 MPa). Replacement of the hydroxyl groups on the CNF surface by esterification may have broken down the hydrogen bonding within the CNF structure, resulting in lower tensile strength.

**Table 3. Tensile properties of CNF films and LA-grafted CNF films.**

	Tensile Properties		
	MOE (GPa)	Strength (MPa)	Elongation (%)
Ungrafted CNF	18.8 <b>(2.5)</b>	125 <b>(23.4)</b>	3.27 <b>(0.86)</b>
LA-grafted CNF	19.1 <b>(4.9)</b>	66 <b>(8.3)</b>	0.75 <b>(0.24)</b>

Although analysis of the PLA-CNF composites is not complete, initial observations are promising. Images of the CNF samples compounded with PLA at 2 wt% is shown in Figure 3. Visual inspection of the samples indicate that the LA-grafted CNF produced a more transparent composite sample with no signs of the presence of the CNF (Figure 2A). On the other hand, the ungrafted CNF displays a poor dispersion as the samples appear more opaque with visible signs of agglomeration of the CNF (Figure 2B).



**Figure 3.** PLA composites containing A) LA-grafted and B) Ungrafted CNF.

## Conclusions

Surface esterification of CNF was carried out through lactic acid grafting in aqueous medium. Ester carbonyl peaks were observed in the FTIR spectra of LA-grafted CNF, an indication that the esterification was successful. The samples displayed similar thermal and dynamic mechanical properties, meaning that esterification had no pronounced effect on these properties of the CNF. Similarly, tensile results revealed that LA-grafted CNF exhibit comparable tensile modulus. On the other hand, tensile strength was found to decrease in the LA-grafted CNF relative to the ungrafted sample. Also, the LA-grafted CNF produced composites with apparently better dispersion than the ungrafted CNF. Therefore, aqueous medium esterification of CNF has resulted in a modified CNF with improved compatibility with PLA. This holds a promise for a better reinforcement material aimed at improved properties when compounded with PLA.

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