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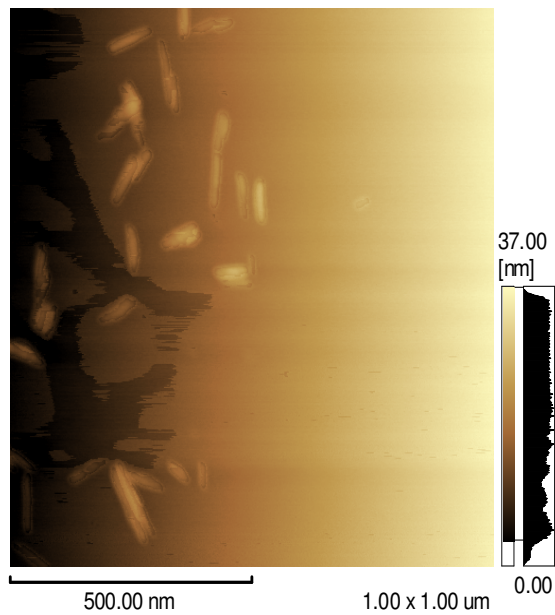


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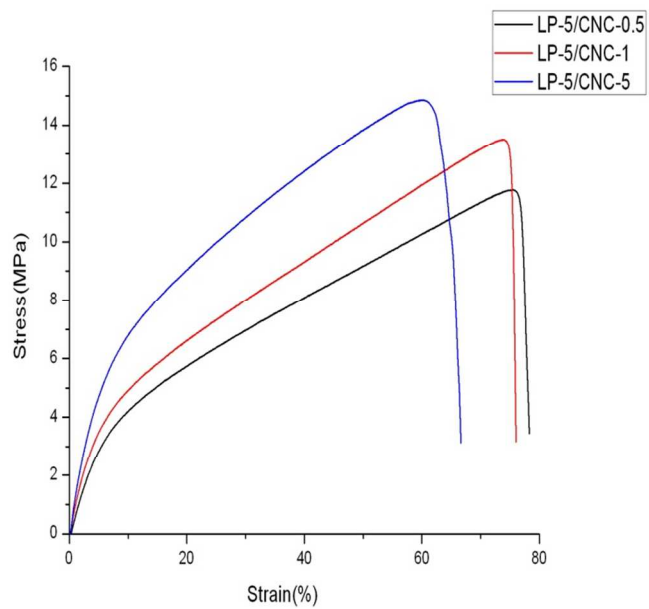
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Cellulose nanocrystals (CNC)



Lignin-based polyurethane (LP)

Lignin-based polyurethane film reinforced with cellulose nanocrystalsBai-Liang Xue,^a Jia-Long Wen,^a Ming-Qiang Zhu,^{a,c} Run-Cang Sun*^{a,b}

Novel nanocomposite films were synthesized using cellulose nanocrystals (CNC) as a reactive reinforcing filler and lignin-based polyurethane (L-PU) as the matrix through casting and evaporating method. A series of L-PU films were prepared by replacing polyol with lignin from 10 to 50% (molar percentage). The L-PU film with maximum addition of lignin content was used as the matrix, which were reinforced with 0.5, 1 and 5 wt% dosage of CNC. The structural, mechanical and thermal properties of the resulting films were evaluated by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), tensile test and thermal gravimetric analysis. The mechanical measurement showed that the tensile strength of the L-PU films was significantly improved by the addition of CNC as a reinforcement. Thermal gravimetric analysis results demonstrated that the thermal stability of the L-PU film after the addition of CNC was slightly increased.

Key words: lignin; polyurethane; cellulose nanocrystals; tensile property; thermal stability

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1. Introduction

Lignin is one of the three major components in plant cell walls and the most abundant aromatic polymer in the nature. It is an irregular aromatic biopolymer consisting primarily of three different types of phenylpropane units linked by ether and carbon-carbon bonds.¹ In spite of its high availability, there are few lignin added products because of its complex structure, low reactivity, different sources and poor processability.^{2,3} Extensive efforts have been made to explore high-value applications of lignin, in particular in polymeric materials, such as phenolic resins, epoxy polymer and polyurethane (PU).⁴

PU is one of the most useful polymer materials in the plastic industry due to their versatile characteristics such as solid elastomers, fibers, foams, solid plastics, and coating and adhesive materials.⁵ PU consists of a chain of organic units joined by urethane linkages. It is formed through a step-wise polymerization by the reaction of isocyanate groups with hydroxyl groups.⁶ Considering the fact that lignin is a polymer with high concentrations of hydroxyl units (phenolic and aliphatic) and carboxylic groups that own reactive hydrogen, lignin has the potential to replace polyols in PU production.⁷⁻⁹ For example, PU film can be prepared from organosolv lignin with polyethylene glycol as co-polyol and soft segments with or without catalyst.^{10,11} PU film can be also prepared from flax soda lignin with polyethylene adipate and ethylene glycol as co-polyol and soft segments.¹²

CNC is a highly crystalline rod-like nanomaterial hydrolyzed from sustainable and renewable resources, which has positive environmental benefits and general biological compatibility.¹³ It has been incorporated into the polymer matrix as a reinforcing phase due to its intrinsic properties such as nanoscale dimension, high surface area, unique morphology, low density, high specific strength and Young's modulus, and low coefficient of thermal expansion.^{14,15} Previously, CNC has been used as the reinforcing filler in PU/CNC nanocomposites,¹⁶⁻²⁰ and it is expected that their tensile strength and Young's modulus increases with increasing CNC content. CNC could be isolated from various cellulose materials, for example, cotton,¹⁶ flax fiber,¹⁷ cottonseed linter pulp,¹⁸ microcrystalline cellulose,¹⁹ bacterial cellulose.²⁰ Although the lignin-based PU foams

reinforced with CNC had been prepared previously,²¹ to our best knowledge, the incorporation of CNC into the lignin based polyurethane (L-PU) films has not been reported.

In the present work, a number of our attempts were made to produce flexible L-PU films by varying the amounts of polyethylene glycol (PEG-400), lignin and methyldiphenyl diisocyanate (MDI). After maximum replacement of polyol with lignin was achieved, CNC was introduced into the L-PU films to reinforce the nanocomposites. Changes in surface structure of the prepared films were investigated by ATR-FTIR, XRD and SEM. Mechanical and thermal behaviors of the prepared films were also investigated.

2. Experimental

2.1 Materials

Methyldiphenyl diisocyanate (MDI) with 50% 4, 4 and 50% 2, 4-isomers was supplied by Yantai Wanhua Co., Shandong, China. NCO value in MDI is 7.5 mmol/g. Polyethylene glycol, used as the polyether polyol, PEG-400 (Mw = 400g/mol) was obtained from Sinopharm Chemical Reagent Co., Shanghai, China. The hydroxyl values in PEG-400 (5.75 mmol/g) was quantified by ³¹P NMR. Cotton linter was kindly supplied by Silver Hawk Fiber Corporation (Shandong, China). Lignin, extracting with mild alkaline solution from the corncob residue after hydrolysis of hemicelluloses, was supplied by the Longlive Biological Technology Co., Shandong, China. The alkaline lignin contained 94.65% Klason lignin, 5.02% acid-soluble lignin, and 0.33% polysaccharides. All other chemicals were reagent grade and used as received without further purification.

2.2. Methods

2.2.1 Characterization of the lignin

Molecular weight of the lignin was estimated by GPC using an Agilent 1200 HPLC system equipped with a Knauer differential refractometer, and PL-gel Mixed Bed HPLC Column (Inner Diam: 7.5 mm; Length: 300 mm; Particle Size: 10 um; Mid-Weight

range: 500-10M). The column was eluted with tetrahydrofuran (THF) at a flow rate of 1.0 mL/min.²²

Functional groups (phenolic and aliphatic hydroxyl) were determined by ³¹P NMR spectra using a previous literature.²³ ³¹P NMR spectra were recorded with 65536 data points and a spectral width of 32467 Hz. A relaxation delay of 5 s was used, and the number of scans was 1024. Samples (20 mg) were dissolved in 500 μ L of anhydrous pyridine and deuterated chloroform (1.6:1, v/v) under stirring. This was then followed by the addition of 100 μ L of cyclohexanol (22.01 mg/mL) as an internal standard, and 50 μ L of chromium (III) acetylacetonate solution (5.6 mg/mL in anhydrous pyridine and deuterated chloroform 1.6:1, v/v) as a relaxation reagent. Finally, the mixtures were treated with 100 μ L of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) and then transferred into a 5 mm tube for subsequent NMR analysis.

2.2.2 Preparation of the CNC

Cotton linter (5 g) was hydrolyzed with a 60 wt% H₂SO₄ solution (200 mL) in a water-bath at 50 °C for 2 h under constant stirring. After hydrolysis, the CNC aqueous suspension was collected by centrifugation, and then dialyzed against water until neutrality.²⁴ To avoid the agglomeration of CNC in the synthesis of PU composites, CNC was freeze-dried from aqueous suspension and re-dispersed in tetrahydrofuran (THF) solution by ultrasonic treatment without additives to avoid any surface modification. Sonication was repeated until complete re-dispersion took place.²⁵

2.2.3 Synthesis of the PU biofilms

L-PU films were prepared by adding various amounts of lignin, MDI and polyol. Weighed quantities of lignin and MDI were each solubilized at room temperature in THF solution. The mixtures were stirred at 60 °C for 0.5 h, the polyol dissolved in THF solution was then added. The resultant solution was stirred for another 2 h at 60 °C. After the polymerization reaction, the solution was casted on 14×7 cm glass plates. Thicknesses of the films were from 0.1 to 0.5 mm. After drying the film overnight at room temperature, it was placed in a vacuum desiccator for 3 days to ensure complete

removal of THF.²⁶

The amount of lignin and polyol were determined by different molar ratio of the hydroxyl groups from lignin to those from polyol (1:9, 2:8, 3:7, 4:6 and 5:5), which corresponded to the sample L-PU1, L-PU2, L-PU3, L-PU4 and L-PU5. The molar ratio of isocyanate to hydroxyl (NCO/OH) was set to 1.0. The NCO/OH ratio was calculated using the equation below:

$$\text{NCO/OH} = \frac{W_{\text{MDI}}[\text{NCO}]_{\text{MDI}}}{(W_{\text{L}}[\text{OH}]_{\text{L}} + W_{\text{P}}[\text{OH}]_{\text{P}})}$$

Where W_{MDI} , W_{L} and W_{P} represent the weights (g) of MDI, lignin and polyol, respectively; $[\text{NCO}]_{\text{MDI}}$ is the molar content of isocyanate groups in MDI; $[\text{OH}]_{\text{L}}$ and $[\text{OH}]_{\text{P}}$ are the molar content of total hydroxyl groups in the lignin and polyol, respectively.

To prepare L-PU reinforced with CNC, the sample L-PU5 was selected as the matrix, which was reinforced by various amounts of CNC. The THF suspension of the CNC was firstly added to the polyol, and the entire system was mechanically stirred and subsequently sonicated. With the exception of CNC addition, the procedure was same for the preparation of L-PU. L-PU reinforced with 0.5, 1 and 5 wt% CNC (based on the weight of lignin and polyol) were successfully prepared, and termed as L-PU5/CNC-0.5, L-PU5/CNC-1 and L-PU5/CNC-5, respectively. All the films were prepared in five duplicates, and the average result from the five samples was reported.

2.2.4. Characterization of the PU biofilms

Atomic force microscopy (AFM) was conducted by depositing an aqueous dispersion of the CNC (0.1 mg/mL^{-1}) on a freshly cleaved mica surface and dried at 60°C under vacuum for 24 h. A JPK SPM Control Station III with a NanoWizard II stand-alone atomic force microscope (AFM) head was used to acquire images in tapping mode. All micrographs were presented in top-view with no filtering to ensure that all images were produced with the same quality.

ATR-FTIR spectra were recorded using a Thermo Scientific Nicolet iN10 FT-IR Microscope (Thermo Nicolet Corporation, Madison, WI) equipped with a liquid nitrogen cooled MCT detector. Samples were mounted on the germanium crystal of a

variable angle ATR attachment and their spectra were recorded in the range from 4000 to 700 cm^{-1} and 128 scans per sample.

X-ray diffraction (XRD) was performed by XRD-6000 instrument (Shimadzu, Japan). The preparations were laid on a glass sample holder and analyzed under plateau condition. X-ray diffractograms were recorded from 5° to 40° (2θ) with a scanning speed of 2°min^{-1} .

Scanning electron microscopy (SEM; Hitachi S-3000, Hitachi High Technologies Inc., Tokyo, Japan) was used to observe the fracture surfaces of the composite films pre-chilled in liquid nitrogen. Sample was coated by a sputter-coating (BOT 341F) with evaporated gold, and subsequently its morphology was examined using a SEM at an acceleration voltage of 15 kV.

Tensile property of the films was measured with a tensile testing machine (Zwick Universal testing machine Z005) fitted with a 200 N load cell. The films were cut in the rectangular specimens with a width of 20 mm and length of 60 mm, and five replicate specimens were tested. The initial distance between the grips was 20 mm, and the separation rate of the grips was kept constantly at 5 mm/min. The tensile strength and elongation at break were recorded, and their modulus was calculated from the increase in load detected from an elongation of 5–30%. The measurements were performed at 25°C and relative humidity of 50%.

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were performed using a simultaneous thermal analyzer (SDT Q600 TGA/DSC, TA Instrument). The samples were heated from room temperature to 600°C at a heating rate of $10^\circ\text{C}/\text{min}$ under an inert atmosphere of N_2 .

3. Results and discussion

3.1 Characterization of CNC and lignin

AFM micrograph of the CNC obtained from acid hydrolysis of cotton linter is presented in Figure 1. The CNC had an average length of 134 nm, diameter of 27 nm, and therefore an aspect ratio of ~ 5 . The hydrolysis process introduced a small amount of sulfate groups on the surface of the CNC, which caused electrostatic repulsion between

the nanocrystals and led to its good dispersibility in many polar solvents.²⁷ Before the L-PU films were prepared by varying the amounts of polyol, lignin and MDI, the hydroxyl content of the lignin was firstly determined by ³¹P NMR spectra. In Supplementary Information, Figure S1, the content of hydroxyl groups (6.86 mmol/g) was obtained by integration of the following region: aliphatic hydroxyl units (148–146 ppm), phenolic hydroxyl groups (143–137 ppm).²³ The effect of the lignin content on the properties of the L-PU films was firstly investigated. By varying different molar ratio of the hydroxyl groups from the lignin to those of the polyol, the L-PU film containing the highest lignin content was chosen as the matrix. The replacement content of the polyol with the lignin influenced the lignin in dispersing the polyol, and finally affected the films formed by casting and evaporating method. Thus, the maximum replacement of the polyol with the lignin content was selected as 50% (molar percentage). Secondly, another series of experiments were done in an effort to investigate the variation of CNC for reinforcing the L-PU film at the maximum addition of the lignin.

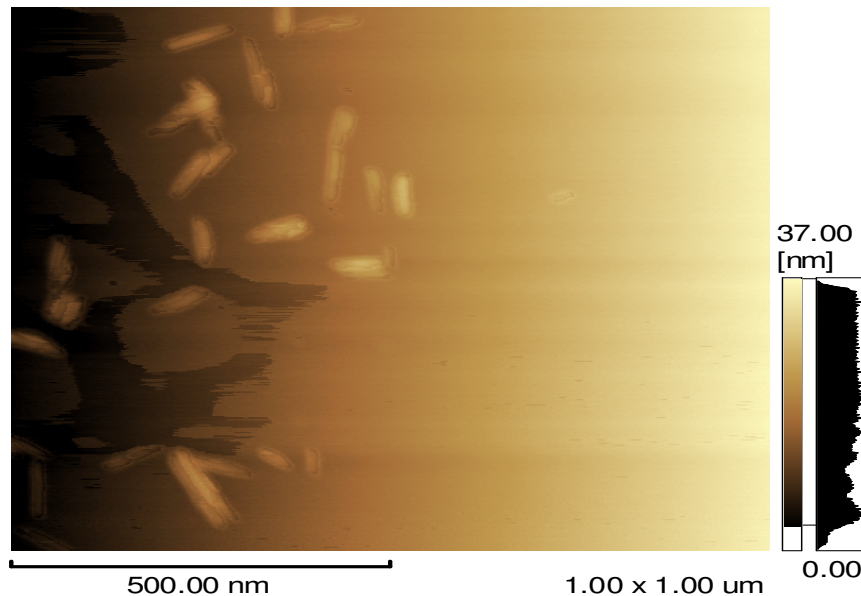


Figure 1. Atomic force microscopy of the CNC obtained from acid hydrolysis of cotton linter.

3.2 Chemical structure of the prepared films

FT-IR spectroscopy was used to study the chemical structures of PU films. Compared with the spectrum of the lignin (Supplementary Information, Figure S2), the relative intensity of the OH band at 3414 cm^{-1} decreased and the peak shifted to lower frequencies around 3322 cm^{-1} in the spectra of L-PU and L-PU5/CNC films (Figure 2), indicating that the consumption of the former groups to give the corresponding NH functions in the urethane moieties. In Figure 2(a), the strong increase in the relative intensity of the bands at $2800\text{-}2950\text{ cm}^{-1}$ demonstrated the incorporation of MDI and corresponding inclusion of numerous aliphatic moieties in the L-PU films.²⁸ The band at 1727 cm^{-1} attributed to the free carbonyl groups was obviously presented in the L-PU films except the sample L-PU5. However, this absorption shifted to 1706 cm^{-1} due to the hydrogen-bonded carbonyl groups formed in the sample L-PU5.²⁹ These results suggested that the free carbonyl groups of MDI probably reacted completely in the sample L-PU5. Moreover, the intensity of this peak decreased when the CNC was added into the L-PU5 films as shown in Figure 2(b). One of the potential reasons was probably nanoscaled CNC hindered the hydrogen bonding between the hard segments of the L-PU films.¹⁶ Additionally, the relative intensities of the bands at 1597 , 1535 and 1508 cm^{-1} corresponded to the aromatic skeletal vibrations of lignin, were rather similar in the spectra, confirming that the lignin was not altered essentially during the prepolymerization reaction.²² Thus, the lignin was covalently bonded to PU molecular chains under the prepolymer reaction, and CNC was expected to affect the hydrogen bonding and phase separation of the hard segmented L-PU films.¹⁶

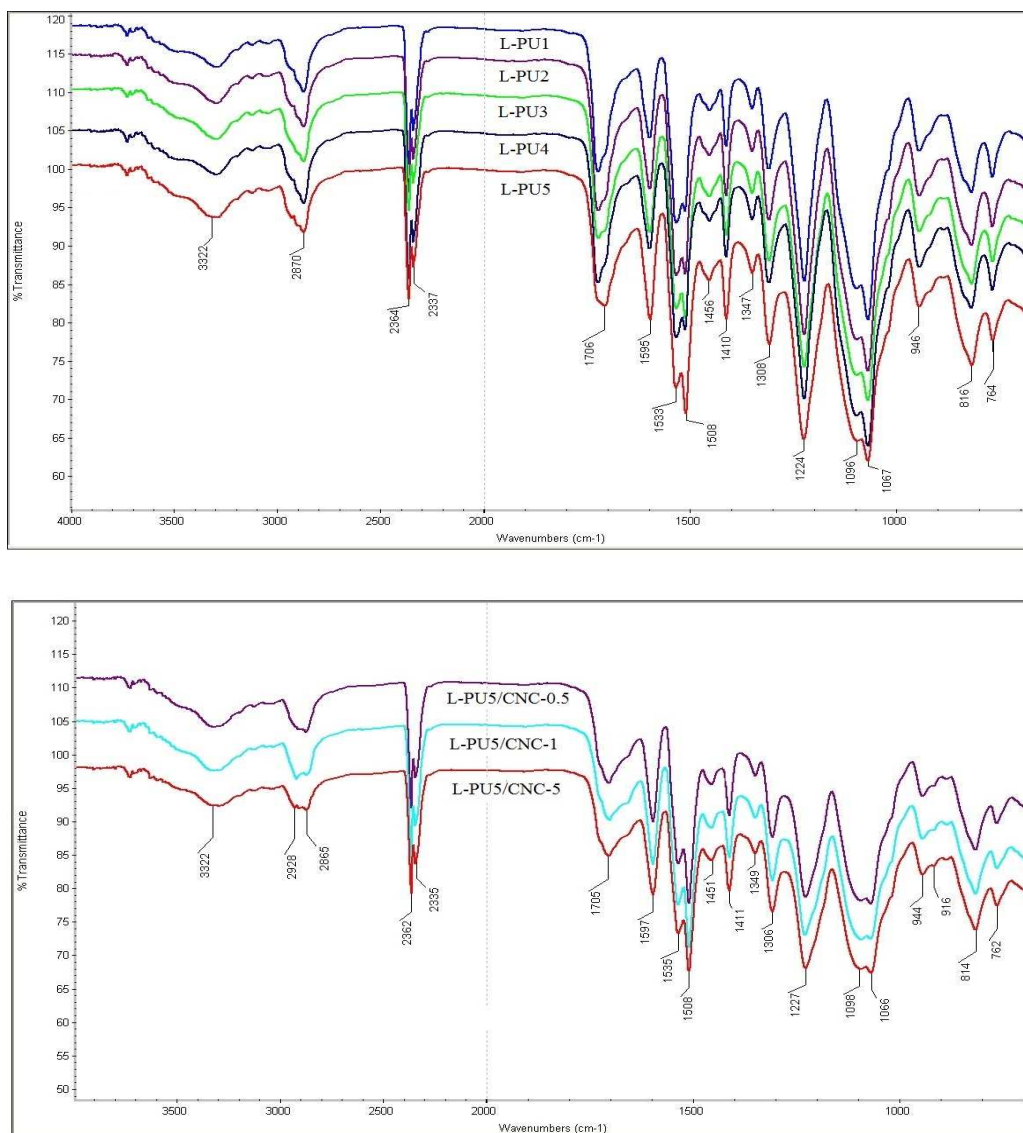


Figure 2. FT-IR spectra of L-PU films (a), and L-PU5/CNC films (b).

XRD spectra of CNC, L-PU5 and L-PU5/CNC films are presented in Figure 3. XRD comparative pattern of cotton linter and CNC was shown in Supplementary Information, Figure S3. Compared to the raw material, the crystallinity was much higher for the CNC, indicating that the CNC obtained by acid hydrolysis is properly prepared. The spectra of L-PU5 and L-PU5/CNC films showed similar characteristic peaks, no obvious difference can be observed. Interestingly, the 2θ angle at 22.6° from the cellulose I were not visible in the sample L-PU5/CNC-0.5 and L-PU5/CNC-1 due to the low content of CNC, in contrast, the peak at 22.6° was slightly identified in the

sample L-PU5/CNC-5.^{30,31} These results indicated that the crystal structure of cellulose I was well preserved in the L-PU5/CNC films at low loading of CNC content, and chemical reaction between MDI and cellulose only occurred on the surfaces of CNC, which was in accordance with the conclusion of Pei et al.¹⁶ Furthermore, the morphology of the nanocomposite films was studied by SEM in Figure 4. Compared to the fracture surface of the samples L-PU5, the sample L-PU5/CNC-5 became rougher and contained ripples and ridges. This result was due to the increased energy dissipation and changed crack deflection during fracture as the L-PU5 film was reinforced with CNC. The CNC used as a rigid filler material was well distributed and separated in L-PU5 film, indicating that L-PU nanocomposite films were successfully prepared by casting from THF solution/suspension.³²

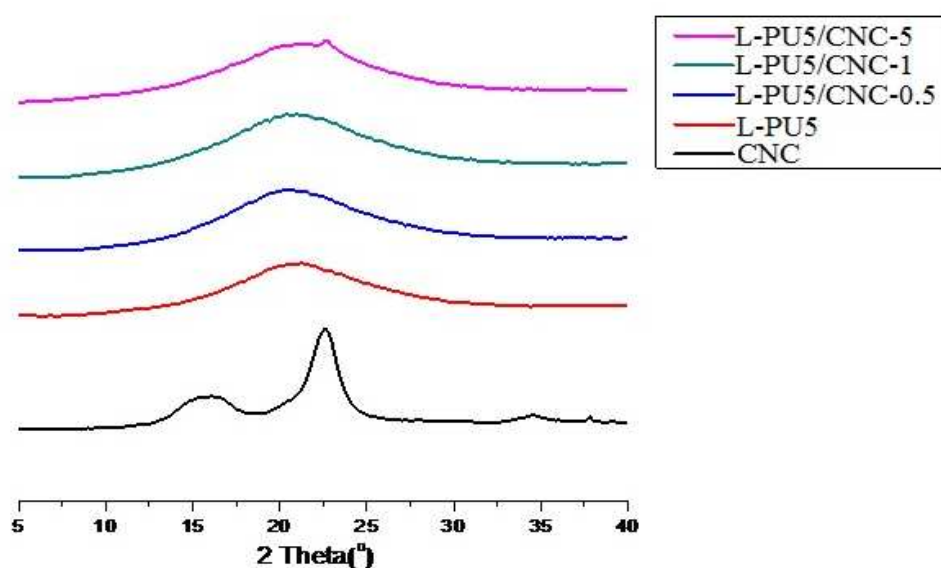


Figure 3. XRD pattern of CNC, L-PU5, and L-PU5/CNC films.

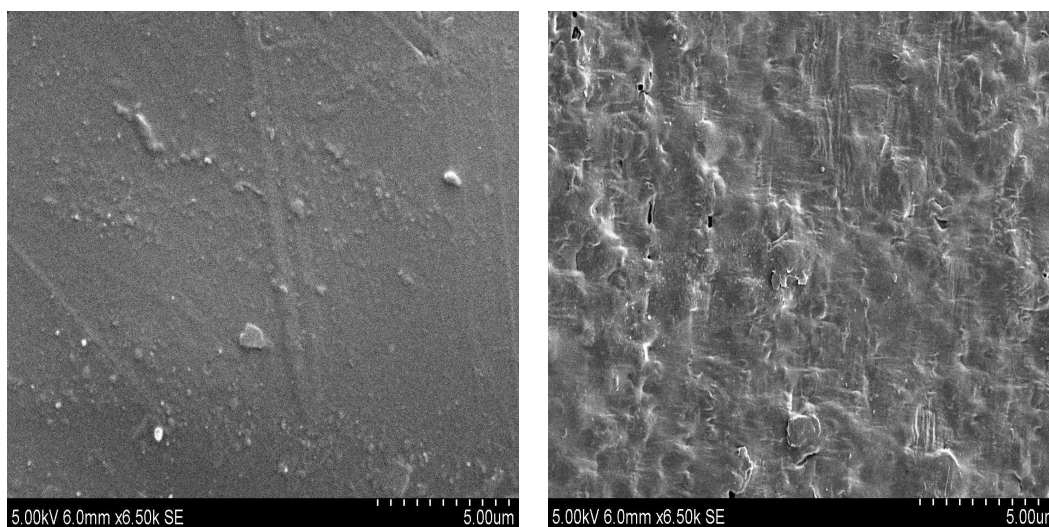


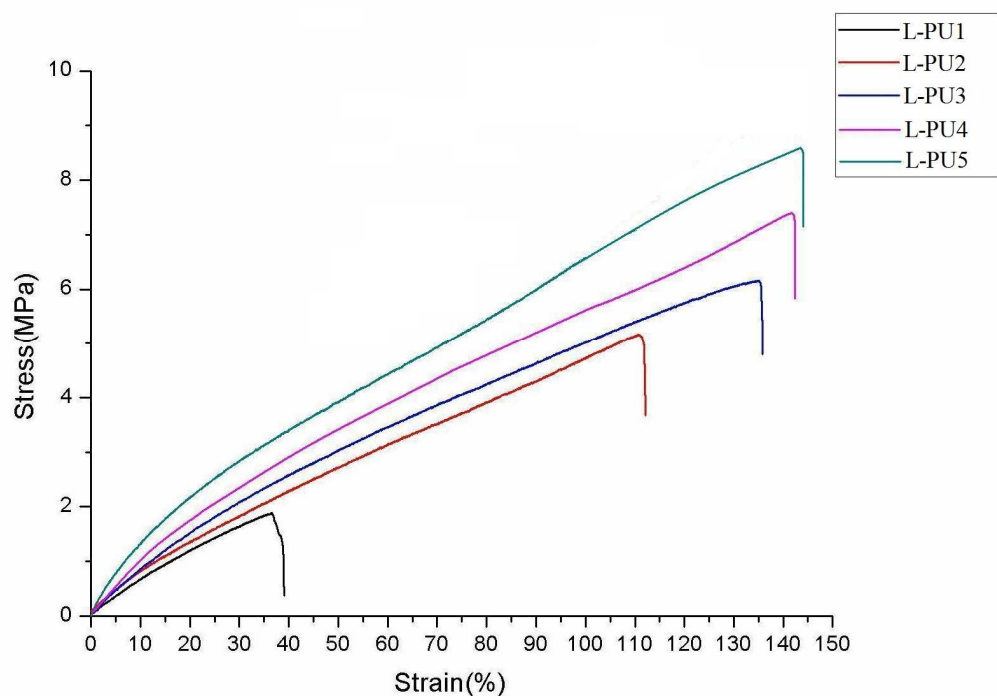
Figure 4. Scanning electron microscopy of low temperature fractured surfaces of L-PU5, and L-PU5/CNC films.

3.3 Mechanical property of the prepared films

The stress–strain curves of the L-PU and L-PU5/CNC films are shown in Figure 5, the results for tensile strength, modulus and elongation at break are summarized in Table 1. As shown in Figure 5(a), it can be obviously seen that the tensile strength, modulus and elongation at break of the L-PU films increased as a function of the lignin content. The lignin was incorporated into PU matrix, the tensile modulus remained very low at low lignin content. As the lignin content increased, the rigidity of the L-PU films increased due to a reduction in the amount of soft segment and an increase in the degree of crosslinking between the hydroxyl group functionality of the lignin and MDI. Thus, the sample L-PU5 was chosen as the matrix reinforced with various amounts of CNC.

Compared with the sample L-PU5, L-PU5/CNC films showed higher tensile strength and modulus in Figure 5(b), the enhancement in tensile strength and modulus was directly attributed to the reinforcement provided by CNC dispersed in the L-PU films. The tensile strength increased from 8.86 MPa for the sample L-PU5 to 11.71 MPa for the sample L-PU5/CNC-0.5, further to 13.51 MPa for the sample L-PU5/CNC-1 at 1 wt% CNC, finally increased to 14.86 MPa for the sample L-PU/CNC-5 containing 5 wt% CNC. Similarly, their tensile modulus increased with increasing CNC content, and reached the highest value of 24.56 MPa at 5 wt% CNC. These results indicated that the

CNC preferentially reinforced the hard domains rather than the soft segments of the L-PU films, avoiding the undesired stiffening of the soft domain.¹⁶ The reinforcement mechanism was due to the CNC reinforcement and increased cross-link density of the PU-CNC interaction, which was in accordance with the published literatures about PU composites reinforced by conventional microscale fillers.³³⁻³⁴ However, it is interesting to note that the elongation at break of L-PU5/CNC films decreases with increasing additions of CNC. This phenomenon suggested that L-PU5/CNC films exhibited strain hardening especially at larger elongations, which were in agreement with the interpretation of Pei et al.¹⁶ and Marcovich et al..³² The potential reason for their low elongation at break was that CNC did not arrange astatically under high strength and also induced the apparent strain decline.³⁵



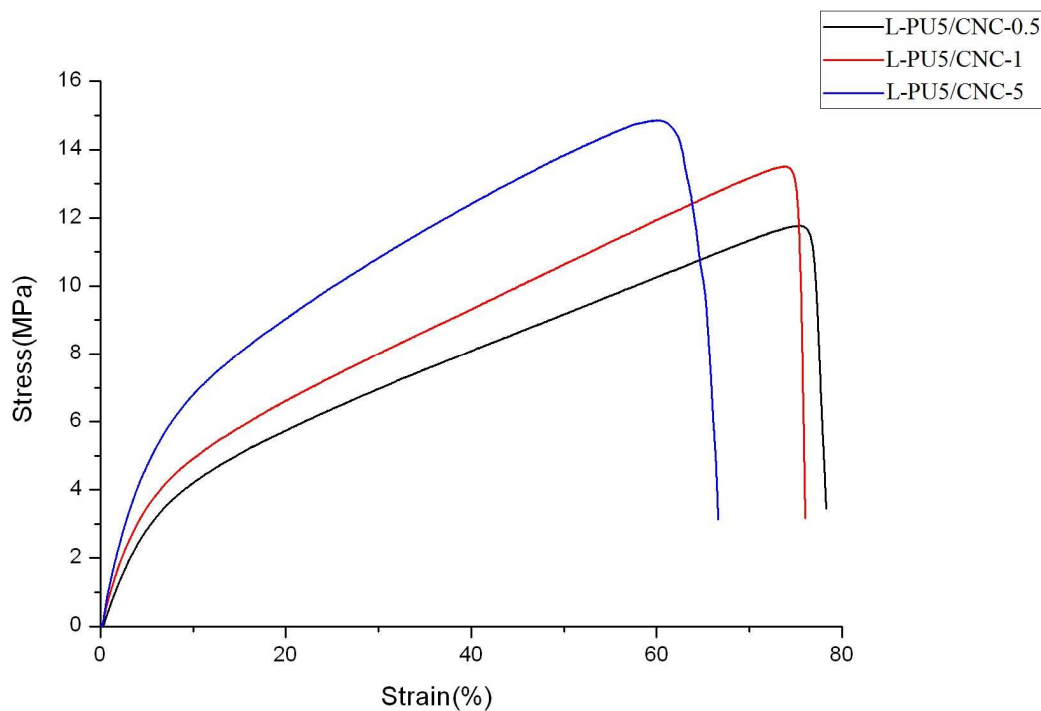


Figure 5. Stress-strain curves of L-PU films (a), and L-PU5/CNC films (b).

3.4 Thermal property of the prepared films

TG curves were used to study the thermal stability of L-PU films, while DTG curves showed the characteristic peaks corresponding to the rate of weight loss. As shown in Figure 6(a), the thermal degradation curves could be mainly divided into two stages. The first stage (200–300 °C) was the weight loss of unreacted products in the prepolymerization reaction. The second stage (300–450 °C) was the decomposition of urethane links between the hydroxyl groups and isocyanate groups.³⁶ With respect to the “char residues” in the TG curves, it was found that the “char residues” at 600 °C were about 30%. The initial decomposition temperature can be defined as the point where the rate of weight loss exceeded 0.5 %/min.³⁷ In Figure 6(b), the two sample L-PU5 and L-PU5/CNC-5 displayed the initial decomposition temperature at 213 and 230 °C, respectively. Thermal decomposition temperature of their largest rate of weight loss were at 343 and 379 °C, respectively, which was in accordance with their initial decomposition temperature in the order. The increase of the decomposition temperature may be due to the increased crosslink density of the PU films reinforced with the CNC,

which lead to a dense construction and a higher heat resistance. These results were in agreement with the conclusion of lignin based PU foam reinforced with CNC.²¹ In conclusion, the thermal stability property of the L-PU film reinforced with CNC slightly increased.

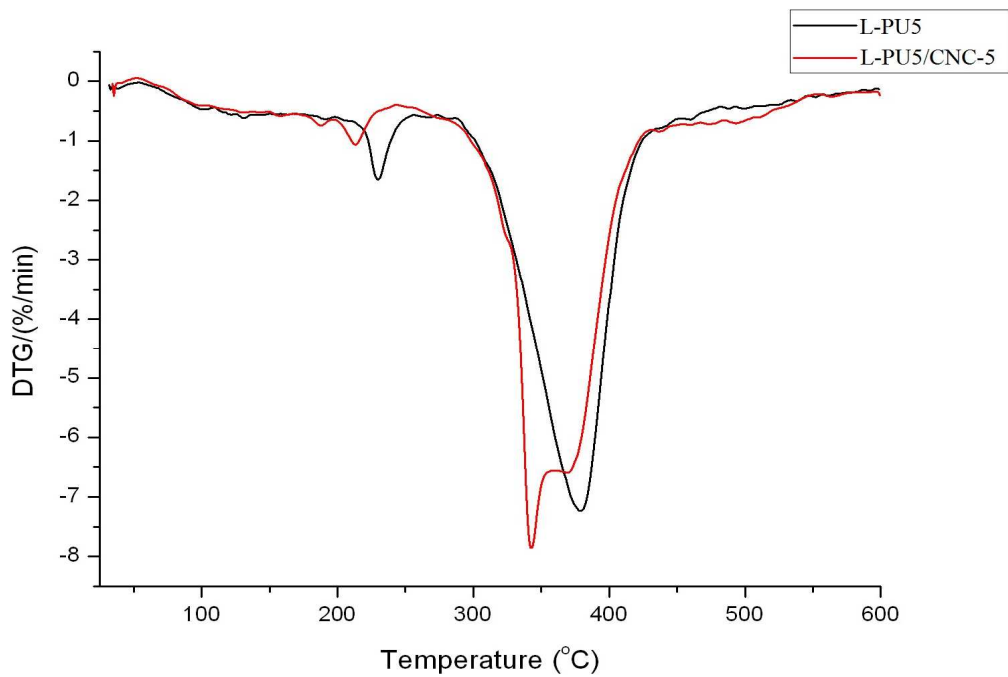
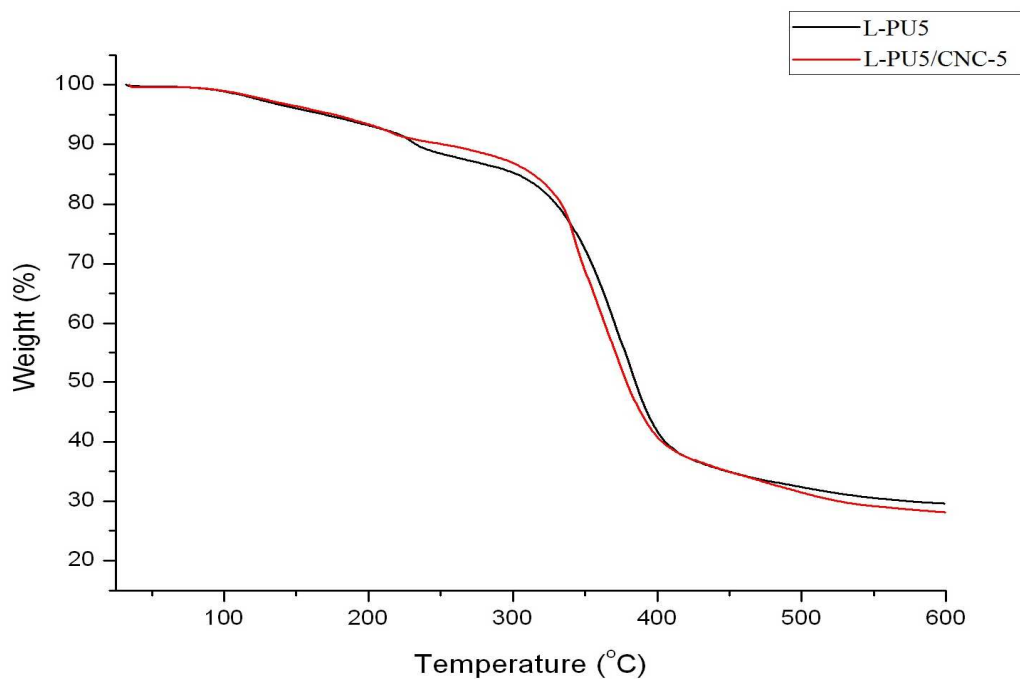


Figure 6. The degradation TGA curves (a), and the rate of weight loss (b) of L-PU5 and L-PU5/CNC-5 films.

4. Conclusion

Lignin-based PU films reinforced with CNC were synthesized by lignin, polyol and MDI using CNC as a reinforcing phase, which were prepared by a solution-casting technique after repolymerization reaction. Changing the molar ratio of lignin and polyol at the [NCO]/[OH] ratio of 1.0 was an effective way to control the mechanical properties of L-PU films. The increase of CNC content in the L-PU films significantly enhanced their tensile strength and modulus, and reduced corresponding maximum elongation at break. The application of CNC into L-PU films results in a slight increment in the thermal property of the CNC reinforced lignin composite materials. This investigation will broaden the practical utilizations of CNC enforcement in packaging and construction industry of the lignin composite materials.

Table 1. Mechanical properties of L-PU and L-PU5/CNC films

Sample	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
L-PU1	4.20	1.83	39.06
L-PU2	3.64	5.19	112.12
L-PU3	5.12	6.24	134.59
L-PU4	7.76	7.18	141.12
L-PU5	8.60	8.86	143.85
L-PU5/CNC-0.5	16.52	11.71	78.28
L-PU5/CNC-1	18.12	13.51	76.03
L-PU5/CNC-5	24.56	14.86	66.63

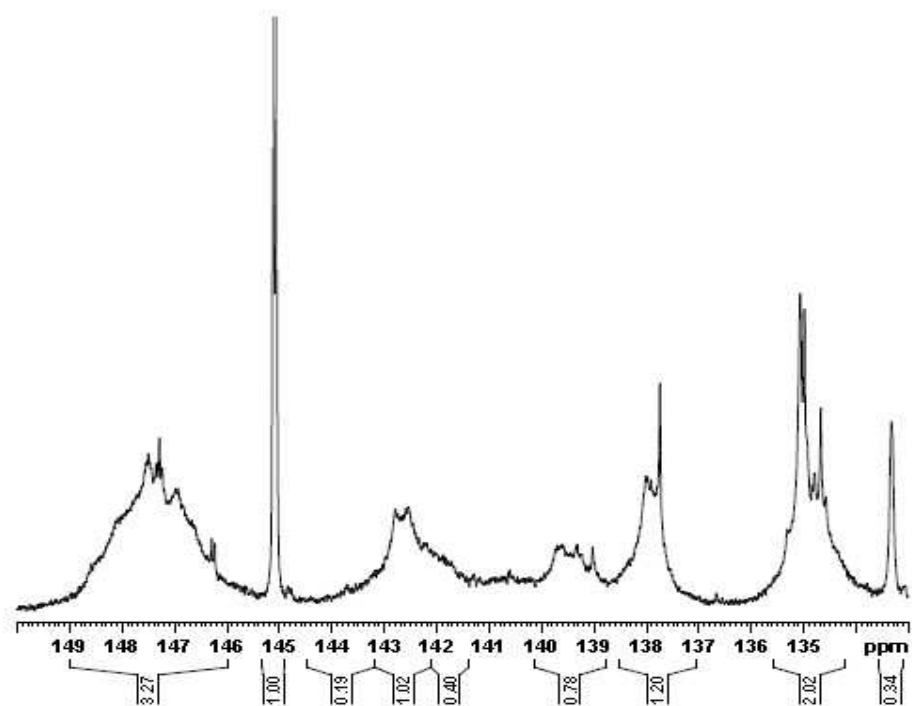


Figure S1. ^{31}P NMR spectra of the lignin

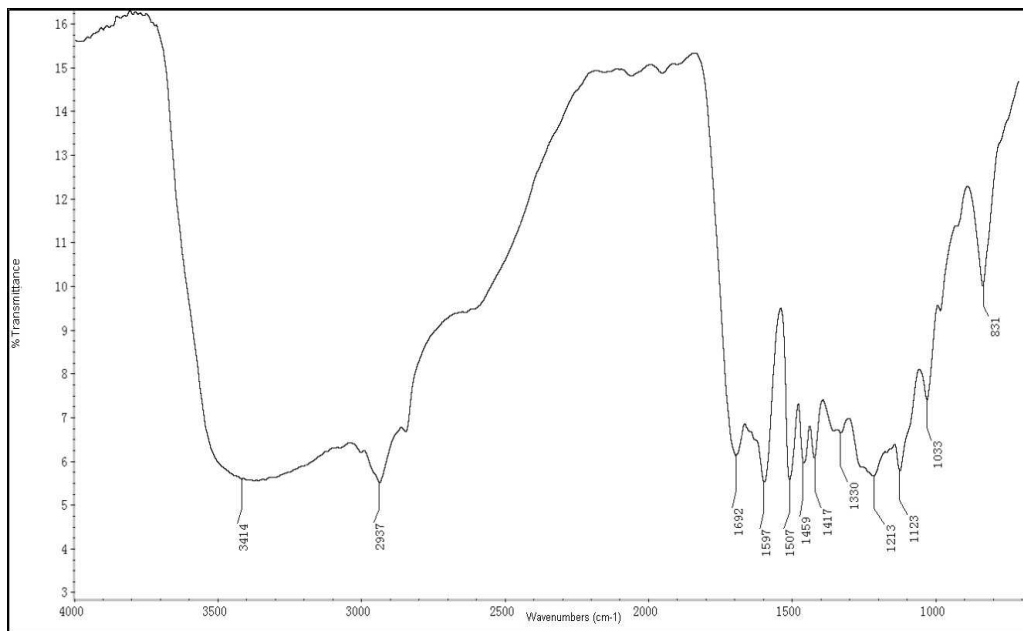


Figure S2. FT-IR spectra of the lignin

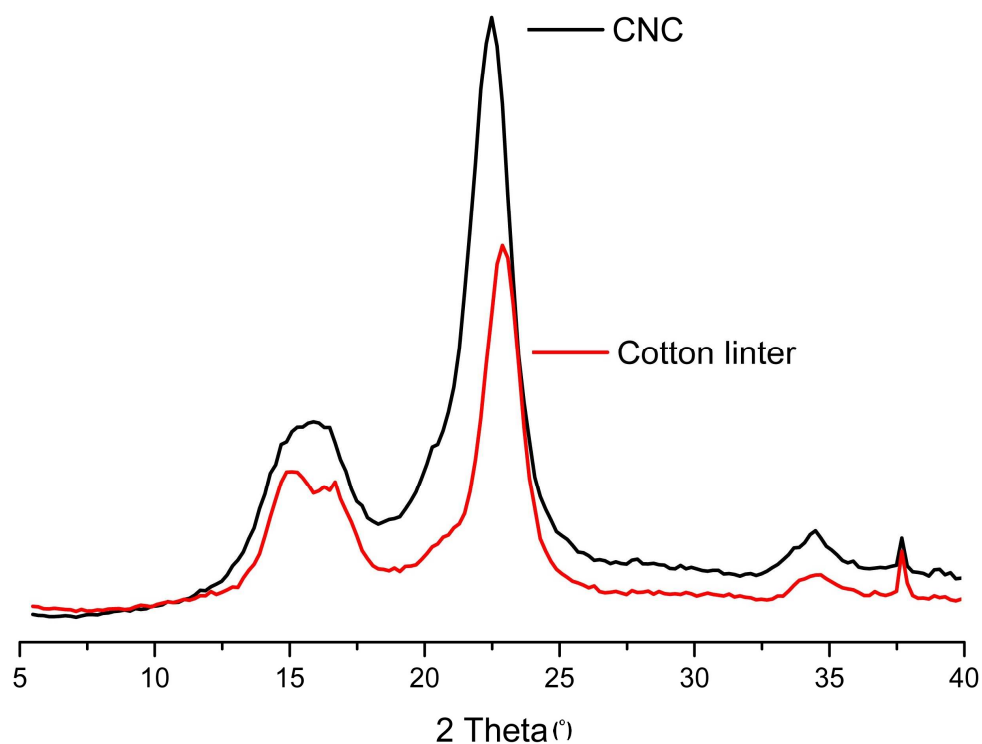


Figure S3. XRD pattern of cotton linter and CNC

Acknowledgements

The authors are extremely grateful for the financial supports from the Fundamental Research Funds for the Central Universities (BLYJ201312), the National Natural Science Foundation of China (31110103902), and the Major State Basic Research Projects of China (973-2010CB732204).

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