

FABRICATION AND CHARACTERIZATION OF ELECTROSPUN POLYLACTIC ACID FILMS REINFORCED WITH CHILEAN BAMBOO CELLULOSE NANOFIBERS

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Films with uniform fibers composed of polylactic acid (PLA) reinforced with cellulose nanofibers (CNF), with loadings of 1%, 3% and 5%, have been fabricated by electrospinning. The CNF were obtained from Kraft pulp of *Chusquea quila*, by mechanical high shear treatment in a microfluidizer. For the reinforcement treatment, the CNF were acetylated before preparing the PLA electrospun solution. The obtained CNF were observed using atomic force microscopy (AFM) and analyzed after acetylation using FT-IR spectroscopy to confirm their modification. Morphology studies on the films were conducted using scanning electron microscopy (SEM). The films were tested via tearing tests according to ASTM D1938 (2014). Besides, the films were subjected to photodegradation experiments according to ASTM D4329 (2013) and to mechanical testing to analyze the influence of photodegradation on their mechanical properties. The addition of 1% CNF was translated into an important increase in tear strength, which in some cases reached a 37% increase. After the photodegradation test, the films lost up to 46% of their original tensile strength.

Keywords: acetylation, cellulose nanofibers, electrospinning, mechanical properties, polylactic acid

INTRODUCTION

The plastics industry has traditionally relied on petroleum-derived polymers, which generate serious environmental problems mainly because of their low biodegradability. Because of this, industries, such as the food packaging one, have begun the search for new environmentally friendly materials to substitute for synthetic polymers.^{1,2} Biopolymers have attracted much attention in this respect, due to suitable physical and mechanical characteristics as well as biodegradability properties.³

Such as a biopolymer is polylactic acid (PLA), which is derived from lactic acid, and is a great alternative to synthetic polymers, also being safe to humans and to the environment. PLA has similar characteristics to those of synthetic polymers, it is hydrophobic and resistant to fats, moisture and deformation.⁴ However, biopolymers should also comply with specific characteristics required for certain applications, such as packaging.⁵ Biocomposites are often a solution in this case, by combining the advantages

of the matrix material and of the reinforcement for achieving enhanced physical and mechanical properties.⁶ In line with this, cellulose, which is the most widely available biopolymer in nature, being present in most plant matter, may serve as a reinforcement material.⁷ Cellulose nanofibers (CNF) can be extracted by chemical and mechanical methods involving grinding and high shear processing,⁸ and then used as reinforcement in biocomposites manufacturing.

Previous research has been reported on developing biocomposites based on PLA reinforced with CNF. Researchers have shown that the mechanical properties of PLA can be effectively improved by the addition of cellulose nanofibers.^{9,10,11} Bamboo species are an attractive source of cellulose, being widely available in tropical and warm temperate regions. In this study, we considered extracting cellulose nanofibers from a Chilean bamboo species *Chusquea quila*, and then using them for

enhancing the mechanical properties of PLA based composites.

In manufacturing nanofiber reinforced biocomposites, the electrospinning technique has attracted much interest.¹² Electrospinning is an electrostatic process, where a polymeric solution is exposed to high voltages, forming fibers that can have micro- and nano-dimensions.¹³ Using this technique, films or membranes can also be formed from layers of interlaced micro-fibers.

The objective of this study was to develop a biocomposite based on PLA reinforced with CNF using electrospinning. Cellulose nanofibres were extracted from bleached Kraft pulp of *Chusquea quila*, and were characterized using atomic force microscopy (AFM). The CNF were subjected to acetylation to achieve good mixing with PLA. The morphology of the films was analyzed using scanning electron microscopy (SEM), which allowed measuring the fiber diameter. The films were also characterized in terms of tear resistance, according to ASTM D1938 (2014).¹⁴ Photodegradation tests were carried out on the films according to ASTM D4329 (2013).¹⁵ Additionally, micro-tension tests were performed using Microtest equipment, before and after the photodegradation test.

EXPERIMENTAL

Materials

Polylactic acid (Natureworks® 2002D; Morgan S.A., Santiago, Chile), with a molecular weight of 200,000 g/mol, density of 1.24 g/cm³, glass transition temperature (*T_g*) of 58 °C, and melting point (*T_m*) of 153 °C, was used. For extracting CNF, bleached *Chusquea quila* bamboo kraft pulp was used. Laboratory-grade NaOH was purchased from Merck KGaA, (Darmstadt, Germany) and used to pretreat the fibers. For the acetylation of CNF, laboratory-grade glacial acetic acid and anhydrous acetic from Merck KGaA, (Darmstadt, Germany), tartaric acid from Furet Ltd., (Concepción, Chile) and acetone supplied by Winkler Ltd. (Santiago, Chile) were used. For fabricating the films, analytical grade chloroform purchased from Merck KGaA (Darmstadt, Germany), and analytical grade acetone obtained from Winkler Ltd. (Santiago, Chile) were used.

Synthesis of cellulose nanofibers (CNF)

The CNF were extracted from bleached *Chusquea quila* kraft pulp at the Center of Biomaterials and Nanotechnology, University of Bío-Bío, Chile. The process to obtain CNF was based on mechanical treatments of high shear and homogenization.^{16,17,18} At first, 70 g of bleached kraft pulp of *Chusquea quila* was immersed in distilled water for 12 hours. NaOH

(5% w/v) was added to distilled water for loosening the fibers. After 12 hours of immersion, the fibers were subjected to a mechanical dispersion process by means of Ultra Turrax equipment (T 25; IKA Works Inc., Staufen, Germany), for 10 minutes at 14,000 rpm.

The product of the dispersion was passed through a colloidal mill, for grinding the fibers. For this, a Supermasscolloider (series MKCA6-2; Masuko Sangyo Ltd., Kawaguchy, Japan) was used, where the fibers were subjected to continuous passes at 1,500 rpm, for 2 hours, using a disc aperture calibrated to 0.5 micron. The fibers obtained were of micrometric size.

In the following step, the cellulose microfibers were continuously passed 8 times through high pressure shearing equipment (LM10 Microfluidizer; Microfluidics Corp., Westwood, USA) at 1,000 bar until a gel composed of cellulose nanofibers was obtained. A sample of the CNF gel was used for characterization using atomic force microscopy (AFM) (MultiMode 8; Bruker; Massachusetts, USA).

Finally, the CNF gel was subjected to centrifugation in an Ultracentrifuge (DDL6; Yingtai Instrument, Changsha City, China) at 12,000 rpm for 30 minutes. This allowed separating the residual moisture from the fibers. Subsequently, an acetylation treatment was carried out, in order to generate surface modification of the CNF for good dispersion in the biopolymer (PLA).

AFM characterization of CNF

Sample preparation: CNF obtained from the high pressure shear process was dispersed in distilled water (to 0.01% by CNF dry weight). Then, one drop of this dispersion was placed in a sample holder, introduced into the spin-coater equipment (WS-400-6NPP; Laurell Technologies Corporation, North Wales, USA) for 30 seconds at 750 rpm. The samples were kept in Petri dishes at room temperature for 12 hours.

Acetylation of CNF

The acetylation was carried out in three stages. In the first stage (activation), 1 gram of CNF gel was immersed in 40 mL of acetic acid and then agitated in a magnetic plate for 15 minutes. Then, the CNF was ultracentrifuged at 8,000 rpm for 10 minutes in the Ultracentrifuge (DDL6; Yingtai Instrument, Changsha City, China); this process was repeated three times.¹⁹

In the second stage (acetylation), CNF were added to a solution of 100 mL of anhydrous acetic and 0.94 grams of tartaric acid. The mixture was stirred at 650 rpm and 120 °C for 3 hours. The sample was then centrifuged at 8,000 rpm for 15 minutes.

In the third stage (purification), the acetylated sample was immersed in 60 mL of acetone, then stirred at room temperature for 15 minutes and ultracentrifuged at 8,000 rpm for 15 minutes; this process was repeated twice.

Fourier transform infrared spectra of CNF and acetylated CNF were acquired using a FT-IR

Spectrometer (FTIR Spectrum Two; Perkin Elmer, Massachusetts, USA), to analyze surface changes on nanofibers.

Preparation of PLA, PLA+CNF solutions and film fabrication by electrospinning

Polymeric films were manufactured, where the percentage of CNF in the film corresponds to the weight, in grams, of the acetylated CNF gel. Thus, 10 mL of solution were prepared, where 10% of this solution corresponds to the PLA and the remaining

90% to the solvent (solvent prepared with the ration of chloroform:acetone of 2:1). PLA was statically dissolved in chloroform for 12 hours, then acetone was added and homogenized in a magnetic plate for 1 hour at room temperature. Subsequently, the solution was loaded into a syringe and introduced into the electrospinning equipment (Inovenso NE-300; Inovenso Ltd., Istanbul, Turkey), where the inner diameter of the electropinning injector nozzle was 0.8 mm (Fig. 1).

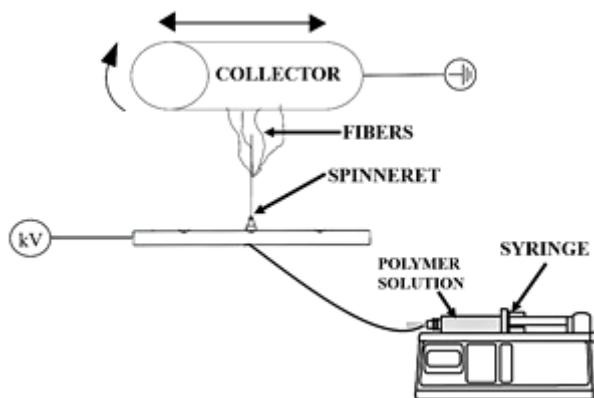


Figure 1: Set-up of electrospinning apparatus, configuration of ascendant vertical fabrication

The electrospinning equipment was calibrated with a distance from injector to collector of 20 cm and 24 kV of fabrication voltage.²⁰ The solution flow was set to 0.1 mL/h. The collector used was a drum rotatory collector (Inovenso Ltd., Istanbul, Turkey).

The PLA+CNF solutions were prepared as previously described, with the addition of acetylated CNF gel in percentages of 1%, 3% and 5%, based on polymer weight. After the homogenization of the PLA and acetone, the CNF amount corresponding to each experiment was added. The homogenization was applied for 1 hour at room temperature. The solution was then loaded into a syringe and then carried to the electrospinning equipment.

Morphological characterization of electrospun films

The morphology of the films was observed using a scanning electron microscopy (JEOL JSM- 6610LV SEM; Jeol Ltd., Tokyo, Japan), with an accelerating voltage of 5 kV, where the samples were previously gold coated for 30 seconds (Denton Vacuum, New York, USA). The fiber diameter in the films was measured using ImageJ Image Processing and Analysis Java software (National Institutes of Health, Version 1.46r, Bethesda, MD, USA).

Tear test

The tear strength of the films was measured with a universal testing machine (Model Z2020; Zwick Roell Group, Ulm, Germany). Tear propagation resistance tests were performed according ASTM D1938-14

(2014) standard.¹⁴ Three replicates were used and the average value was analyzed for each film.

Photodegradation test

The test was performed in accordance to ASTM D4329-13 (2013), in an accelerated weathering chamber (QUV; Q-LAB Corporation, Cleveland, EE. UU).¹⁵ Cycle A was chosen for the exposure of PLA and PLA+CNF films to UV light, with typical irradiation test parameters of 340 nm and 0.89 W/(M2 * nm), 8-hour UV exposure at a controlled temperature of 60 °C and 4 hours of temperature-controlled condensing of 50 °C. The cycle had 12 continuous repetitions for a total of 144 hours of exposure.

Before and after the photodegradation test, the films were characterized by micro tensile tests on Microtest equipment (Deben UK Ltd., Suffolk, UK). The deterioration of mechanical properties upon photodegradation was analyzed: tensile strength and elongation data were obtained and compared. Rectangular specimens of 5 mm x 20 mm were cut from each film, considering the electrospinning orientation of the fiber mats. The samples were clamped with a separation of 10 mm between clamps, and the speed rate was fixed at 1.5 mm/min. Three replicates were used and the average value was analyzed for each film.

RESULTS AND DISCUSSION

The measurements of the diameter of CNF and of the fibers forming the films were done

following the method described by Xie *et al.* (2014).²¹ One hundred random diameter measurements were taken using the ImageJ software, so that an average could be estimated, and a representative histogram could be made.²¹

The AFM micrograph obtained for the CNF is shown in Figure 2. The capture area was $2 \times 2 \mu\text{m}$, the measured average diameter of the nanofibers was 30.3 nm. The AFM image also reveals the high surface area of the nanofibers, which is very useful for enhanced interaction between the polymer matrix and the nanofiber in the films.

FTIR spectra of CNF and acetylated CNF are shown in Figure 3. The spectrum of the acetylated cellulose nanofibers exhibit the signal corresponding to the vibrations of the carboxyl group at approximately 1728.7 cm^{-1} ($\text{C}=\text{O}$ stretching). The appearance of this band indicates

the presence of acetyl groups resulting from the acetylation of primary hydroxyl groups.

Morphological analysis of films

Fiber diameter variation in the films prepared with various CNF loadings is shown in Figure 4. It may be seen in the images in Figure 4 that randomly oriented, bead free and uniform electrospun fibers were formed from the PLA solution and the PLA+CNF blend. According to the measurements, the Fibers in the films fabricated with PLA and PLA with the addition of 1% and 3% CNF have a diameter of 2 μm .

When 5% CNF was added for reinforcement, the fiber diameter increases to 2.2 μm . This could be related to the increase in the viscosity of the solution due to the large amount of nanofibers present, which may result in thicker fibers.

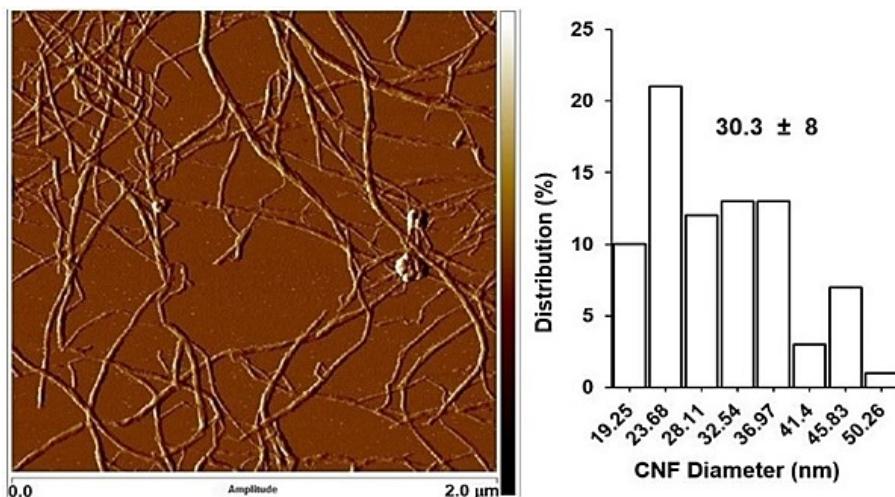


Figure 2: AFM image of cellulose nanofibers and their size distribution

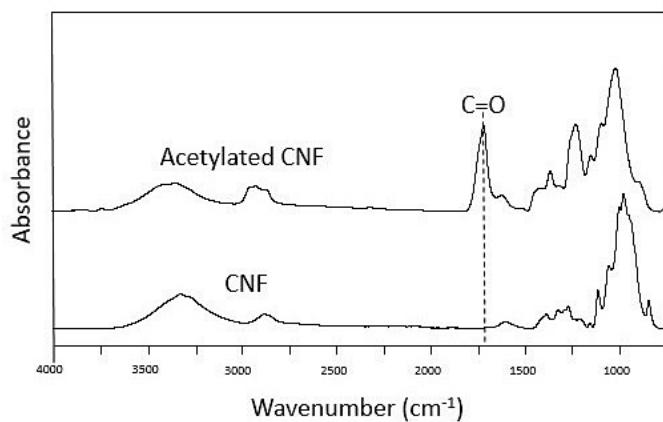


Figure 3: FT-IR spectra of CNF and acetylated CNF

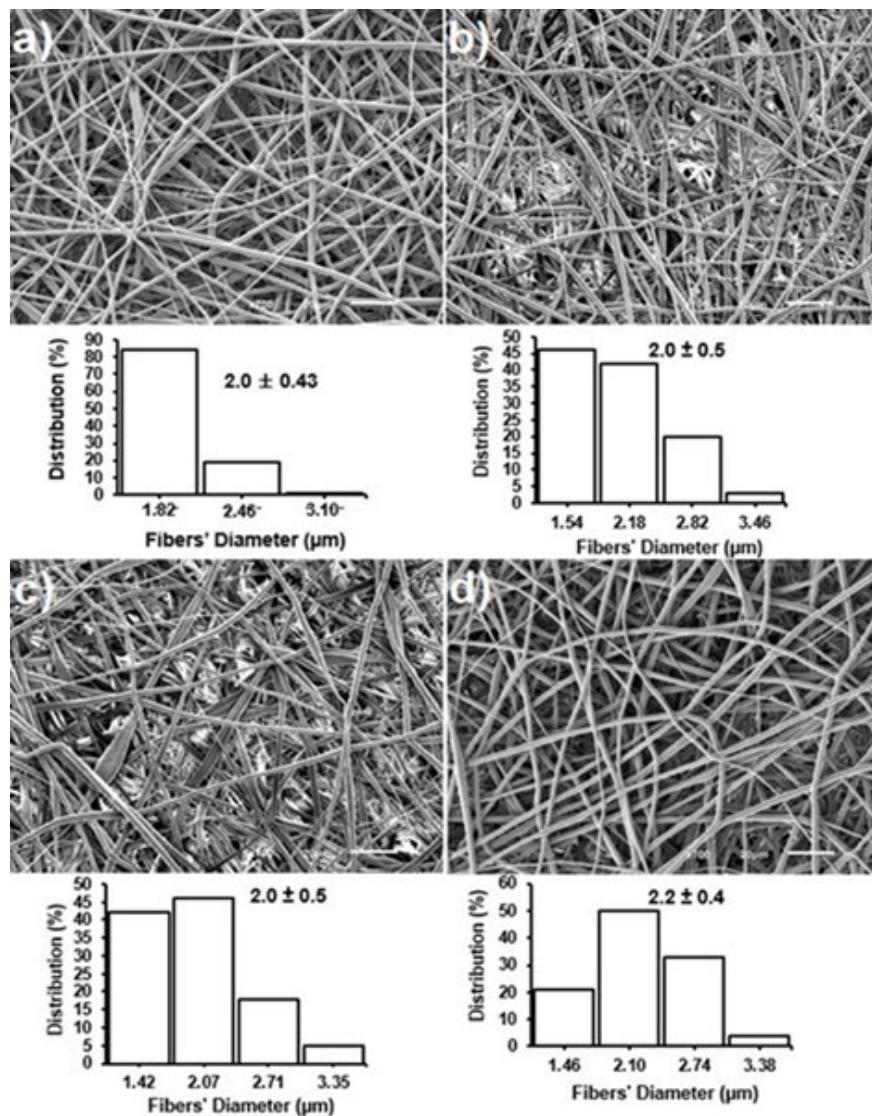


Figure 4: Diameter distribution of microfibers in films based on a) PLA, b) PLA+1% CNF, c) PLA+3% CNF and d) PLA+5% CNF

Tear resistance

The results of the tear resistance tests are shown in Table 1. It is observed that the addition of 1% CNF reinforces the material. It is evident that the films manufactured without the addition of CNF show low resistance to tear, while the addition of 1% CNF as reinforcement of the PLA gives an increase in the tear resistance of 37%. However, it can be observed that, when 3% and 5% CNF was added, the tear resistance of the material decreased, suggesting that the higher loading of CNF causes a reduction of mechanical properties of the films. These findings are in agreement with previously reported results in the literature, which also indicated that the addition of CNF in percentages of 3% and 5% leads to lower tear strength in relation to films reinforced with

1% CNF.²²⁻²³ However, the tear strength values obtained with the addition of 3% and 5% CNF were still higher than those obtained for the neat PLA films.

Photodegradation and mechanical properties

The effects of photodegradation on the mechanical properties of the films were investigated. In Figure 5, the behavior of the films in terms of their tensile strength is shown before and after the photodegradation experiment. Figure 6 presents the results obtained for the strain behavior of the films before and after photodegradation. It can be observed that the mechanical properties of both the films prepared from PLA and those from PLA+CNF were affected by the UV radiation. Ultraviolet radiation

causes photo-oxidative degradation, which leads to breaking of the polymer chains, reducing the molecular weight.²⁴ As a result, the deterioration of the material occurs, with a consequent loss of mechanical properties. After photodegradation, the biopolymer films become brittle, are easily broken into small particles and scattered, which are, however, harmless to the surrounding environment and living beings.²⁴

Furthermore, it can be observed that the presence of CNF does not affect the degradability of the films upon photodegradation. However, the CNF do have a reinforcing effect. Thus, it is noted in Figure 5 that the PLA films subjected to aging exhibit a decrease in tensile strength up to 46%, whereas in the films of PLA+1% CNF,

there is a decrease of 43%. Meanwhile, the films composed of PLA+3% CNF and PLA+5% CNF show a decrease of up to 29%.

As may be remarked in Figure 6, the photodegradation also affects the elasticity of the material because of the fracture of polymeric chains caused by the exposure to UV radiation. When the polymer chains break, the material loses its mechanical stability and the elongation capacity in the material decreases.

In the photodegradation test, it can be observed that the films made of PLA and PLA+CNF react with the energy delivered by ultraviolet rays, this leads to the degradation of the material, indicating a natural tendency towards disintegration.

Table 1
Tear resistance of the films

Sample	Tear resistance	
	N (Newton)	SD
PLA	0.3030	0.06
PLA+1% NFC	0.4161	0.07
PLA+3% NFC	0.3161	0.06
PLA+5% NFC	0.3127	0.08

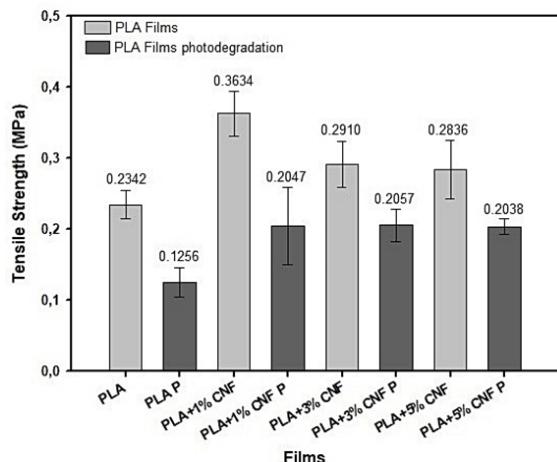


Figure 5: Tensile strength of PLA and PLA+CNF films before and after photodegradation (mean value and 95% confidence interval)

CONCLUSION

Polylactic acid (PLA) films reinforced with cellulose nanofibers (CNF) were successfully prepared and characterized. The morphological characteristics, and the mechanical and photodegradation behavior of the blend films were investigated to compare with those of pure PLA films.

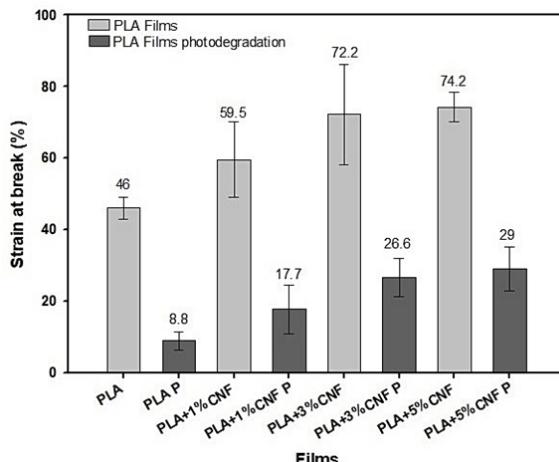


Figure 6: Strain at break of PLA and PLA+CNF films before and after photodegradation (mean value and 95% confidence interval)

Nanofibers with 30 nm in diameter were obtained. In the neat PLA films and those with the addition of 1% and 3% of CNF, a fiber diameter of 2.0 μm was measured. Meanwhile, when 5% of CNF was added, the fiber diameter increased to 2.2 μm . The modification of CNF by acetylation was evidenced by new signals in the FTIR spectra, characteristic of acetylated CNF. The evaluation of the mechanical properties of the

PLA showed a decreasing trend in tear resistance with increasing nanofiber content. Compared to the neat PLA films, the tear resistance increased from 0.30 N to 0.41 N when 1% CNF was added. The photodegradation of PLA and PLA+CNF films has a great impact on the mechanical properties of the films. The photodegradation of PLA films results in a reduction of tensile strength of up to 46%. Similarly, the PLA+1% CNF films showed a decrease of 43%; with a less significant decrease in the PLA+3% NFC and PLA+5% CNF films, which showed a decrease in tensile strength of 29%.

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