Renewable Rice Straw Cellulose Nanofibril Reinforced Poly (ε-caprolactone) Composite Films

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Abstract

In this study, cellulose nanofibrils (CNFs) fabricated from rice straw were utilized to reinforce poly (ε-caprolactone) (PCL), and the structure and properties of these CNF/PCL composite films were analyzed by morphology observation and the characterization of X-ray diffraction (XRD), differential scanning calorimeter (DSC), thermogravimetric analyzer (TGA), mechanical property and water absorption tests. The experimental results revealed that in PCL matrix, CNF exhibits a homogeneous distribution at low content, but shows some aggregates at high content. The incorporation of CNFs doesn't change the crystal type, crystallinity and melting temperature of PCL, but accelerates the crystallization of PCL due to the heterogeneous nucleating agent effect of CNF. Compared with PCL film, the CNF/PCL composite films show obvious improvement of mechanical strength and Young's modulus. However, after the CNF content exceeds 10%, the tensile strength of the composite films begins to decrease, and high loading of CNFs also causes remarkable negative influences on the thermal stability and hydrophobicity of the composite films.

Introduction

Traditional petroleum-derived polymeric materials lead to serious environmental problems induced by the accumulation of plastic wastes due to an even growing landfiling rate and their resistance to microbial degradation (Cocca et al. 2015). Therefore, the development of biodegradable polyesters, such as polylactide (PLA), poly(vinyl alcohol) (PVA), poly(ε-caprolactone) (PCL) (Gunatillake et al. 2006; Okada et al. 2002; Chandra et al. 1998) and their composites with natural reinforcing fillers (Kowalczyk et al. 2011; Avella et al. 2009), has attracted increasing attentions for solving these problems. The blending of biodegradable polymers and natural reinforcing fillers offers the possibility of obtaining a new type of eco-friendly and fully compostable composites. Among the reinforcing fillers, the environmentally friendly cellulose has a wide range of sources and is one of the most abundant natural polymeric materials in the world (Siró et al. 2010). When cellulose fiber reinforced plastics are subjected at the end of their life cycle to a combustion process or landfill, the released amount of CO₂ of the cellulose fiber is neutral with respect to the assimilated amount during the growth (Bledzki et al. 1999).

Poly(ε-caprolactone) (PCL) is a thermoplastic aliphatic polyester produced by chemical synthesis from crude oil via the ring opening polymerization of caprolactone monomer (Khan et al. 2013). PCL is easy to be processed due to its low melting point (58-64°C) and low melt viscosity (Nair et al. 2014), and it can be employed in packaging, tissue engineering, and biomedical applications (Khan et al. 2013). However, the applications of PCL are still limited due to its poor mechanical properties and high cost, and the addition of natural fibers found in biodegradable agricultural residues seems to be a good method to solve the problems (Wu et al. 2012). Straw is a kind of abundant, renewable and fully biodegradable agricultural residue, and its components of biopolymer cellulose make it valuable as additives in plastics after being recovered. Moreover, the biodegradability and mechanical properties can be controlled by filler loadings, and maleated polymer can be used as compatibilizer to improve the miscibility of the composites (Jawaid et al. 2011). The development of biobased products is very helpful for minimizing the
widespread dependence on fossil fuel (Zhen et al. 2016). SEM images indicated poor adhesion between rice straw fiber (RSF) and PCL matrix, and the thermal stability of the composite decreased with the increasing of RSF content, but the tensile modulus of the composite showed an increase with the loading of RSF from 1–7% (Khandanlou et al. 2015). Compared with the RSF/PCL composites, the RSF/maleic anhydride-grafted PCL (PCL-g-MA) composites exhibited noticeably superior mechanical properties, due to the improvement of compatibility with the ester formation between the anhydride groups of PCL-g-MA and the hydroxyl groups of RSF. Water resistance of the RSF/PCL-g-MA composite was higher than that of the RSF/PCL composite (Wu et al. 2012).

Cellulose nanofibrils (CNFs), with diameters between 1 and 100 nm and a few microns in length, are expected to show high stiffness since the Young's (elastic) modulus along the axis of CNF is above 150 GPa and the tensile strength was assessed to be approximately 3 GPa by modeling (Dhakal et al. 2018). They are regarded as unique components to construct some functional nanomaterials that can be applied in the fields of coatings, functional papers, biodegradable plastics and biomedical materials (Vilela et al. 2019). It was reported that CNFs prepared by enzymatic pretreatment of never-dried pulp were utilized to reinforce PCL by one-step wet-feeding method with the addition of fragmentation chain transfer-mediated surfactant-free poly(methyl methacrylate) (PMMA) latex nanoparticles (Vilela et al. 2019; Lo Re et al. 2018) or the esterified and quaternized copolymer of 2-(dimethylamino) ethyl methacrylate and 2-hydroxy methacrylate (Kaldéus et al. 2019). After the addition of PMMA latex or the reactive copolymer compatibilizer, both the CNF dispersion and the mechanical properties of composites were obviously improved due to the electrostatic interaction between CNF and the compatibilizer. The hydrophobic modification of CNF, that is produced from microfibrillated cellulose through the synergy of mechanical and chemical actions derived from the gentle ball milling, is beneficial for preparing both strong and ductile CNF/PCL nanocomposites in a wide range of fiber content, because of the strengthening of interfacial interaction and the improvement of CNF dispersion in the PCL matrix (Deng et al. 2018). It was found that the nanocellulose network is generally formed by the physical entanglement of cellulose nanofilbers in the polymer matrix, and the reinforcing mechanism can be explained by the independent deformation of the continuous nanocellulose network which helps to consume the applied energy under the loading strain (Li et al. 2021).

Until now, the investigations on the straw or CNF reinforced PCL composites were less reported. In this study, CNFs, produced by the 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation and mechanical treatment of the steam exploded rice straw fibers, were utilized to reinforce PCL by melt-blending method, and the morphology, thermal stability, mechanical strength and water absorption of these renewable rice straw CNF/PCL eco-composite films were investigated in detail. It is anticipated that the CNF/PCL nanocomposites may provide high value-added new generation PCL materials with superior performance and extensive applications, due to the filling of excellent reinforcing agent with outstanding mechanical properties, large aspect ratio, low density and biodegradability. Meanwhile, the consumption of natural agricultural waste residues contributes to the solution of low-carbon and environmental protection problems.
Experimental

Materials

Poly (ε-caprolactone) (PCL) was purchased from Solvay Group (Brussels, Belgium), and its number-average molecular weight and polydispersity index were $M_n=9.0 \cdot 10^4$ and $M_w/M_n=1.2$. The bleach reagent hydrogen peroxide ($\text{H}_2\text{O}_2$) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sodium hydroxide (NaOH), sodium chlorite (NaCl), sodium hypochlorite (NaClO) solution, 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) and other chemicals were purchased from Shanghai Titan Scientific Co., Ltd. (Shanghai, China). All the chemicals were used as received without further purification. The steam exploded rice straw fibers used in this study are a commercial product from Zhangjiagang Grain Forage Feed Co., Ltd. (Zhangjiagang, China).

Preparation of rice straw cellulose nanofibrils

The steam exploded rice straw fibers with a length of 2-5 cm were soaked in a 2% NaOH solution at 80°C and stirred for 4 h. The alkali treated fibers were washed with distilled water until the pH of filtrate became neutral, and then immersed in an 8% H$_2$O$_2$ solution at 50°C for 24 h to remove lignin. The bleached fibers were suspended in a 0.05 M sodium phosphate buffer (pH 6.8) dissolving TEMPO (1 mM) and NaCl (0.1 M) with a subsequent addition of 7.5% NaClO solution in an airtight flask. Afterwards, the fiber suspension (0.01 g/mL) was sealed, stirred at 60°C for 24 h, cooled to room temperature, and washed until a neutral pH of filtrate was obtained (Saito et al. 2009). Finally, these TEMPO-oxidized fibers were suspended in de-ionized water at 1% content and agitated at 15,000 rpm for 15 min by using a mechanical homogenizer. The resulting CNF suspension was stored at 4°C before usage. Transmission Electron microscopy (TEM) observation verifies that the rice straw fibers have been fibrillated to nanoscale by the above treatments. Most rice straw CNFs have diameters in the range of 5-12 nm and length longer than 1200 nm, and the aspect ratio of CNFs is more than 100. Moreover, the CNFs exhibit entangled network structures in TEM images (Wang et al. 2018).

Preparation of CNF/PCL composite films

The CNF suspension obtained above was concentrated, and then melt blended with PCL in a 50EHT 3Z “Plastograph” Mixer (Brabender, Germany) at 150°C and a screw speed of 100 r/min. After the torque reached equilibrium, the obtained blend was dried in an oven at 38.5°C, and then hot-pressed into films of 0.2 mm in thickness at 150°C for 10 min by using a LP-S-50 Vulcanizing Press (Labtech Engineering, Thailand). According to the content of rice straw CNFs, these CNF reinforced PCL composite films were named as $n$CNF/PCL, in which $n$ represents the mass percentage of rice straw CNFs. The concentration of CNFs ($C_{\text{CNFs}}$) ranges from 0.5–15%. At the same time, the pure PCL was also hot-pressed into a film for comparison. PCL and CNF/PCL composite films were cut into suitable samples before measurements.
Characterization of CNF/PCL composite films

The morphology of the CNF/PCL composite films was observed by a JSM-7800F Prime Scanning Electron Microscopy (SEM, JEOL, Japan) at room temperature. Before measurements, the CNF/PCL composite films were cryo-fractured after freezing pretreatment by liquid nitrogen, and then sputter-coated with gold to improve the conductivity through an E-1045 Ion Sputter & Carbon Coating Unit (HITACHI, Japan).

A Rigaku D/max2550VL/PC system (Rigaku, Japan) equipped with a Ni-filtered CuKa radiation was operated to obtain the XRD diffractograms. The measurements were carried out at 35 kV and 200 mA from 5 to 30° at a scanning rate of 5°/min and an interval of 0.02°.

During the differential scanning calorimeter (DSC) measurements, the CNF/PCL composite films were placed in a 204 F1 DSC system (NETZSCH, Germany), heated quickly to 100°C and kept for 5 min to eliminate the thermal history, cooled to 0°C at 10°C/min, and then reheated to 100°C at 10°C/min. The test atmosphere was nitrogen.

The thermal stability of CNF/PCL composite films was evaluated by the weight change of the samples in a Q5000IR Thermogravimetric Analyzer (TGA, TA, USA). The measurements were performed in a nitrogen atmosphere from 50 to 600°C with a heating rate of 20°C/min.

The tensile strength and elongation at break of the CNF/PCL composite films were measured by a Z020 static materials testing system (Zwick Roell, Germany) according to the standard of GB13022-91 at a cross-head speed of 5 mm/min. The tensile samples were obtained by cutting the films into a dumbbell shape with dimensions of 50 mm in length and 4 mm in narrow width. Five specimens were tested for each sample, and the reported results were average values.

As for the water absorption tests, the CNF/PCL composite films were dried in a vacuum oven at 38.5°C until a constant weight was obtained ($W_1$), and then immersed in distilled water for 24 h at room temperature. Afterwards, these films were taken out, wiped with a tissue to remove surface water and weighed ($W_2$). Three specimens were tested for each sample to obtain the average value for evaluation. The water absorption of each sample was determined by the following equation (Ibrahim et al. 2013):

$$\text{Water absorption (\%) } = \frac{(W_2 - W_1)}{W_1} \times 100$$

Results And Discussion

Morphology observation

Figure 1 shows SEM images of the cryo-fractured surface of PCL and CNF/PCL composite films. As can be seen from Figure 1, compared with pure PCL, there are many white dots on the fractured surface of the CNF/PCL composite films, which should be formed by the CNF particles. It is obvious that in PCL matrix,
CNF exhibits a homogeneous distribution at $C_{CNFs}$≤1%, but shows some agglomerates at $C_{CNFs}$=5%, just as the CNFs prepared from never-dried pulp did in PCL matrix (Vilela et al. 2019). At low $C_{CNFs}$, with the interactions of the hydroxyl groups in CNF and the carbonyl groups in PCL chains and the loading of mechanical shear force, it is easy for CNFs to disperse uniformly in PCL matrix without aggregation (Wu et al. 2006). However, when CNF addition increases up to 5%, the excessive CNFs cannot interact with PCL well and begin to aggregate into larger particles, which make the surface become much rougher. Meanwhile, some filaments (pointed out by arrows) can be seen clearly from the fractured surfaces of pure PCL film and the PCL composite films of 0.5CNF/PCL and 1CNF/PCL. The formation of filaments indicates the strong toughness of PCL. Nevertheless, the 5CNF/PCL composite film shows no apparent filaments, due to the strengthening of rigidity and brittleness caused by a large quantity of CNFs. The early occurrence of CNF aggregation and the increase in the brittleness and roughness of PCL composite film should be attributed to the weak compatibility between the hydrophobic PCL matrix and hydrophilic CNF fillers. However, according to the tensile test results shown later, the weak compatibility between PCL and CNF does not affect the reinforcing effect of CNF, and the tensile strength and Young’s modulus of the CNF/PCL composite films still exhibit a remarkable improvement.

X-ray diffraction (XRD)

Figure 2 shows the X-ray diffraction patterns of CNF, PCL and CNF/PCL composite films. In Figure 2, CNF exhibits two overlapped weak peaks at around 14.7° and 16.2° and a sharp and strong peak at around 22°, which originate from the diffraction of the (1-10), (110) and (200) crystalline planes of cellulose I (Junior et al. 2018). However, these diffraction peaks cannot be clearly visible for the CNF in the PCL composites because of its small crystallite size. PCL and CNF/PCL composite films present three peaks at around 21.4°, 22° and 23.7°, and these peaks correspond to the diffraction of the (110), (111) and (200) crystalline planes of PCL, respectively (Wu et al. 2006). It can be found that the position of the diffraction peaks of PCL does not change obviously after the addition of CNFs, which implies that the CNF fillers have not altered the crystal type of PCL, similar to the results of nanocellulose/PCL and cellulose nanocrystal/PCL composites (Li et al. 2020; Hivechi et al. 2021). Nevertheless, with the increase of CNF addition, the intensity of the diffraction peaks of PCL gradually decreases due to the reduction of PCL concentration.

Differential scanning calorimetry (DSC) measurements

DSC cooling and heating thermograms of PCL and CNF/PCL composite films are shown in Figure 3. The values of phase transition temperatures (crystallization temperature $T_c$ and melting temperature $T_m$) and enthalpies (crystallization enthalpy $\Delta H_c$ and melting enthalpy $\Delta H_m$) recorded by DSC are summarized in Table 1. The degree of crystallinity was calculated by the following equation:

$$\chi = \frac{\Delta H_m}{\Delta H_{m100\%}(1 - W_{CNFs})}$$
where $\Delta H_m$ is the melting enthalpy of the composite films, $\Delta H_m^{100\%}$ is the melting enthalpy of 100% crystalline PCL (142 J g$^{-1}$ (Tsuji et al. 1998; Crescenzi et al. 1972)), and $W_{CNFs}$ is the mass fraction of CNFs in the composite films. It can be found from Table 1 that the $T_m$ of pure PCL is 56.2°C, and the $T_m$ of 5CNF/PCL and 10CNF/PCL composites is 56.5°C and 56.6°C, respectively. The crystallinity of pure PCL is 49.1%, and the crystallinity of 5CNF/PCL and 10CNF/PCL composites is 50.8% and 50.7%, respectively. Thus it can be seen, the addition of CNFs has no significant effect on the melting temperature and crystallinity of PCL. Similar behaviors were also found for the PCL composites containing the CNFs from never-dried pulp or cellulose nanocrystals from cotton waste or cellulose nanofibers obtained by gentle ball milling (Vilela et al. 2019; Deng et al. 2018; Hivechi et al. 2021).

Although $T_m$ of PCL is nearly the same for all the CNF/PCL composite films, the $T_c$ of PCL in the CNF/PCL composite films exhibits a remarkable increase, presenting an increment of about 12°C at $C_{CNFs}$=10%. Clearly, the incorporated CNFs do not change the thickness of PCL crystals (Li et al. 2020), but their heterogeneous nucleating agent effect does accelerate the crystallization of PCL. In general, the crystallization of polymers consists of nucleation and crystal growth. Larger number of CNFs provide higher-density nucleation sites, but faster crystallization will cause space constraints and influence the orderly organization of molecular chains (Li et al. 2020). Therefore, the crystal growth of PCL is restricted, and the crystallinity of PCL does not increase obviously. Moreover, the gradual decrease in the enthalpies of PCL composite films with the increase of CNF addition should be related to the decline of PCL concentration in the composites.

| Sample      | $T_m$ (°C) | $T_c$ (°C) | $\Delta H_m$ (J/g) | $\Delta H_c$ (J/g) | $\chi$ (%) |
|-------------|------------|------------|---------------------|---------------------|------------|
| PCL         | 56.2       | 21.9       | 69.7                | 70.4                | 49.1       |
| 5CNF/PCL    | 56.5       | 34.1       | 68.6                | 68.4                | 50.8       |
| 10CNF/PCL   | 56.6       | 33.9       | 64.8                | 64.6                | 50.7       |

Thermal stability analysis

Figure 4 presents the TGA curves of CNF, PCL and CNF/PCL composite films. As can be observed from Figure 4, the thermal stability of CNF is significantly lower than that of PCL, and both PCL and CNF/PCL composite films exhibit a single step decomposition process, similar to the thermal decomposition behaviors of PCL composites containing CNFs from never-dried pulp (Vilela et al. 2019) or nanocellulose obtained from microcrystalline cellulose by sulfuric acid hydrolysis (Celebi et al. 2021). The main pyrolysis weight loss zone of pure PCL film is concentrated between 320-550°C. With the increase of temperature, the weight of PCL quickly decreases, and then tends to plateau after 550°C. When the mass loss is 10%, the decomposition temperatures of PCL and PCL composite with 5%, 10% and 15% CNF are
382.6°C, 381.1°C, 366.0°C and 357.1°C, respectively. Clearly, lower loading of CNF \( (C_{\text{CNFs}}=5\%) \) does not have significant influence on the thermal stability of CNF/PCL composite, but higher loading of CNF \( (C_{\text{CNFs}}\geq10\%) \) remarkably destroys the thermal stability of CNF/PCL composite. It seems that the thermal stability of CNF/PCL composite is superior to that of cellulose nanocrystal/PCL composites, which exhibit a rapid decline of onset degradation temperature when the filler content is only 4% (Hivechi et al. 2021). Better thermal stability of CNF/PCL composites may be attributed to the homogenous distribution of CNFs in the PCL matrix. Therefore, enhancing the compatibility between cellulose fillers and PCL matrix is beneficial for improving the thermal stability of PCL composites (Celebi et al. 2021).

Mechanical properties evaluation

Figure 5 shows the tensile properties of PCL and CNF/PCL composite films. It can be noted from Figure 5 that the addition of CNFs obviously enhances the mechanical properties of PCL material. With the increase of \( C_{\text{CNFs}} \), the tensile strength of CNF/PCL composite films first increases and then decreases, showing a maximum of 16.4 MPa at \( C_{\text{CNFs}}=10\% \), 7.5% higher than that of pure PCL film. However, the Young’s modulus of CNF/PCL composite films continues increasing with the addition of CNFs, attaining 595 MPa at \( C_{\text{CNFs}}=15\% \), 76% higher than that of pure PCL film. Thus it can be seen, smaller number of CNFs can disperse in the PCL matrix well and exhibit reinforcing effects by transferring the external loading stress, but larger number of CNFs will result in the aggregation of excessive nanofibrils and reduce the reinforcing efficiency. Nevertheless, it seems that the dispersion state of CNFs does not cause significant negative effects on the improvement of the modulus of PCL composite films.

Obviously, good dispersion of CNFs in PCL matrix plays a very important role in the reinforcing efficiency of CNF for PCL. It was reported that there are a lot of hydroxyls exposed on the surface of CNFs that lead to the self-aggregation of CNFs (Deng et al. 2018). The CNFs obtained by gentle ball milling of microfibrillated cellulose seem to aggregate more easily than our CNFs obtained by TEMPO-oxidization, and the resultant CNF/PCL composite shows a maximal tensile strength at a very low filler loading below 1% (Deng et al. 2018). Earlier appearance of isolated entangled fibril aggregates will restrict the further improvement of the mechanical strength of PCL composites. According to the results of the PCL composites containing CNFs obtained from the enzymatic pretreatment of never-dried pulp (Lo Re et al. 2018), the dispersion of CNFs in PCL matrix can be greatly improved by the use of wet feeding technique and latex compatibilizer, and the tensile strength and Young’s modulus of the PCL composites were remarkably promoted.

Our previous research results reveal that most CNFs have diameters in the range of 5-12 nm and length longer than 1200 nm (Wang et al. 2018). Clearly, the diameters of CNFs isolated from rice straw are much smaller than those of CNFs obtained from flax, cotton, soy hulls and para rubber wood, which are typically in the range of 20-90 nm (Qua et al. 2009; Alemdar et al. 2008; Kamphunthong et al. 2012). The aspect ratio of the rice straw CNFs is more than 100, much higher than that of the above CNFs reported. In this case, the CNFs from rice straw might give a greater reinforcing efficiency due to their higher aspect ratio. In addition, the entangled fiber networks can be observed for these rice straw CNFs in the TEM
images, and these network structures will also be beneficial for the improvement of fiber reinforcing effects (Wang et al. 2018).

Water absorption

Figure 6 gives the values of water absorption for the CNF reinforced PCL composite films after being soaked in distilled water for 24 h. As can be observed from Figure 6, the water absorption of pure PCL film is almost 0%, indicating that PCL is a hydrophobic polymer. It is the nonpolar hydrocarbon groups accumulated on the surface of PCL that generate a hydrophobic surface for PCL to resist the water adsorption (Lo Re et al. 2018). The values of the water absorption of the 5CNF/PCL, 10CNF/PCL and 15CNF/PCL composite films are 0.33%, 0.73% and 1.34%, respectively, which implies that the hydrophobicity of CNF/PCL composite films decreases with the increase of CNF addition, similar to the behaviors of the PCL composite containing the CNFs obtained by the sulfuric acid hydrolysis of microcrystalline cellulose (Celebi et al. 2021). CNF is a kind of hydrophilic material with large quantities of hydroxyl groups in the molecular chains. After being immersed in water, the hydroxyl groups on the CNF surface form a lot of intermolecular hydrogen bonds with water molecules, thus remarkably enhancing the water absorption of PCL composite films. It can be noted from Figure 6 that with the increase of $C_{\text{CNFs}}$, the curve tilts up, revealing that the increase in the water absorption of CNF/PCL composite becomes faster and faster. This phenomenon can be explained by the interfacial compatibility between CNF and PCL and the dispersion state of CNFs in PCL matrix. When $C_{\text{CNFs}}$ is low, CNFs can be evenly dispersed in the PCL matrix, and the microstructure of PCL composite is compact with CNF fillers mainly encapsulated by PCL matrix, thus making the water absorption of CNFs to be hindered due to less voids and water absorption channels. However, when $C_{\text{CNFs}}$ is high, CNFs form agglomerates in the PCL matrix, and it is difficult for PCL matrix to completely enclose the CNF particles. In this case, the structure of CNF/PCL composite is loose with more voids and water absorption channels, so the water absorption of CNF/PCL composite increases rapidly.

Conclusions

The rice straw CNF reinforced PCL composite films were prepared by melt blending method. A small number of CNFs can be uniformly dispersed in the PCL matrix, but when the content of CNFs reaches 5%, CNFs will partially agglomerate. After the addition of CNFs, the crystal structure and melting temperature of PCL do not change, but the crystallization temperature and water absorption increase and the thermal stability decreases for the CNF/PCL composites. CNF exhibits obvious reinforcing effect for PCL, and the CNF/PCL composite films show a continuous increase of the Young’s modulus but a maximal tensile strength at a 10% CNF content.

Declarations

Conflict of interest
There are no conflicts to declare.

Author Contributions

All the authors participated, discussed the results, and reviewed the manuscript.

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Figures
Figure 1

SEM micrographs of the cryo-fractured surface of PCL and CNF/PCL composite films: (a) PCL, (b) 0.5CNF/PCL, (C) 1CNF/PCL, (d) 5CNF/PCL. The filaments were pointed out by the arrows.

Figure 2

X-ray diffraction patterns of CNF, PCL and CNF/PCL composite films. The inset is the magnified X-ray diffraction pattern of CNF.

Figure 3

DSC curves of PCL and CNF/PCL composite films: (a) heating curves; (b) cooling curves.
Figure 4

TGA results of CNF, PCL and CNF/PCL composite films.

Figure 5

Tensile properties of PCL and CNF/PCL composite films: (a) tensile strength, (b) Young's modulus.
Figure 6

Water absorption of PCL and CNF/PCL composite films.