

Degradable Nursery Containers Made of Rice Husk and Cornstarch Composites

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The degradation behavior was investigated for eco-composite nursery containers (NCs) prepared with rice husk and cornstarch adhesive modified with urea formaldehyde (UF) as a wet strength agent. The wet shear strength, water absorption capacities, and biological degradation of NCs within soil were also investigated. Quantitative analysis of the thermal degradation behavior of different NC versions was performed by thermo-gravimetric analysis (TGA). The results demonstrated that the introduction of the UF agent accelerated the soil degradation of the NCs matrix to a certain extent. The maximum cumulative mass loss was 51.1% when the UF content of NCs was 8 wt.%. Moreover, the dry strength of the mixed urea formaldehyde-cornstarch adhesive (UCA) was increased by 108.9% compared with cornstarch adhesive (CA). The results of this work indicate the improved biodegradability of the NC eco-composites, which could make them potential sustainable alternatives for conventional plastic pots.

Keywords: Rice husk; Nursery containers; Eco-composites; Morphological structure; Biodegradable materials

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INTRODUCTION

Rice is one of the world's most prominent agricultural crops. Rice straw, a major by-product of the rice crop, is undeservedly treated as a waste product in many countries that lack efficient utilization technology (Gao *et al.* 2008; Huang *et al.* 2008). The current practices for managing straw waste are detrimental to the environment and are potentially hazardous to human health (Kristensen and Kristensen 2004). Using straw waste to produce composite materials is both economically and environmentally beneficial (Ramamoorthy *et al.* 2015). The use of straw waste in the preparation of biodegradable materials to replace plastic bowls is one of the more attractive ways to utilize agricultural waste (Wu *et al.* 2013). An abundant variety of container types and configurations are available to growers for producing seedlings, and until recently, plastic containers were the most commonly used (Dunn *et al.* 1997). Countless plastic containers are discarded once the plant dies or is replanted. Because plastic containers do not degrade, the resulting pollution is more serious. Moreover, with plastic containers there is a need to remove the seedling to transplant it, which can cause root damage. Transplanting from plastic containers is also time consuming and leads to higher manufacturing costs.

Natural polymers have the potential to ultimately biodegrade through natural environmental processes, and they can also be thermally processed into various articles (Middleton and Tipton 2000; Williams and Hillmyer 2008). Starch is a popular

biodegradable material that has many applications due to its abundance, renewability, thermo-process ability, and adequate thermal stability for melt blending with synthetic plastics (Yu *et al.* 2006; Shah *et al.* 2008; Liu *et al.* 2012; Wu *et al.* 2013). The incorporation of starch into plastics to enhance their fragmentation and degradability in the environment has generated considerable interest. Also, starch is extensively used as a binder (Wang *et al.* 2012). There are many reports on the synthesis, characterization, and properties of starch graft copolymers (Bruyn *et al.* 2007; Liu *et al.* 2012). Grafting is an important technique for modifying the physical and chemical properties of polymers, and the grafting of synthetic polymers onto a starch backbone is one of the best ways to improve the binding properties of starch. Wang *et al.* (2012) reported that a renewable starch-based wood adhesive, useable at room temperature, was prepared by grafting vinyl acetate (VAc) onto starch using ammonium persulfate (APS) as the initiator. Compared to the blend of commercial polymer vinyl acetate (PVAc)/gelatinized starch, the shear strength of the grafted starch adhesive increased by 59.4% in the dry state and by 32.1% in the wet state, while its water resistance increased by 61.1%. Therefore, starch must be modified to improve the strength and water resistance of starch-based adhesives (Liu *et al.* 2012; Wu *et al.* 2013). Chai *et al.* (2009) showed that the addition of corn starch modified by a reaction with sodium trimetaphosphate could enhance its water uptake property. When the modified corn starch was blended with different amounts of PVAc, the resulting blend displayed a maximum weight loss during the enzymatic degradation and improved degradability.

However, there is very limited research on the degradation of nursery containers based on rice husk and cornstarch adhesives in soil medium or how the cornstarch content affects the rate and extent of degradation. To develop improved degradable NCs based on rice husk and cornstarch adhesives, urea formaldehyde resin (UF) was added into cornstarch adhesive to produce urea formaldehyde-cornstarch adhesive (UCA) for making the NCs in this study. The main objectives of this study were to characterize the water absorption and mass loss rate of the nursery containers made from rice husk and UCA adhesives (cornstarch adhesive and UF), determine the internal structure and thermo-stability of the rice husk and adhesive composites, and investigate the biodegradation process and biodegradation mechanism of the NCs.

EXPERIMENTAL

Materials

Rice husk (RH) feedstock was collected from an experimental station of the Jiangsu Academy of Agricultural Sciences in Nanjing, China, in August 2013. The RHs were powdered into particles with lengths less than 0.45 mm using a pulverizer. The moisture content of the prepared powder was approximately 12% after drying under ambient conditions.

The cornstarch adhesive, which was used as the crosslinking component to produce the nursery containers, was synthesized in the laboratory as described previously (Wu *et al.* 2013). A series of urea formaldehyde-cornstarch adhesive (UCA) derivatives were prepared by adding UF resins in different amounts (4, 8, 12, and 16% w/w, as wet strength agent) to improve the shear strength of cornstarch adhesives. The products were named UCAI, UCAII, UCAIII, and UCAIV, respectively. Ammonium chloride (NH₄Cl, 20 wt.% solution) was used as a curing catalyst with a concentration of 0.01 w/w of UF resin.

Preparation of Biodegradable Nursery Containers

Four types of NCs were prepared with rice husk and the four UCA variants (UCA I, II, III and IV), which were named NCI, NCII, NCIII and NCIV, respectively.

A measured quantity of UCAI (II/III/IV) adhesive (the amount of UCA used was 50% by weight of rice husk) was mixed with the catalyst (NH_4Cl) and then poured on a pre-weighed amount of rice husk. The mixture was placed in a 10-L high-speed mixer equipped with a 2.2 kW motor and a fixed speed spindle that reached up to 200 rpm. Next, 200 g of paraffin wax was added as a release agent, and the mixture was stirred evenly for about 30 min until the moisture content of the blended material was about 14%. The semi-finished materials were placed in a hot-press machine with nine-cavity molds at a temperature of 100 °C and a compaction pressure of 13 MPa for 25 s. The physical and chemical characteristics of the NCs are given in Table 1.

Table 1. Physico-Chemical Characteristics of Nursery Containers

NC	Organic Matter (g/kg)	TOC (mg/kg)	TN (g/kg)	C/N ratio
NC I	77.12 ± 1.94a	44.73 ± 1.13a	17.23 ± 0.56d	25.96
NC II	71.47 ± 4.23a	41.46 ± 2.46a	30.81 ± 1.15c	13.46
NC III	58.69 ± 1.71b	34.04 ± 0.99b	40.79 ± 2.79b	8.35
NC IV	56.93 ± 7.65b	33.02 ± 4.44b	56.61 ± 8.18a	5.83

Data are given as mean ± standard deviation for n=3 trials; values within the same column followed by different letters are significantly different at $P < 0.05$; TOC means total organic carbon; TN means total nitrogen; C/N means the ratio of carbon/nitrogen.

Analytical Methods and Related Theory

Kinetic studies of water absorption

The water absorption (WA) value is a useful indicator of the swelling capacity of NC, and this test was performed according to ASTM D570-98 (2010). Pre-dried samples were weighed and then were immersed in a distilled water bath at 25 °C for different time durations. They were removed during the first day of immersion at specific time intervals of 0.15 h, 0.3 h, 0.5 h, 1 h, 2 h, 3 h, 8 h, and up to 30 h. The water on the surface was wiped off, and the samples were weighed again to determine the amount of absorbed water. The uptake of water was recorded until there was no significant change in weight, indicating that an equilibrium was attained. The percentage of moisture content (M_t) was determined using the following equation,

$$M_t(\%) = \left(\frac{W_t - W_0}{W_0} \right) \times 100 \quad (1)$$

where W_t was the weight of the sample at time t , and W_0 was the initial weight of the sample.

The water absorption behavior in the samples can be studied as a Fickian behavior. For short immersion times, the diffusion coefficient, D , is determined using the following formula (Reddy *et al.* 2010; Alamri and Low 2013),

$$\frac{M_t}{M_\infty} = 4 \left(\frac{Dt}{\pi h^2} \right)^{1/2} \times 100 \quad (2)$$

where M_t was the moisture content at time t , M_∞ was the equilibrium moisture content, and h was the sample thickness. Therefore, the diffusivity, D , was determined from the

initial slope of the moisture absorption *versus* the square root of time.

Soil burial degradation test

The degradability of the NC was tested under controlled conditions in a laboratory scale, homemade, soil burial system consisting of four incubators. The specimens were first placed inside net bags with small holes, which were buried in incubators with soil at a depth of 100 mm. The test was similar to the methods published by Yoon *et al.* (2012) with a slight modification. The moisture content of the soil was maintained at 65% by sprinkling water with an ambient temperature of 30 °C. The specimens were taken out at irregular time intervals, washed with distilled water, and vacuum-dried at 103 °C to reach constant weight. Weight loss of the specimens over time was used to indicate the degradation rate of NC in the soil burial test, according to the below Eq. 3,

$$\text{Weight Loss}(\%) = \left(\frac{M_0 - M_i}{M_0} \right) \times 100 \quad (3)$$

where M_0 was the initial weight of sample after drying, and M_i was the weight of degraded sample after vacuum drying.

Surface morphology

The microstructures of the samples were analyzed by scanning electron microscopy (SEM, FEI Quanta 200, Hillsboro, OR, USA) operated at 20 kV and 20 mA. Samples were fractured in liquid nitrogen and gold-coated before SEM observation.

IR analysis

Infrared (IR) spectra were recorded by a FT-IR spectrometer (J200, Thermo Fisher Scientific, Waltham, MA, USA) with a golden gate ATR attachment and diamond crystal. The samples were sliced into small pieces and ground in an agate mortar. A total of 32 scans in the region of 4000 cm^{-1} to 400 cm^{-1} were acquired with a resolution of 4 cm^{-1} .

Thermo-stability analysis

Isothermal thermal gravimetric analyzer (TGA) measurements were carried out using thermo-gravimetric equipment (SII-7200, Hitachi Limited, Tokyo, Japan). Nitrogen was used as the carrier gas at a flow rate of 25 mL/min. The heating rates were controlled at 20 °C/min from 40 °C to 800 °C. The sample weight in all tests was approximately 8 to 10 mg. The initial decomposition temperature (T_0) was defined as the onset of weight loss taken at 1%, and the temperature at maximum decomposition rate (T_{max}) was obtained from the maximum of normalized derivative curves (DTG). An empty alumina crucible was used as reference. The Coats and Redfern's integral method (Genieva *et al.* 2010) was applied for the mathematical analysis of the thermo-degradation kinetic parameters of the NCs based on the TG/DTG data (Yang *et al.* 2010). This method is defined by the Arrhenius equation (Eq. 4),

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = \ln \left(\frac{AR}{\beta E_a} \right) - \frac{E_a}{RT} \quad (4)$$

where $\alpha = (w_0 - w)/(w_0 - w_f)$, $\beta = (dT)/(dt) = \text{constant}$, T was the absolute temperature (K), A was the pre-exponential or frequency factor (s^{-1}), R was the gas constant with a value of 8.3145, E_a was the activation energy (kJ/mol), w was the mass fraction present at any time, w_0 was the initial mass fraction, and w_f was the mass fraction at infinity. Plotting $\ln[-\ln(1-\alpha)/T^2]$ *versus* $1/T$ results in a straight line with a slope of $(-E_a/R)$ and a y

intercept of $\ln[(AR)/(\beta E_a)]$, providing the values of E_a and A (Ke *et al.* 2011).

Statistical analyses

Data were analyzed using the Software Statistical Package for Origin Pro (Ver. 9.0, OriginLab, Northampton, MA, USA) and SPSS (Version 22.0, SPSS Inc., Chicago, IL).

RESULTS AND DISCUSSION

Water Absorption Capacity

Water absorption (WA) was measured to evaluate the swelling capacity of the different NC versions. Figure 1 shows the results of the water absorption for NCs with different treatments. The water absorption capacity for all samples increased quickly during their initial swelling, then increased slowly, and finally reached equilibrium. Typical Fickian diffusion behaviors were observed for all samples (Alamri *et al.* 2013). The NC I and NC II samples had WA values of 39.39% and 38.42%, while the NC III and NC IV samples had lower WA values of 32.31% and 24.78%, respectively, after 30 h of immersion in distilled water. The water absorption for NCs reinforced with UF was lower than that of the blank, which indicated that these samples were more water resistant. The samples (blank) bonded by pure CA were delaminated when they were immersed in water, so their WA could not be measured. This result was expected due to the hydrophilic nature of both CA and rice husk, which causes them to absorb a large amount of water, depending on the environmental conditions.

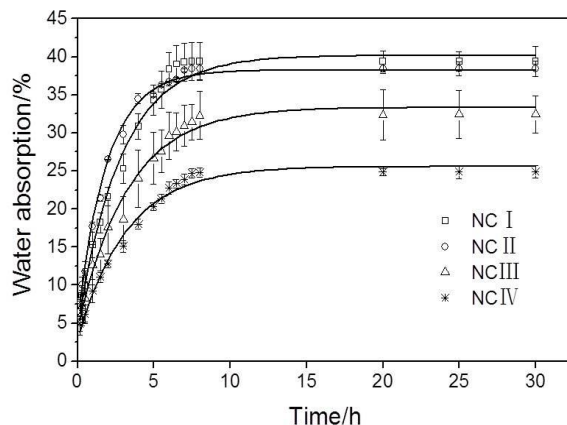


Fig. 1. Water absorption curves at 25 °C for nursery containers (NCs) prepared with rice husk and cornstarch adhesives modified with urea formaldehyde (UF); The error bars represent the standard deviation of actual test values ($n=3$).

These observations were confirmed with the performance indicators of UCA (Table 2). UCA adhesives showed a wet strength of 0.33 MPa or higher. It was expected that the NCs bonded with UCA adhesives would absorb moisture at a slower rate than the pure NCs because CA reacts with UF to form a strong cross-linking network that provides more hydrophobicity. The modification of the NCs with UF may induce two effects: (1) hydrophilic hydroxyl groups of rice husk fiber and cornstarch adhesive are more effectively covered by wet strength agent (UF adhesive), which causes the resulting

hydrogen bonding between the fiber and water to slow down the absorption of water molecules; (2) the structure of UF reacts with CA to form a cross-linking network that can improve water resistance, thus making it an essential ingredient in the adhesive system.

Table 2. Properties of Cornstarch Adhesives

Matrix Resin	Shearing Strength (MPa)		Water Resistance (h)	Solids Content (%)	pH
	Dry state	Wet state			
CA	1.12 ± 0.11c	/	0.75 ± 0.08d	27.46 ± 0.38b	4.98 ± 0.13b
UCA I	2.15 ± 0.23b	0.33 ± 0.04c	72 ± 1c	28.27 ± 0.54b	5.12 ± 0.15b
UCA II	2.34 ± 0.19b	0.37 ± 0.06c	75 ± 2c	30.26 ± 0.64a	5.36 ± 0.04a
UCA III	2.47 ± 0.13a	0.45 ± 0.05b	108 ± 3b	31.08 ± 0.46a	5.49 ± 0.06a
UCA IV	2.51 ± 0.24a	0.49 ± 0.05a	124 ± 4a	32.05 ± 0.81a	5.54 ± 0.04a

"/", no shearing strength. Data are given as mean ± standard deviation, for n=3 trials; values within the same column followed by different letters are significantly different at $P < 0.05$.

Mohan and Kanny (2011) stated that the maximum water uptake depends on the rate of water absorption into the composites rather than on rate of water diffusion, which was measured along the thickness direction of the samples. The equilibrium moisture content (M_{∞}) and D values are summarized in Table 3. The NC immersed in distilled water showed lower values of both M_{∞} and D compared to the sample bonded by pure CA. It can be seen that the addition of the wet strength agent decreased the rate of water diffusion. Diffusivity decreased slightly as the UF adhesive content was increased from 4 wt.% to 16 wt.%. The maximum water uptake of NCIV decreased significantly to about 37.09% when 16 wt.% of wet strength agent was added. However, the D value of NCII was similar to that of NCI, at 8 wt.% UF adhesive loading. The diffusivity of NCII decreased by 6.25% compared to NCI, while the D value of NCIII significantly decreased by 18.18% compared to NCII. This can be attributed to the increased content of the wet strength agent.

Table 3. The Effect of Wet Strength Agent (UF Adhesive) on the Maximum Moisture Content (M_{∞}) and Diffusion Coefficient (D) of NC in Distilled Water

Samples	Wet Strength Agent Content (wt.%)	M_{∞} (%)	D ($\times 10^{-4}$ mm ² /sec)
NC I	4	39.39	1.76
NC II	8	38.42	1.65
NC III	12	32.31	1.35
NC IV	16	24.78	1.15

Comparison of Degradability

Figure 2 illustrates the variation of weight retention with degradation time of NCs. All the samples in soil degraded rapidly in the first 60 days, and the weight retention increased as the UF content increased, in general.

From the weight retention curves, a long active phase (days 0 to 60) was clearly distinguished. In addition, water entered into the polymer matrix of NC, which caused some swelling of the fibrous material. The intrusion of water initiates the hydrolysis of the polymer, leading to the creation of oligomers and monomers. Consequently, microbial attack was more feasible at this stage.

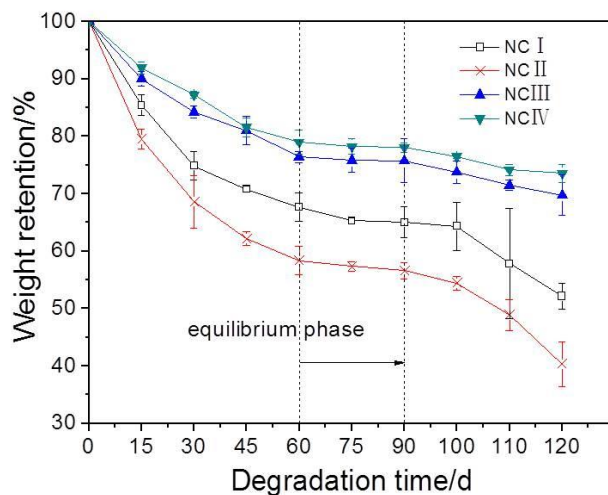


Fig. 2. Weight retention of NCs I, II, III, and IV. The error bars represent the standard deviation of actual test values (n=3).

In this second stage (days 60 to 90), NC I and II samples showed lower weight retention, while NC III and IV samples showed a higher weight retention. At the end of 120 days, all the NCs reached their lowest weight retention levels. NCIII and NCIV had weight retention of about 71.45% and 74.17% after 120 days, while NCI and II had weight retention of 52.6% and 39.85%, respectively. The degradation of NCI and NCII was faster than that of NCIII and NCIV (Fig. 2). It was speculated that the small amount of wet strength agent left in the soil degrades much faster due to its weaker bonding strength, increased distance between fibers, reduced bonding forces in the fibrous network, and loss of its structural rigidity (Pushpadass *et al.* 2010). Interestingly, Figure 2 indicates that NCII lost more mass than NCI. This result was consistent with the results of the WA analysis. Adding the right amount of nitrogen-containing UF resin gave a larger weight loss rate, as the appropriate C/N ratio provided better growth conditions for microorganisms (Table 1). From these results, it is evident that the NCI and II made from UCAI and II had higher degradation rates than the other NCs, and could be potentially suitable for the desired application.

Surface Morphology

The surface morphology of NCII samples before and after degradation was observed by SEM (Fig. 3). Prior to degradation, the morphology of the untreated degradation samples showed that the rice husk was closely bound with the polymer matrix (UCA). The interface presented a relatively compact and smooth surface, which suggested that particles in the adhesive had gathered together (Fig. 3(a)).

After 30 days of incubation, the surfaces became rough. This phenomenon suggested that the interfacial adhesion between the filler and the matrix polymer was weak after degradation in soil (Fig. 3(b)). It was possible to observe the decrease in area and in size of the adhesives, and the fiber was clearly visible as well after 60 days (Fig. 3(c)). The surfaces of NCII became rough, and deep erosion pits with large size could be clearly observed.

Figure 3(d) and (e) showed that several fine voids appeared on the surface of the rice husk, as the hemicellulose and cellulose of the rice husk fiber were degraded, making

the fiber surface rough (Fig. 3(d) and (e)). As reported previously, the wet strength agent acts as a water repellent for the reinforcing material. Because a higher area of wet strength agent started to disintegrate at the same time, there was less strength for the support framework, which decreased the weight retention for NCII.

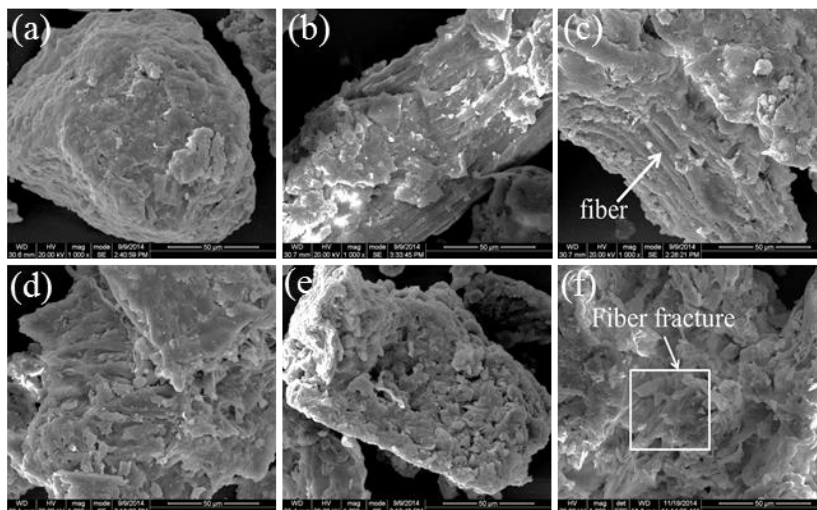


Fig. 3. Scanning electron micrographs (SEMs $\times 1000$) of the surface of NC II before (a), and after degradation for (b) 30, (c) 60, (d) 75, (e) 90, and (f) 120 days

As degradation proceeded, there were obvious histological changes in the longitudinal section of rice straw. After 120 days of degradation, the surfaces showed considerable erosion, and the original surface could hardly be identified. Significant morphological changes occurred (Fig. 3(f)).

Structural Characterization

FT-IR was used to confirm the grafting and modification of CA and to determine the effect of wet strength agent (UF) on the chemical structure of the CA based adhesive. The results are shown in Fig. 4(a). UF showed peaks of relevance at 1666 cm^{-1} , 1542 cm^{-1} , and 1340 cm^{-1} , which were characteristic of amide I (C=O stretching), amide II (N—H bending), and amide III (C—N and N—H stretching), respectively (Essawy *et al.* 2010). The peak at 1124 cm^{-1} and its shoulder at about 1022 cm^{-1} were ascribed to C—H and C—O—C stretching of the carbohydrate fraction in UF, while the broad, strong peak of UF at around 3200 cm^{-1} to 3500 cm^{-1} was due to the stretching vibration of the hydroxyl and amine groups in UF (Essawy *et al.* 2010). The O—H and N—H groups in the UF adhesive form inter- and intra-molecular hydrogen bonding with the C=O group of the amidogen in the UF structure. The bands at 2966 cm^{-1} and 2905 cm^{-1} were related to the asymmetric and symmetric stretching vibrations of —CH₂, respectively. Although hydrogen bonding between cornstarch molecules typically increases the bonding strength of the cured adhesive, it may also decrease its water resistance (Table 2). The band at 3428 cm^{-1} corresponding to the hydroxyl groups of UCAII showed an obvious decrease, which suggested that the water resistance of UCAII was increased. With the introduction of urea-formaldehyde resin, starch adhesive undergoes the grafting reaction. Thereby, urea-formaldehyde segments can be copolymerized into the network structure of CA. The ratio of intensities of the typical infrared absorption bands at 1631 cm^{-1} , 1409 cm^{-1} , and

1240 cm^{-1} for amides I, II, and III, respectively, was an indicator of the successful graft polymerization of CA and the absence of the UF monomer in UCA. Furthermore, the enhancement of the significant band around 1402 cm^{-1} suggested that the —NH_2 group reacted with COO— to form an amide bond. A conclusion could be drawn from Fig. 4(a) that water-resistance of the UCA adhesive improved due to a small amount of UF graft polymerization.

During the decomposition, the peaks related to the UCA resin waned, while the peaks related to the aromatic ring became increasingly dominant (Fig. 4(b)). After 90 days of degradation, the spectrum of NCII showed changed intensities for the peaks at 1653 to 1611 cm^{-1} , 1560 to 1545 cm^{-1} , and 1491 to 1406 cm^{-1} regions, which corresponded to the aromatic ring vibrations and C=O stretching vibrations (Ke *et al.* 2011). This result indicated that the holocellulose of NCII had degraded; thus, the characteristic peak for the aromatic ring vibrations of lignin appeared in the degraded sample when compared to the original NCII composite. Moreover, this result was confirmed by the presence of the sharp bands at 1033 cm^{-1} , which are due to the deformation vibrations of C—H bonds in aromatic rings. The absorption band at 3324 cm^{-1} , due to —OH , became weaker, indicating that the water-resistance increased (Table 2). Interestingly, upon comparing the FT-IR spectra of the degraded NC II and the untreated NCII, the peak at 2916 cm^{-1} shifted to 2966 cm^{-1} and 2990 cm^{-1} , respectively, and the peaks at 2847 cm^{-1} and 2916 cm^{-1} became weaker, which indicated that C—H , C—C , and C—O bonds were influenced by the degradation of cellulose. Moreover, the sharp characteristic peak of SiO_2 at 783 cm^{-1} in the spectrum of decomposed NCII was close to that in the spectrum of rice husk, confirming the presence of SiO_2 in the sample. This phenomenon was due to two reasons: (i) the cornstarch-based adhesive and fiber were decomposed, and (ii) the NCII degradation was due to the fact that bonding strength and water resistance of NCII were lower in the soil medium.

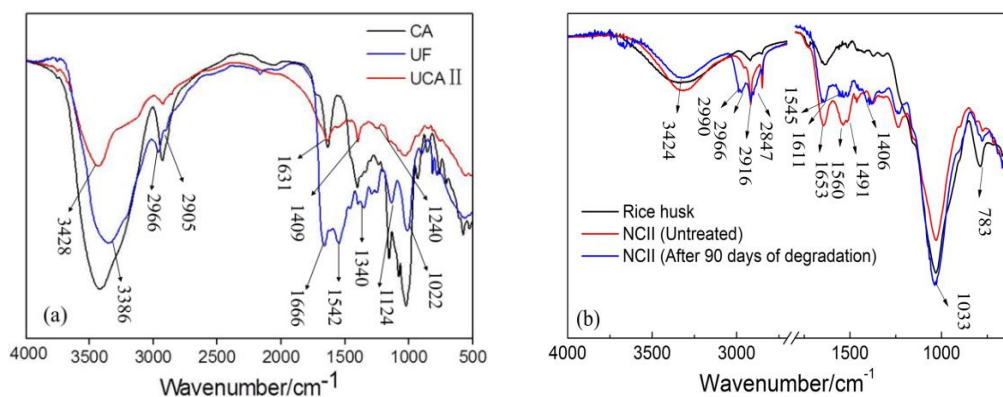


Fig. 4. FT-IR spectra of the different kinds of samples, adhesive (a) and NC II samples (b)

Thermal Stability and Degradation Evaluation

Thermo-gravimetric analysis

Evaluation of the thermal stability of the material is also of great importance for composite applications. Figure 5 shows the TGA and DTG curves of NC II. The first step extended up to 138 $^{\circ}\text{C}$ and accounted for about 8% of the total mass loss. This step was a result of the volatilization of absorbed moisture present in all samples.

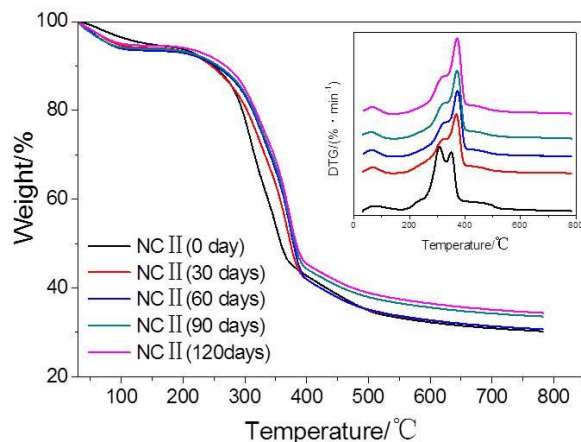


Fig. 5. Weight loss curves and DTG curves for NC II at heating rate of 20 °C/min

The main degradation stage, which occurred at around 220 °C to 420 °C, accounted for approximately 58% of the total weight loss, and it was attributed to the degradation of the main components of NCII. As shown in Fig. 5, there were two significant peaks in the DTG curves of NCII (0 day) in the main degradation stage. A deconvolution method was used as the first approach for splitting the peaks and evaluating the relative contribution of each component. The first peak (309 °C) was assigned to the decomposition of the cornstarch moiety and de-polymerization of the hemicelluloses and amorphous cellulose which degrade more easily than crystalline cellulose (Ciannamea *et al.* 2010). The second peak (352 °C) was related to the random cleavage of glycoside linkages in the remaining cellulose (Ndazi *et al.* 2007; Ciannamea *et al.* 2010). However, there was only one significant peak in the DTG curves of NCII (30 days), NCII (60 days), NCII (90 days), and NCII (120 days), and the T_{max} values of these samples were shifted to 369 °C, 373 °C, 373 °C, and 374 °C, respectively, due to the slight increase in the crystalline cellulose content among the degraded samples.

It is worth mentioning that the peaks at around 317 °C to 332 °C sharply decreased after degradation treatment in soil medium. Moreover, the reverse trend was seen with an increase in degradation time compared to pure NCII, which could be mainly due to the de-polymerization of the functional groups or linkages present in the eco-composite chains under microbial action. This could also be attributed to the decrease in hemicellulose and amorphous cellulose and/or lignin content. Lignin decomposition usually occurs over a wide temperature range between 300 °C and 500 °C (Ke *et al.* 2011).

Additionally, the residue at 800 °C was mostly composed of carbonaceous products and silica from the original samples, and accounted for about 30.12%, 30.61%, 30.64%, 33.46%, and 34.35% of the total weight loss, after degradation treatment for 0 days, 30 days, 60 days, 90 days, and 120 days, respectively. The apparent activation energies (E_a) of the main degradation stage of the studied systems were determined using the Coats and Redfern method (Genieva *et al.* 2010). The Arrhenius plot of $\ln[-\ln(1-\alpha)/T^2]$ and $1/T$ gave a straight line (Fig. 6). Equation 4 was used to calculate the values of E_a at each selected level of degradation time from the Arrhenius plot. The results are given in Table 4. The E_a values for NC II were 8.03 kJ/mol, 5.18 kJ/mol, 4.52 kJ/mol, 5.56 kJ/mol, and 8.50 kJ/mol for samples degraded for 0 days, 30 days, 60 days, 90 days, and 120 days, respectively, at the heating rate of 20 °C/min (Fig. 5). These results

indicated that each step of the degradation had different activation energy throughout the pyrolysis process.

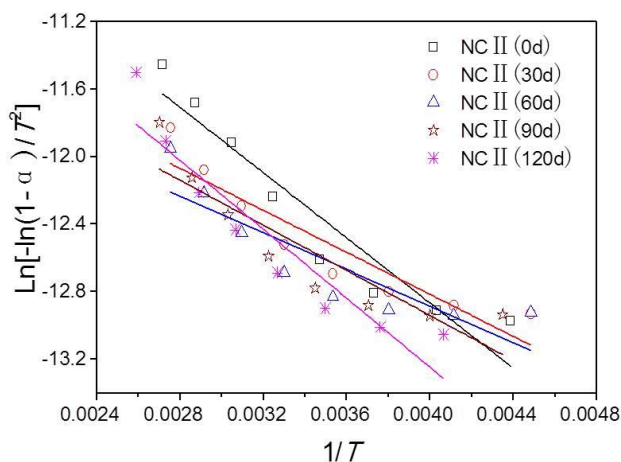


Fig. 6. Arrhenius plot of $\ln[-\ln(1-\alpha)/T^2]$ vs. $1/T$ at heating rate of 20 °C/min obtained by the Coats and Redfern method

Table 4. Kinetic Parameters of the Thermal Degradation of NC II at Heating Rate (β) of 20 °C/min

Days Treated	T_0 (°C)	T_{max} (°C)		Residue at 800 °C (%)	E_a (kJ/mol) Coats and Redfern method
		First peak	Second peak		
0	228	309	352	30.12	8.03
30	223	317	369	30.61	5.18
60	223	323	373	30.64	4.52
90	230	327	373	33.46	5.56
120	246	332	374	34.35	8.50

The decrease in the activation energy for the residual carbohydrates of NCII might contribute to the lower stability during this temperature range. E_a decreased with the increase in incubation time (from 8.03 kJ/mol down to 4.52 kJ/mol), then sharply increased when the degradation time was extended (up to 8.50 kJ/mol). The activation energy showed a peak of 4.52 kJ/mol at the degradation time of 60 days and the E_a varied in a “V”- shape for the different samples during the pyrolysis process. This may be due to the synergistic effect of both cornstarch adhesive and rice husk fibers. Using the kinetic parameters obtained from the Coats and Redfern method, the calculated TG/DTG curves agreed with the experimental results.

Degradation Evaluation

The degradation evaluation was performed on the eco-composite nursery containers to assess their degradation efficiency. Degradation is necessary for water-soluble or water-immiscible polymers because they eventually enter water streams, after which they cannot be recycled nor incinerated. The degradation process of the NCs is illustrated in Fig. 7. Figure 7(a) shows the network structure of NCs. One can envision that the bonding strength was better when rice husk fiber reacted with cornstarch adhesives modified with UF. The introduction of urea-formaldehyde resin maintained the

mechanical strength of NCs during the seeding period. The structural features of cornstarch adhesives modified with UF were confirmed by the FT-IR spectra. In addition, the composite material of the nursery containers degraded faster, and into small oligomers or segments, when the NCs were placed in the natural soil environment (Fig. 7(b) and (c)). This means that the introduced urea formaldehyde not only ensured the mechanical strength properties of the NCs composite, but also improved the biodegradability of eco-composite NCs prepared with rice husk and cornstarch adhesives modified with UF.

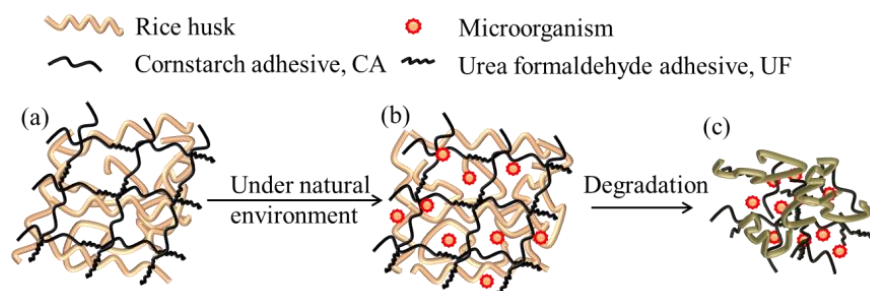


Fig. 7. Schematic illustration of the degradation of NCs: the structure of NCs (a); NCs in natural environment (b); the degradation of NCs (c)

CONCLUSIONS

1. A series of novel, degradable, eco-composite nursery containers (NCs) were prepared using rice husk and cornstarch adhesive modified by urea formaldehyde, and their degradation behavior was analyzed.
2. The maximum cumulative mass loss was 51.13% when the UF content of NCs was 8 wt.%. The dry strength of the mixed urea formaldehyde-cornstarch adhesive (UCA) was increased by 108.92% compared with corn-starch adhesive (CA).
3. The results in the soil burial system showed that the NCI and II eco-composites had higher levels of degradation after 120 days of incubation. Quantitative analysis of the degradation behavior of the components revealed that the incorporation of UF modifying agent accelerated the degradation of the NC matrix, and the optimum amount of UF was 8 wt.% by weight of the CA content.
4. Based on the results, the NC eco-composite with cornstarch adhesive modified by UF wet strength agent meets the requirements for maintaining biological stability. Thus, this work indicated that the NC eco-composites with improved biodegradability could potentially be used as a sustainable alternative to conventional plastic pots.

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