Preparation and Degradation of Seedling Containers Made from Straw and Hydrolyzed Soy Protein Isolate Modified Urea-Formaldehyde Resins

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Straw powders were blended with hydrolyzed soy protein isolate (HSPI) modified urea-formaldehyde (UF) resins to produce biodegradable seedling containers. The tensile strength and the degradability of the seedling containers were characterized. Moreover, the degradation behavior of modified UF resins was investigated using ^{15}N isotopic tracing, dynamic mechanical analysis, ^{13}C CP/MAS NMR spectroscopy, and a scanning electron microscope-energy dispersive spectrometer. The results showed that the best tensile strength of the seedling containers made from HSPI-modified UF resins was improved by 6% compared with the seedling containers made from UF resins. The degradability of the seedling containers made from modified UF resins was improved 8.8 times more than that of unmodified UF resins. HSPI can lower the cross-linking degree of UF resins. The HSPI and urea-formaldehyde molecular chains in the resins were decomposed simultaneously in the soil. After degradation, nodular particles that appeared to be coalesced by small globular particles remained. In the process of degradation, modified UF resins can provide a nitrogen source for crops.

Keywords: Seedling container; Straw; Urea-formaldehyde resin; Hydrolyzed soy protein isolate; Degradability

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INTRODUCTION

Commercial producers may encounter disposal issues for plastic seedling containers, particularly if plant materials are not sold during a season. Consumers must also dispose of plastic seedling containers once the plants are removed (Evans and Hensley 2004). There are biodegradable seedling containers that can be composted, or planted directly into the soil, eliminating the need for plastic containers (Rodda 2008). These biodegradable seedling containers can be made of a combination of adhesives and fibers. These fibers include spruce fibers, sphagnum peat, wood fiber and lime, grain husks, and rice hulls (Evans and Karcher 2004; Wu *et al*. 2013). Urea-formaldehyde (UF) resins are currently the major binders in the industry, due to advantages such as fast curing, good performance, water solubility, and lower prices.

However, a critical disadvantage is that UF is difficult to degrade (Otake *et al*. 1995). Therefore, the present work examines whether UF could be designed to become susceptible to microbial attack, thus becoming degradable in a microbial active

environment while still maintaining favorable properties. Among all the various structures of chemical modifiers, there is particular interest in hydrolyzed soy protein isolate (HSPI) and its functional groups, such as the primary amine, secondary amine, guanidyl, indolyl, *etc*. Also, HSPI is sticky, allowing it to be used as an adhesive. Soy protein-based adhesives are abundant, inexpensive, renewable, and easy to handle (Qi and Sun 2011). Previous results by the authors showed that the bonding strength of HSPI-modified UF was improved by 56% when compared with UF. In addition, the formaldehyde emission is dramatically reduced. The degree of hydrolysis, and additional amount of HSPI, can be used to control the degradation rate of the modified resins (Qu *et al*. 2015).

In this study, HSPI was used to partially substitute urea. The HSPI-modified UF was synthesized using copolymerization. Straw powers were blended with the modified UF resins to prepare biodegradable seedling containers. The tensile strength and the degradability of the seedling containers were characterized. Moreover, the degradation behavior was investigated. Isotopic tracing using ^{15}N-labeled resins was applied to elucidate the degradation behavior of HSPI-modified UF resins. In addition, the degraded samples were characterized *in situ* using a ^{13}CP/MAS NMR, SEM-EDS. The cross-linking degree of unmodified UF and modified UF was performed using DMA.

EXPERIMENTAL

Materials

Stable isotope compounds of ^{15}N urea (enrichment: 10.12 atom%) were purchased from the Shanghai Research Institute of Chemical Industry. Urea (≥99.0%), formaldehyde (37.5%), potassium hydroxide (≥96.0%), and phosphoric acid (≥85.0%) were purchased from the Shantou Xilong Chemical Factory, Guangdong, China. All chemicals utilized in this study were of analytical reagent grade. Soy protein isolate was purchased from the Anyang Detianli Food Co., Ltd., Henan Province, China. Alkaline protease (protease activity >100 U/mg) was purchased from the Shanghai Ruji Biological Technology Development Co., LTD. Rice straw (moisture content: 12%) was obtained from a rice field in Jiangsu Academy of Agricultural Science and then smashed to pass through a 0.35 mm (40 mesh) screen.

Methods

The hydrolyzation of soy protein isolate

The soy protein isolate was treated in a 0.4 wt.% potassium hydroxide (KOH) aqueous solution for 1 h at 70 °C. The solids content of the hydrolyzed soy protein isolate was 13.04%. The amount of HSPI was calculated according to its ability to react with formaldehyde. The formaldehyde reacting ability of HSPI is 30 mg HCHO/g HSPI, and 5%, 10%, and 15% of the urea molar was substituted. The synthesized resins under the same conditions but without the HSPI were defined as the blank UF. The formulation of HSPI-modified UF is shown in Table 1.

Synthesis procedure of the HSPI-modified UF

The HSPI-modified UF was synthesized using three steps, methylolation, polycondensation, and post-treatment. In methylolation, a 2 L four-neck flask equipped with a mechanical stirrer, a thermometer, a condenser, and a septum-seal for feeding was

used. Next, 568.05 g of formaldehyde were added, and the solution was heated slowly until the temperature reached 25 to 30 °, at which point the first portion of urea and HSPI was added. The pH of the mixture was adjusted to 7.8 using a 30 wt.% potassium hydroxide aqueous solution. Afterwards, the mixture was heated at a rate of 1 °C/min, and the temperature reached 60 °C within 30 min. Then the second portion of urea was added. Heating was continued until a temperature of 90 °C was achieved at a rate of 1 °C/min for 30 min, and was then the temperature was held at 90 °C for 1 h. In polycondensation, the pH of the prepared mixture from step 1 was adjusted to 4.5-5.0 using 25 wt.% phosphoric acid aqueous solutions and was maintained until the end of reaction point. After the reactions reached their endpoint, post-treatment began. The pH of the prepared mixture from step 2 was finally adjusted to 7.8 using a 30 wt.% potassium hydroxide aqueous solution. The third urea was added after the temperature decreased to 75 to 80 °C, and kept for 1 h. The obtained resins were cooled to room temperature.

Table 1. Formulation of HSPI-Modified UF Adhesives

	I		II		III		IV	
	Urea (g)	HSPI (g)	Urea (g)	HSPI (g)	Urea (g)	HSPI (g)	Urea (g)	HSPI (g)
1	122	350	122	700	122	1049	140	0
2	85	0	85	0	85	0	85	0
3	125	0	125	0	125	0	125	0

Alternatively, ^{15}N urea (4 wt. %) was added for the synthesis of ^{15}N-labeling the HSPI-modified UF resins. The formulation was the same as II.

Preparation of biodegradable seedling containers

5000 g of rice straw power and 4000 g of adhesives were blended in a mixing tank at 60 °C for 30 min. The blended materials with a moisture content of 15% were hot-pressed at 120 °C under 14 MPa of pressure for 2 min.

Degradation tests: Apparatus and procedure

Degradation tests on the seedling containers were conducted in the soil (soil moisture 60%, temperature 30 °C) at a depth of 10 cm for 90 days. And in 2 L glass flasks, each degradation test was performed in triplicate. All samples were washed gently with distilled water after degradation. The samples were then dried in a drying oven, until a constant weight was obtained. The degree of biodegradation was evaluated as the weight loss divided by the initial sample weight.

Mixing of the soil with resins was used to monitor the degradation of HSPI-modified UF resins. Specimens prepared by mixing of soil with the ^{15}N-labeled and unlabeled HSPI-modified UF resins were defined as the labeled and unlabeled conditions. The soil without mixing with the resins was defined as the blank. Samples of the soil and the degraded resins were taken once per week.

Characterization

Testing was conducted on an HY-0580 Shanghai Hengyi Precision Instrument. The wet samples were prepared according to the following: specimens were immersed into 63 ^{o}C water for 3 h and then cooled to room temperature for 10 min before measurement. The tensile properties were determined according to ASTM D638-03.

The $\delta^{15}N$ values of the extracted liquid from the soil and the degraded samples were analyzed using an automated unit that combines an N C H S elemental analyzer (EA3000, Italy) with an isotope ratio mass spectrometer IR-MS (Isoprime 100, UK).

The dynamic mechanical properties were collected using a DMA Q800 (TA Instruments, New Castle, DE, USA) device operating in double cantilever bending mode at an oscillation frequency of 1.0 Hz. A fixed displacement mode with 100 μm of amplitude and 3 °C/min was used. For preparation, 1 wt.% NH_4Cl was added to the modified and unmodified UF resin adhesives, then thoroughly mixed. The glass microfiber filter (Whatman, USA) was impregnated with the mixed resins, and dried at room temperature for 14 h. Then, the air-dried filter was cut into 60 mm × 13 mm pieces, and then sandwiched between two glass layers. It was then dried again at 50 °C for 30 min.

The solid state ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR spectra were recorded on an AVANCE III WB 400MHz spectrometer (Bruker, Switzerland). The spectrometer was equipped with a 4 mm Bruker MAS probe. The measurements were acquisition parameters: contact time 1 ms, acquisition time 16.98 ms, dwell time 16.533 μs, pre-scan-delay 6.5μs, and recycle delay 1.5 s.

The surface morphologies of samples were evaluated using scanning electron microscopy (SEM Quanta-200, FEI, Czech Republic). The elemental analysis was carried out using energy dispersive spectroscopy (EDS) attached to the SEM.

RESULTS AND DISCUSSION

Tensile Strength of Seedling Containers

The dry and wet tensile strengths are important indicators for seedling containers. The tensile strength of seedling containers is shown in Table 2. It can be seen that the highest dry strength of seedling containers made from HSPI-modified UF resins was 5.08 MPa, which represents a 6% improvement over seedling containers made from unmodified UF resins. The wet strength of the seedling containers made from UF resins was better than the containers made from HSPI-modified UF resins. And, the wet strength decreased as the amount of HSPI increased in the modified resins due to the high water absorbing ability of HSPI.

Table 2. Tensile Strength of Seedling Containers

Samples	I	II	III	IV
Dry strength (MPa)	5.08	4.91	4.13	4.79
(SD)	(0.62)	(0.65)	(0.78)	(0.57)
Wet strength (MPa)	2.58	2.04	1.39	4.81
(SD)	(0.51)	(0.28)	(0.34)	(0.48)

SD: standard deviation.

Degradability of Seedling Containers

The weight loss of seedling containers is shown in Table 3. After the resins were modified by HSPI, the degradability of the seedling containers was increased significantly. The weight loss of seedling containers increased as the amount of HSPI increased in the modified resins. The weight loss of seedling containers made from III resins increased 8.8 times more than the seedling containers made from unmodified UF

resins. The biodegradable HSPI can be decomposed by soil microorganisms. The degradation of HSPI can also lead to the fall off of the length of urea-formaldehyde molecular chains. Therefore, the seedling containers with different degradation periods can be regulated by the additive amount of HSPI in the modified UF resins.

Table 3. Weight Loss of Seedling Containers

Samples	I	II	III	IV
Weight loss (%)	48.8	68.4	79.6	8.1
(SD)	(2.76)	(2.65)	(3.08)	(1.42)

Isotope and Elemental Analyses of Degraded Samples

To verify whether the urea formaldehyde molecular chains in the modified resins could be degraded by microorganisms, ^{15}N-labeled urea was added to synthesize the ^{15}N-labeled HSPI-UF resins. The ^{15}N-labeled HSPI-UF resins exposed *in situ* conditions that may provide more reliable data of urea-formaldehyde degradation. Figure 1 describes the results of the incubation of ^{15}N-labeled HSPI-UF resins in soil. It can be seen from Fig. 1 that the δ ^{15}N values of blank samples increased slightly over time. This is a result of ^{14}N forming weaker chemical bonds than those formed by ^{15}N, due to the higher zero-point energy of ^{14}N. Although the chemical and physical properties of stable isotopes are nearly identical, slight differences arise from a quantum mechanical effect, depending on different zero-point energies of the ^{15}N and ^{14}N. Chemical bonds containing ^{15}N are stronger, to a minute extent, and the activation energy for their cleavage is higher. Therefore in blank soil, usually ^{14}N is preferentially reacted. This principle controls the reactivity of the individual stable isotopes in the environment, and induces isotope fractionation.

The δ ^{15}N value for unlabeled soil was higher than the blank one, and a slight increase during degradation reflected the contribution of HSPI-UF. Therefore, the isotope composition of the soil was altered during decomposition and/or by diagenesis (Nguyen *et al*. 2011). The phenomenon describes the selective degradation of fallen off urea-formaldehyde molecular chains deviating from that of unlabeled HSPI-UF. As blocked urea-formaldehyde molecular chains fall off due to the breakdown of the HSPI, and/or kinetic discrimination during metabolism of urea-formaldehyde by degrading microorganisms, the preferential metabolism of the urea-formaldehyde that is ^{15}N, is depleted (Nguyen *et al*. 2011).

Although both the δ ^{15}N values of unlabeled and blank soil increased over time, the value was below 30%. Regarding the degradation of labeled resins, no latency period was observed, as revealed by the immediately increased δ ^{15}N values. Mineralization seemed to occur nearly instantaneously in the soil. One conclusion that could be drawn was that, not only was the HSPI decomposed, but the urea-formaldehyde molecular chains were degraded simultaneously. As can be seen from the curves of labeled resins, the slope was nearly invariable over time. That is to say that the degradation rate of the urea-formaldehyde molecular chains in HSPI-modified UF resins is constant.

The nitrogen, carbon, hydrogen, and sulphur content of the soil over time are shown in Fig. 2. The nitrogen element of blank soil decreased during degradation, whereas the nitrogen element of soil mixed with HSPI-modified UF resins obviously increased. In addition, the HSPI-modified UF resins released nitrogen elements at a relatively constant rate. That is to say, the HSPI-modified UF resins applied in seedling

containers can be used as a source of nitrogen for the growth of seedlings. The carbon, hydrogen, and sulphur elements of blank soil declined faster than that of the soil mixed with resins. In other words, the modified resins can provide a source of carbon as well, which is beneficial for the growth of seedlings.

As shown in Fig. 3, isotopic analysis of the remaining amounts of ^{15}N-labeled resins showed that almost no alteration of the $^{15}N/^{14}N$ ratio occurred during incubation. The same results have been reported by Geyer *et al*. (2005). Indeed, the isotope composition of HSPI-modified UF resins corresponds to the weighted mean comprised by the isotope composition of HSPI, urea, and formaldehyde. Therefore, the isotope composition of resins can be disproportionately altered if the constituents lost by degradation have an isotope composition which differs substantially from that of the remaining resins (Deines 1980; Balesdent *et al*. 1993). Consequently, the isotope analysis of the degraded resins has high preservation potential (Wiesenberg *et al*. 2004; Yamamoto *et al*. 2010). The results indicated that the constituents lost by degradation had the same isotope composition as that of the remaining resins. That is to say, both the HSPI and urea-formaldehyde molecular chains degraded, and the ratio of degraded HSPI and urea-formaldehyde molecular chains was the same as that of un-degraded resins.

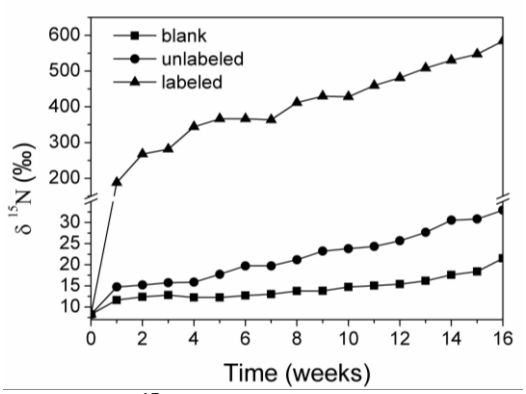

Fig. 1. The ^{15}N abundance of the degradation products over time

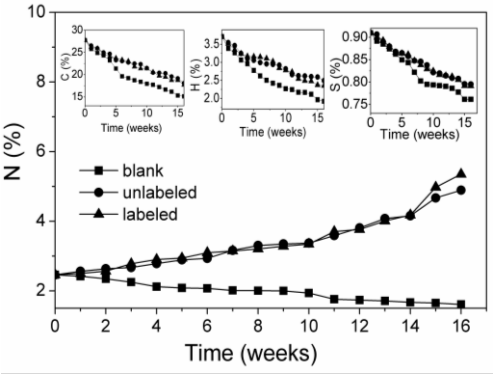

Fig. 2. The nitrogen, carbon, hydrogen, and sulphur content of the degradation products over time

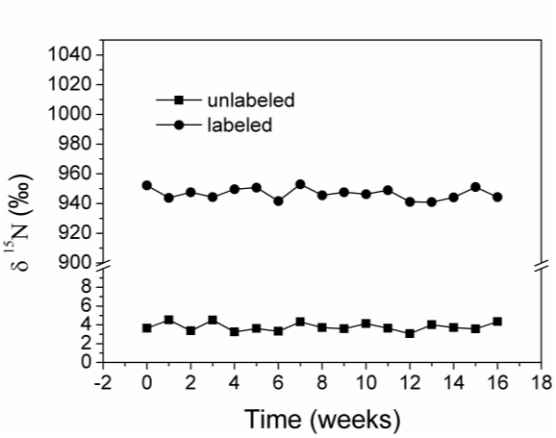

Fig. 3. The ^{15}N abundance of the resins over time

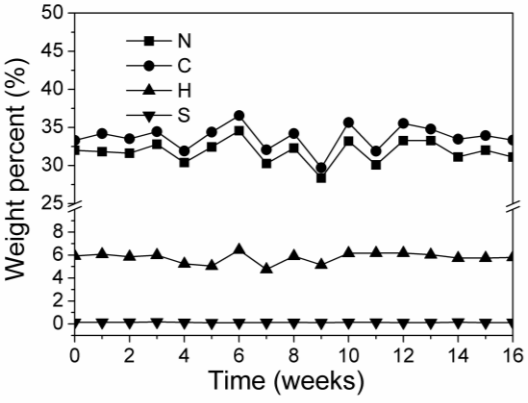

Fig. 4. The nitrogen, carbon, hydrogen, and sulphur content of the resins over time

The nitrogen, carbon, hydrogen, and sulphur content of the degraded resins during degradation time are shown in Fig. 4. The nitrogen, carbon, and hydrogen content of degraded resins fluctuated as a function of time. This was ascribed to the resins that were inhomogeneously decomposed by microorganisms. However, the ratio of C/N, C/H, and N/H was nearly constant, which meant that the degradation of nitrogen, carbon, hydrogen, and sulphur in resins was a fixed ratio. The degradation ratio of C/N, C/H, and N/H was the same as those of HSPI-UF resins.

Dynamic Mechanical Analysis

Lower degrees of cross-linking (Arancibia *et al*. 2014), improved chain flexibility (Okada 2002), and introduced natural molecules may enhance the susceptibility of the modified resin to enzymatic hydrolysis. The DMA was applied to characterize the cross-linking degree of UF and HSPI-modified UF resins. As shown in Fig. 5, the loss modulus (*E*'') of the resins was maximized at *ca*. 192 °C, and its increasing stage could be ascribed to increasing rigidity as the cross-linking degree increased. *E*'' started to decrease after reaching the maximum because the UF resins began to decompose. *E*'' contributes to energy dissipation caused by molecular friction because of the viscose flow of a material (Kim *et al*. 1991; Park and Kim 2008). The peak intensity of modified UF was lower than that of unmodified UF. The results indicated that the molecular friction of the cured resin was reduced after HSPI-modified the UF. This could be attributed to the less branched network structure of a HSPI-modified UF resin, in comparison to those of pure UF resins. In other words, it seems that a cured HSPI-modified UF resin was more flexible than those of unmodified UF resins, which required less energy dissipation under the oscillation. The storage modulus (*E*') first increased to a maximum, then decreased to a minimum, and then reached a maximum again. The first maximum was due to partially cured resins. The subsequent decrease could be ascribed to the softening of resins as a result of the temperature increase (Park and Kim 2008). The second maximum was attributed to further curing of the resins, which indicated that an infinite molecular network was formed. During the increasing stage, the dominant factor was the increasing degree of cross-linking through the curing process. In the second decreasing stage, the main factor was the thermal degradation of the UF resins as the temperature increased.

As shown in the Tan Delta curves, the peak temperature (gel temperature) of UF was 187 °C, which is higher than the 180 °C peak of modified UF. The peak temperature of the Tan Delta was closely related to the viscoelastic property of the resin network (Park and Kim 2008). Therefore, the results indicated that the curing degree of unmodified UF is higher than that of modified UF. In addition, the peak intensity of modified UF was lower than the unmodified UF. The results also indicated that the less branched network structure was formed in HSPI-modified UF resins.

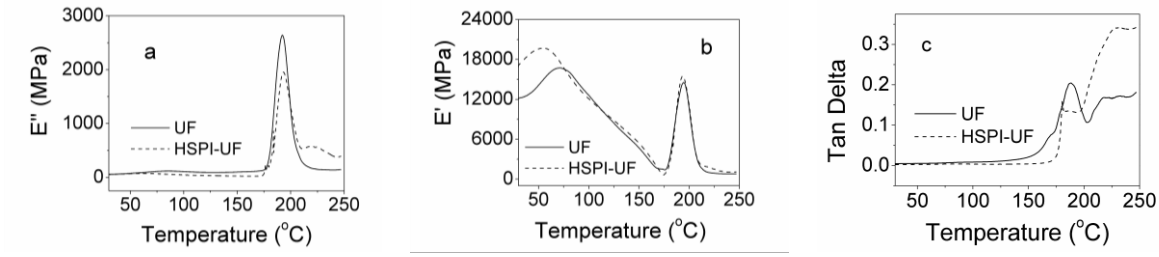

Fig. 5. Loss modulus *E*'' (a),storage modulus *E*' (b), and Tan Delta (c) curves of UF and HSPI-modified UF resins

^{13}C CP/MAS NMR Spectroscopy

Figure 6 shows the spectra of solid-state ^{13}C CP/MAS NMR, for degraded and un-degraded resins. The peak assignments for those spectra are summarized in Table 1. The four kinds of resins have a peak in common at around 47.8 ppm, which indicates the presence of NH-$\underline{C}H_2$-NH in resins; as the chemical shifts at 55 ppm and 65 ppm belong to N(CH_2)-$\underline{C}H_2$-N(CH_2) and NH-$\underline{C}H_2$-O-$\underline{C}H_2$-NH, respectively. Absorption due to $\underline{C}H_2$-O-$\underline{C}H_2$ and $HOCH_2NH$-$\underline{C}$O-N($CH_2OH)_2$ gave peaks at 80 ppm and 160 ppm, respectively. The peaks at around 61.8 ppm and 72 ppm belong to NH-$\underline{C}H_2OH$ and N(CH_2)-$\underline{C}H_2$-OH (Soulard *et al*. 1999; Tohmura *et al*. 2000). The peak areas at 26 ppm and 31 ppm are attributed to the side-chain aliphatics of HSPI. The peaks at around 129 ppm and 173 ppm are ascribed to the aromatics and carbonyl carbons of HSPI (Yoshimizu *et al*. 1991).

Table 4. Chemical Shift Assignment of Solid-State ^{13}C CP/MAS NMR Spectra of Degraded and Undegraded Resins

Chemical structure	Chemical shift (ppm)			
	UF	UF-4	HSPI-UF	HSPI-UF-4
-NH-$\underline{C}H_2$-NH-	47.721	47.802	47.860	47.841
-N(CH_2)-$\underline{C}H_2$-N(CH_2)-	55.880	55.205	55.219	55.235
-NH-$\underline{C}H_2OH$	61.874	61.875	61.873	61.879
-NH-$\underline{C}H_2$-O-$\underline{C}H_2$-NH-	65.726	65.752	65.483	65.419
-N(CH_2)-$\underline{C}H_2$-OH	72.504	72.623	72.632	72.894
Uron -$\underline{C}H_2$-O-$\underline{C}H_2$-	80.694	80.768	80.869	80.655
$HOCH_2NH$-$\underline{C}$O-N($CH_2OH)_2$	160.389	160.383	160.439	160.346
Side-chain aliphatics of HSPI	-	-	26.159	25.982
Side-chain aliphatics of HSPI	-	-	31.216	31.121
Aromatics of HSPI	-	-	128.833	129.270
Carbonyl carbons of HSPI	-	-	173.671	173.571

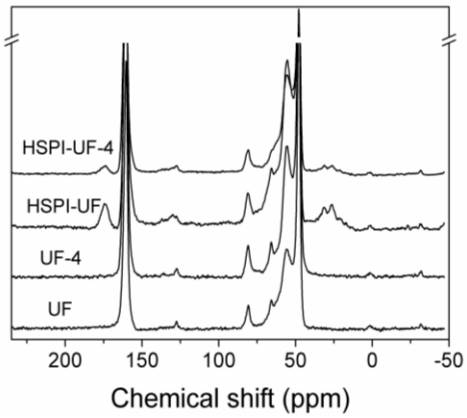

Fig. 6. ^{13}C CP/MAS NMR spectrum of degraded and undegraded resins

Table 5. Elemental Composition of Undegraded and Degraded Resins

Element	Undegraded		Degraded	
	Weight%	Atomic%	Weight%	Atomic%
C	27.82	32.75	27.98	32.92
N	35.32	35.64	35.46	35.76
O	34.60	30.57	34.32	30.28
Na	0.66	0.41	0.65	0.40
Cl	1.60	0.64	1.59	0.63

There was hardly any difference between the spectra of UF and UF-4, which means the UF could not be decomposed after incubation in soil. In other words, no evidence of biodegradation was found for UF resins. After degradation, the intensity

peaks of HSPI decreased significantly. This indicates that the copolymerized HSPI can degrade. Even so, undegraded HSPI also was found after incubation in the soil. Comparing the spectra of HSPI-UF-4 with HSPI-UF, the peak areas of $N(CH_2)$-$\underline{C}H_2$-$N(CH_2)$ and NH-$\underline{C}H_2$-NH decreased significantly. This means the urea-formaldehyde can be degraded by microorganisms as well. One conclusion that can be drawn is that the degradation of HSPI drives the degradation of urea-formaldehyde.

Scanning Electron Microscope-Energy Dispersive Spectrometer

The SEM micrographs of specimens collected before and after degradation are shown in Fig. 7. Before degradation, the cross section was flat (Fig. 7a). After degradation, the HSPI-modified UF resins were worn out (Fig. 7b). Many irregular holes formed and connected with each other. The nodular particles that appeared to be coalesced by small globular particles were left.

The element composition of undegraded and degraded resins is listed in Table 5. It can be seen that the contents of carbon, nitrogen, and oxygen were nearly the same, which is consistent with the results of the elemental analyser.

The Degradation Mechanism

The degradation mechanism of HSPI-modified UF resin is shown in Fig. 8. The degradation was mainly the result of the activity of microorganisms acting by enzymatic, mechanical, and chemical means (Gu 2003). The proteases, ureases, and methylenediurea amidinohydrolase were biosynthesized by the microorganisms. The HSPI was hydrolyzed, yielding amino acids. The methylenediurea amidinohydrolase hydrolyzed urea-formaldehyde moleculars into ammonium, formaldehyde, and urea (Jahns *et al*. 1997; Lugauskas *et al*. 2003).

In addition to their adherence by means of an enzymatic interaction, microbial species can adhere to the resins' surfaces due to the secretion of a kind of glue (Cappitelli *et al*. 2006). This slime matter, made of polysaccharides and proteins, changes moisture degrees and thermal transfers. In addition, the mechanical action of microorganism alters the size of pores and provokes cracks.

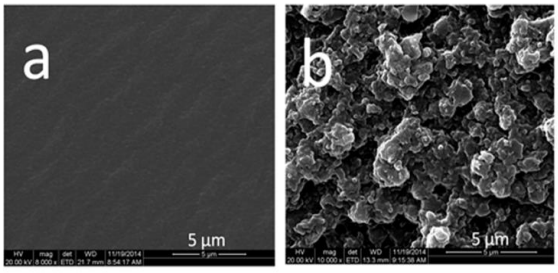

Fig. 7. Scanning electron micrographs of HSPI-modified UF resins before and after degradation (a: Undegraded resins, b: Degraded resins)

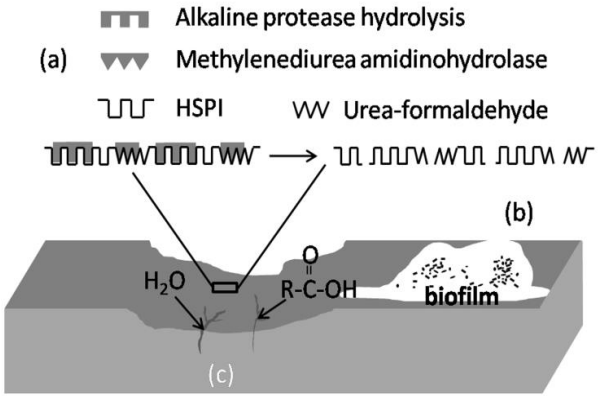

Fig. 8. The degradation mechanism of HSPI-modified UF resins (a: enzymatic way, b: physical way, c: chemical way)

Besides, the hydrophilic groups, such as hydroxymethyl and amino groups in the resins can adsorb water molecules. The intrusion of water initiates the hydrolysis of the

methylene link (-NH-CH_2-NH-, N(CH_2)-CH_2-N(CH_2)) or methylene ether link (-NH-CH_2-O-CH_2-NH-) in resins, leading to the creation of oligomers and monomers. Progressive degradation changes the microstructure of the resins due to the formation of pores, then oligomers and monomers are released. The curing reaction was catalyzed by acids. The acid will also catalyze the hydrolysis of the cured resins.

CONCLUSIONS

1. HSPI-modified UF resins not only improve the tensile strength of seedling containers, they also enhance the biodegradability.
2. The natural, degradable, HSPI can lower the degree of cross-linking of the UF resins. The constituents lost by degradation have the same isotope composition with that of the remained resins. After degradation, the modified resins become loose and porous.
3. The urea-formaldehyde and HSPI degraded simultaneously and transformed the nitrogen into biomass using organisms. Because of this, HSPI-modified UF resins applied in seedling containers may be used as a source of nitrogen.

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