

## Degradation of polyurethane coating materials from liquefied wheat straw for controlled release fertilizers

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**ABSTRACT:** Polyurethane (PU) was synthesized by liquefied wheat straw and isocyanates for controlled release fertilizers (CRFs). CRFs coated by PU were buried in soil for 12 months. The degradation degree and mechanism of PU coating materials were observed by thermogravimetric analysis (TGA), Atomic Force Microscope (AFM), differential scanning calorimetry (DSC), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and Fourier transform infra-red spectroscopy (FTIR). Significant microscopic morphology of PU exhibited many small chips or stereovision holes caused by biodegradation or hydrolytic degradation due to the presence of natural polymer wheat straw. AFM results depicted the plane and height topography changes of PU before and after 12 months burial time, showing the swelling morphology of buried PU. TGA and FTIR results confirmed the disintegration of PU polymer due to the presence of isocyanates monomers in the PU12. XPS revealed an accumulation of biofilm on the surface of buried PU, providing the evidence of biodegradation mechanism. Pot experiment indicated the resin residual coating has a positive effect on soil quality. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44021.

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### INTRODUCTION

Controlled release fertilizers (CRFs) have been greatly studied and used in many countries for decades because they released their nutrient contents gradually in accordance with the nutrient requirement of plants at all stages. These CRFs are commonly prepared by coating granules of conventional fertilizers with various polymer materials.<sup>1</sup> However, these polymer coating materials, such as polystyrene (PS), epoxy resin (EP), and polyethylene (PE) are very difficult to degrade completely in soil after nutrient release of CRFs, and consequently it can lead to the environmental pollution which affect the physicochemistry properties of soil as well as the growth of plants.<sup>2</sup> Additionally, the large-scale application of CRFs in the fields is also limited by the high cost and depletion of petrochemical products, the raw materials of polymer coating in CRFs. Therefore, the further developments of polymer coating in CRFs undoubtedly would focus on the environmentally friendly materials from renewable sources in the future.

Wheat straw as agricultural residues is essentially a renewable biomass resource and easily obtainable, especially in China. Wheat straw was converted to biomass polyols through liquefaction technology, which was used for preparation of polyurethane (PU) films, foams, or adhesives products.<sup>3–7</sup> We have patented the preparation of the PU coating materials with liquefied agricultural residues for CRFs in China.<sup>8</sup> These results showed that the PU coating materials had excellent controlled release properties and good film forming properties on the surface of fertilizers. But the degradation extent and mechanism of PU from liquefied biomass is unknown and not reported in the literature. Although the thermal degradation<sup>9–12</sup> and microbial degradation<sup>13</sup> of PU synthesized by isocyanates and polyols were studied, environmental degradation was not involved. The mechanism of environmental degradation of PU is considerably complicated due to the presence of many substances such as water, oxygen and micro-organisms in the environmental medium.

**Table I.** Experiment Design and Fertilizers Used in the Treatments

NO.	Treatments	N-(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> -KCl (g·pot <sup>-1</sup> )	Urea (g·pot <sup>-1</sup> )	PU-CRFs (g·pot <sup>-1</sup> )	Residual coating (g·pot <sup>-1</sup> )
1	CK	0	0	0	0
2	Urea	0.65-0.88-0.68	1.41	0	0
3	PU-CRF	0.65-0.88-0.68	0	1.51	0
4	PU-CRF1	0.65-0.88-0.68	0	1.51	0.229
5	PU-CRF5	0.65-0.88-0.68	0	1.51	1.145
6	PU-CRF10	0.65-0.88-0.68	0	1.51	2.29
7	PU-CRF50	0.65-0.88-0.68	0	1.51	11.45
8	PU-CRF100	0.65-0.88-0.68	0	1.51	22.9

The present study focuses on the environmental degradation behavior of PU from the liquefied wheat straw and the effect of its residual coating on soil quality in the soil environment. The variation of morphology, chemical groups, and bonding energy of the PU coating materials after 6, 12 months burial time was studied in detail. The major objectives of these researches are to provide some guidance for the further large scale application of CRFs with PU coating materials from the liquefied wheat straw.

## EXPERIMENTAL

### Materials

Wheat straw was harvested from a farm at the National Engineering Research Center for Slow/Controlled Release Fertilizers. The material was milled and only the 60–100 mesh fractions were selected for the liquefaction experiments. Material was dried in an oven at 105 °C for 24 h before being used for liquefaction. Commercial urea prills (from Shanxi Lanhua Coal Mining Group Co. Ltd) with a particle size range of 2–5 mm were used. All reagents used were CP or AR grade and easily obtained from commercial sources.

### Liquefaction of Wheat Straw

Diethylene glycol, sulfuric acid, and wheat straw flour according to mass ratio were added into a three-necked flask equipped with a reflux condenser, a thermometer, and a stirrer. Then the mixture was heated to 150 °C and stirred for 90 min to accomplish liquefaction. Subsequently, the flask was cooled to room temperature, and the resultant liquefied wheat straw (LWS) was collected for the preparation of CRFs.

### Preparation of CRFs

LWS and isocyanates were mixed uniformly to obtain the coating liquid. Urea particles were placed in a rotary drum, and heated to 60–90 °C. The coating liquid was uniformly sprayed onto the urea particles in the rotary drum and cured for about 5 min to accomplish the first coating. After spraying a measured amount of coating liquid, the final CRFs products were obtained, cooled to room temperature, and stored in bags. The CRFs coated with PU materials is denoted as PU-CRFs.

### X-ray Photoelectron Spectroscopy (XPS) Analysis

The surface of samples was analyzed using a Thermo ESCALAB 250XI Multifunctional imaging electron spectrometer (Thermo Fisher Scientific, The United States), incorporating a hemispherical electron energy analyzer. The incident radiation was mono-

chromatic Al Ka X-rays. Survey (wide) spectra were collected using 100 eV pass energy and multiplex (narrow) high-resolution scans, which focus on a particular atom at 30 eV pass energy. Survey scans were carried out over 1400–0 eV binding energy range with 1.0 eV steps. Narrow high-resolution scans were run with 0.05 eV steps.

### Fourier Transform-Infrared Spectroscopy (FTIR) Analysis

FTIR spectra were performed by a Nicolet 380 FTIR spectrometer using a resolution of 4 cm<sup>-1</sup>. The scanning coverage was from 4000 to 500 cm<sup>-1</sup>. The samples were adequately mixed with KBr and disks of sample/KBr mixtures were prepared to obtain the FTIR spectra.

### Scanning Electron Microscopy (SEM) Analysis

The granules of CRFs or coating materials were observed by using JSM-5800 scanning electron microscope (SEM). Samples were split into two halves, and the cross-section or surface of materials was adhered to sample holders with double-sided adhesive tape. Samples were coated by sputtering with gold before observation.

### Atomic Force Microscope (AFM) Analysis

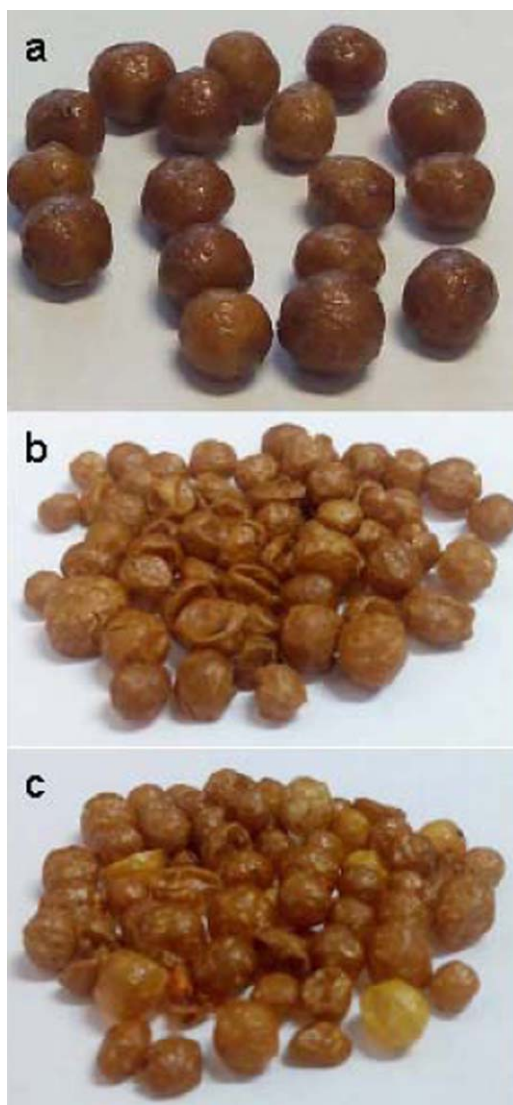
AFM measurements were carried out with a Multimode Nanoscope IIIa controller (Veeco, The United States). Films thickness was about 3 mm. The plane and height topographic image of the PU surface were provided. The tapping mode was used during the measurement.

### Thermogravimetric Analysis (TGA)

The thermal behavior of the materials was determined by using DTG-60A thermogravimetric analyzer (SHIMADZU, Japan) under nitrogen atmosphere with a flow rate of 50 mL/min. The samples were heated from room temperature to 600 °C with a constant heating rate of 20 °C/min.

### Degradation of PU Coating Materials in Soil

Degradation of PU coating materials was conducted in garden soil (the experimental field at the National Engineering Research Center for Slow/Controlled Release Fertilizers, Shandong Agricultural University, Shandong, China). CRFs were buried at least 2 cm apart and 20 cm below the soil surface. The samples were buried for 6 or 12 months. At the end of each period, (i.e., every 6 months) soil was removed from the PU coating materials by immersing in a solution containing 0.25% sodium hypochlorite and dried under vacuum (84 h, 25 °C) according



**Figure 1.** Photographs of PU0 (a), PU6 (b), and PU12 (c). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

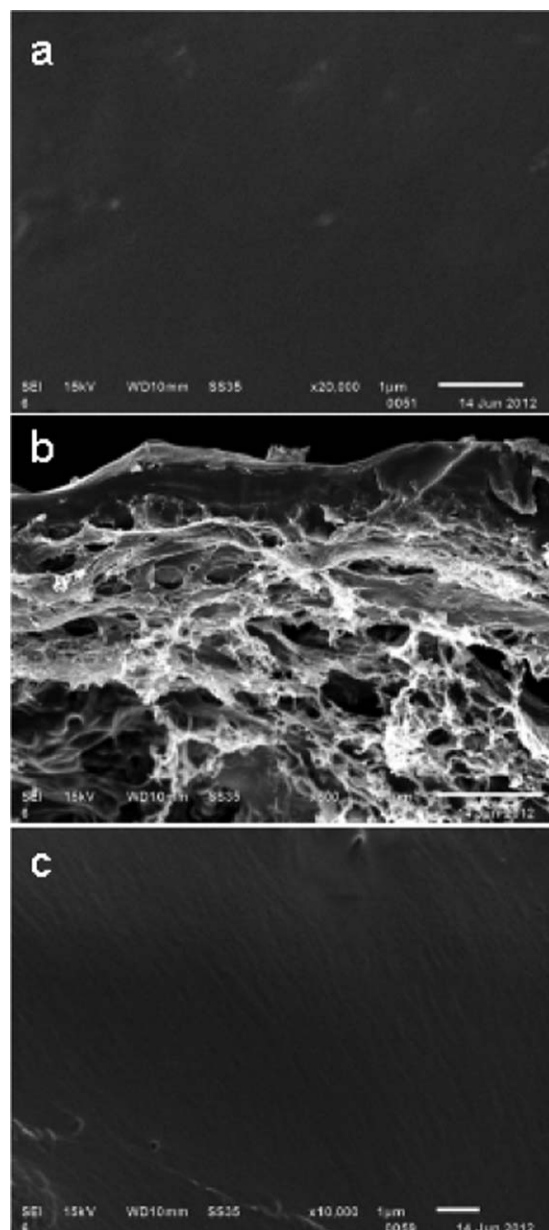
to the method of Mousavioun *et al.*<sup>14</sup> The PU coating materials buried for 6 months are denoted as PU6, and the PU coating materials buried for 12 months are denoted as PU12, and those that was not buried in soil are denoted as PU0.

#### Pot Experiment

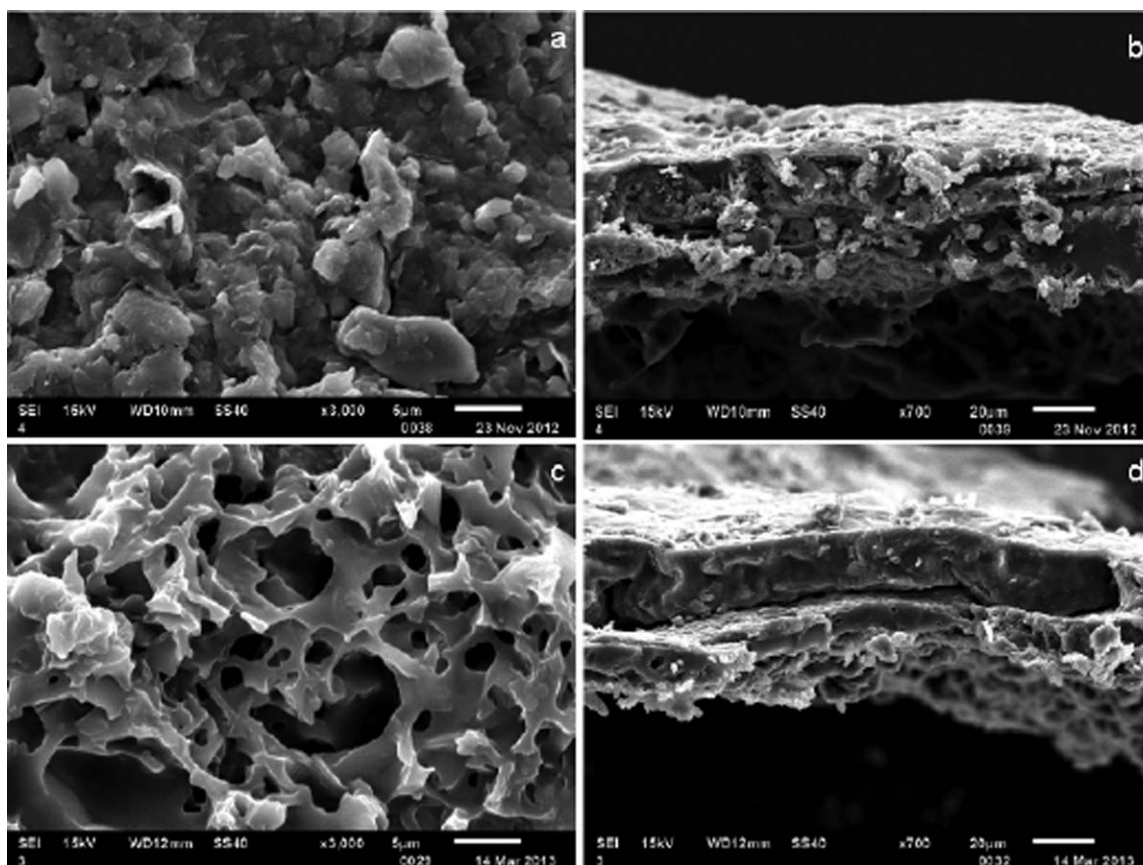
The effects of PU-CRFs and its residual coating on soil quality were conducted at the potted oilseed rape experiment located in a farm at the National Engineering Research Center for Slow/Controlled Release Fertilizers. Main properties of soil during the experiment were: pH, 7.74 (1:5, the ratio of soil to water), available  $\text{NH}_4^+$ -H concentration,  $0.1 \text{ mg kg}^{-1}$ ; available P concentration,  $6.21 \text{ mg kg}^{-1}$ , organic matter concentration,  $14.8 \text{ g kg}^{-1}$ , and available K concentration,  $96.33 \text{ mg kg}^{-1}$ , respectively. The conventional fertilizers used were urea (containing 46% N) as N fertilizer, diammonium phosphate (containing 50% P) as P fertilizer, and potassium chloride (containing 49.8% K) as K fertil-

izer, respectively. The PU-CRFs was used for oilseed rape. In this experiment, there were two nutrient treatments and five treatments including resin residual coatings in comparison with a no-fertilizer application as a control blank (CK). The PU-CRFs with the addition of residual coating (0.229 g, residual coating of 1 year) is denoted as PU-CRF1, and so on PU-CRF5, PU-CRF10, PU-CRF50, and PU-CRF100 were obtained. Eight treatments were listed in Table I. Each treatment was conducted in triplicate. The growing period of oilseed rape was 45 days.

Soil samples were collected in Nov. 15, 2015 after harvest of oilseed rape. Three soil cores in each pot were collected and then mixed as a composite sample. Soil samples were divided into two parts. One part was stored fresh in a  $4^\circ\text{C}$  refrigerator, and another part was air-dried, and ground pass through 1 mm



**Figure 2.** SEM images of PU0 or CRF. (a) surface of CRF, (b) section surface of CRF, and (c) fraction surface of PU0 coating materials.



**Figure 3.** SEM images of PU6 (a) surface, (b) fraction surface and PU12 (c) surface, (d) fraction surface.

sieve and 0.25 mm sieve. The concentrations of  $\text{NH}_4^+$ -N (extraction with 0.01M  $\text{CaCl}_2$ ) in fresh soil samples were measured in extract solution by using the AA3-A001-02E Auto-analyzer (Bran-Luebbe, Germany) within 48 h after collection.<sup>16</sup> Soil available P content was measured using the Olsen-P method. Soil available K content was obtained by a flame photometer. Soil organic matter was determined by using a wet oxidation method with  $\text{K}_2\text{Cr}_2\text{O}_7$  and concentrated  $\text{H}_2\text{SO}_4$ .<sup>15</sup> Soil pH value was measured at the ratio of soil to distilled water (1:5, w:v) using a pH meter (PB-10, Sartorius AG, Germany). Data were compared statistically by one-way ANOVA with least significant difference test (Duncan's multiple range test) at the 0.05 probability level in Statistical Analysis System (SAS) package version 9.2 (2010, SAS Institute, Cary, NC).<sup>16</sup>

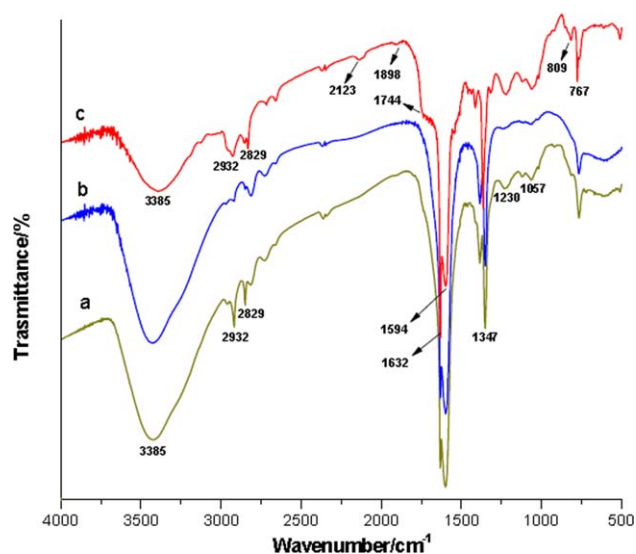
## RESULTS AND DISCUSSION

### Macroscopic and Microscopic Morphology

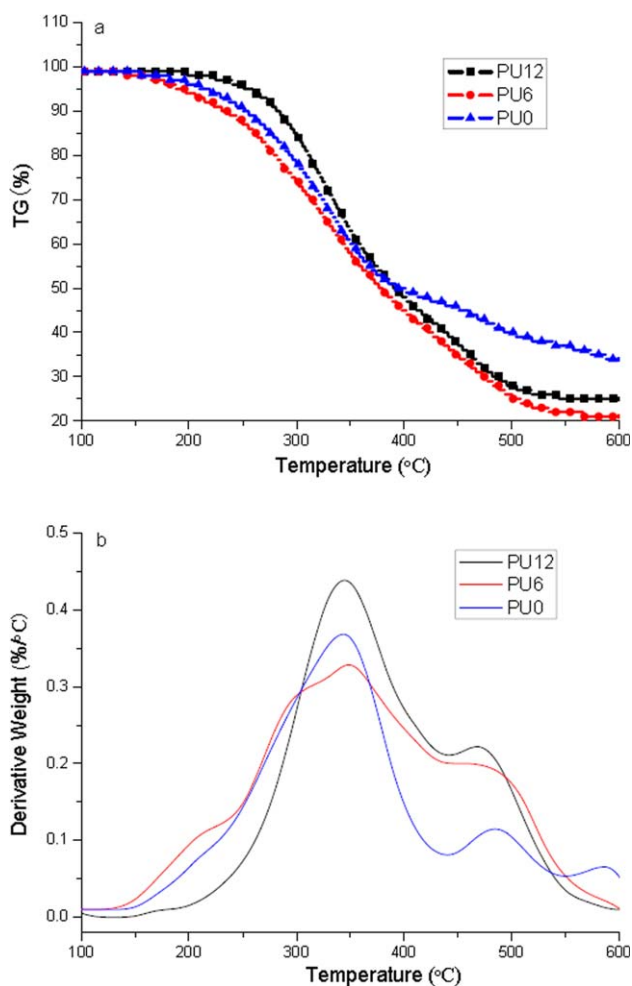
Photograph of PU-CRF is displayed in Figure 1(a), and it was prepared by coating urea with PU film materials. Photographs of Figure 1(b,c) show that the core urea particles fertilizers have been released completely and only it had left the PU coating materials. The degradation of PU coating materials occurred obviously, as evident in the small holes, breakages and many discoloration spots appeared on the surface of PU6 and PU12 coating materials buried in soil. It is noted that the discoloration spots on the surface of PU increased with prolongation of

burial time. These spots should be the main degradation regions.

The microscopic morphology of surface and section surface of PU0<sup>17</sup> or PU-CRF is observed through the SEM images. The



**Figure 4.** FTIR spectra of PU0 (a), PU6 (b), and PU12 (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 5.** TGA (a) and DTG (b) curves of PU0, PU6, and PU12 under nitrogen. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

surface [Figure 2(a)] and section surface [Figure 2(c)] of PU0 exhibit very dense and smooth, even though it has no hole on the surface of PU0 at 20,000 $\times$  magnification. Figure 2(b) displays the section surface of PU-CRF. It can be seen that the white region is urea, and the puce region is the compact PU coating materials, which only has a thickness of 20–30  $\mu\text{m}$  on the CRF.

The SEM images of PU after buried for 6 or 12 months are displayed in Figure 3. It is obviously investigated that the tendency of PU degradation increased with burial time. There are many fragments produced during the degradation process stacked disorderly on the surface of PU6 [Figure 3(a)] forming several loose holes of about 5  $\mu\text{m}$ . After buried for 12 months, the morphology of network state appeared on the surface of PU12 [Figure 3(c)] coating materials, showing innumerable different sizes of stereovision holes. On the basis of these images, the degradation mechanism of PU coating materials buried in soil is inferred as follows. In this research, the PU coating materials were synthesized by the liquefied wheat straw and isocyanates. However, the nature polymer compounds derived from the liquefied wheat straw in the PU were easily hydrolyzed and

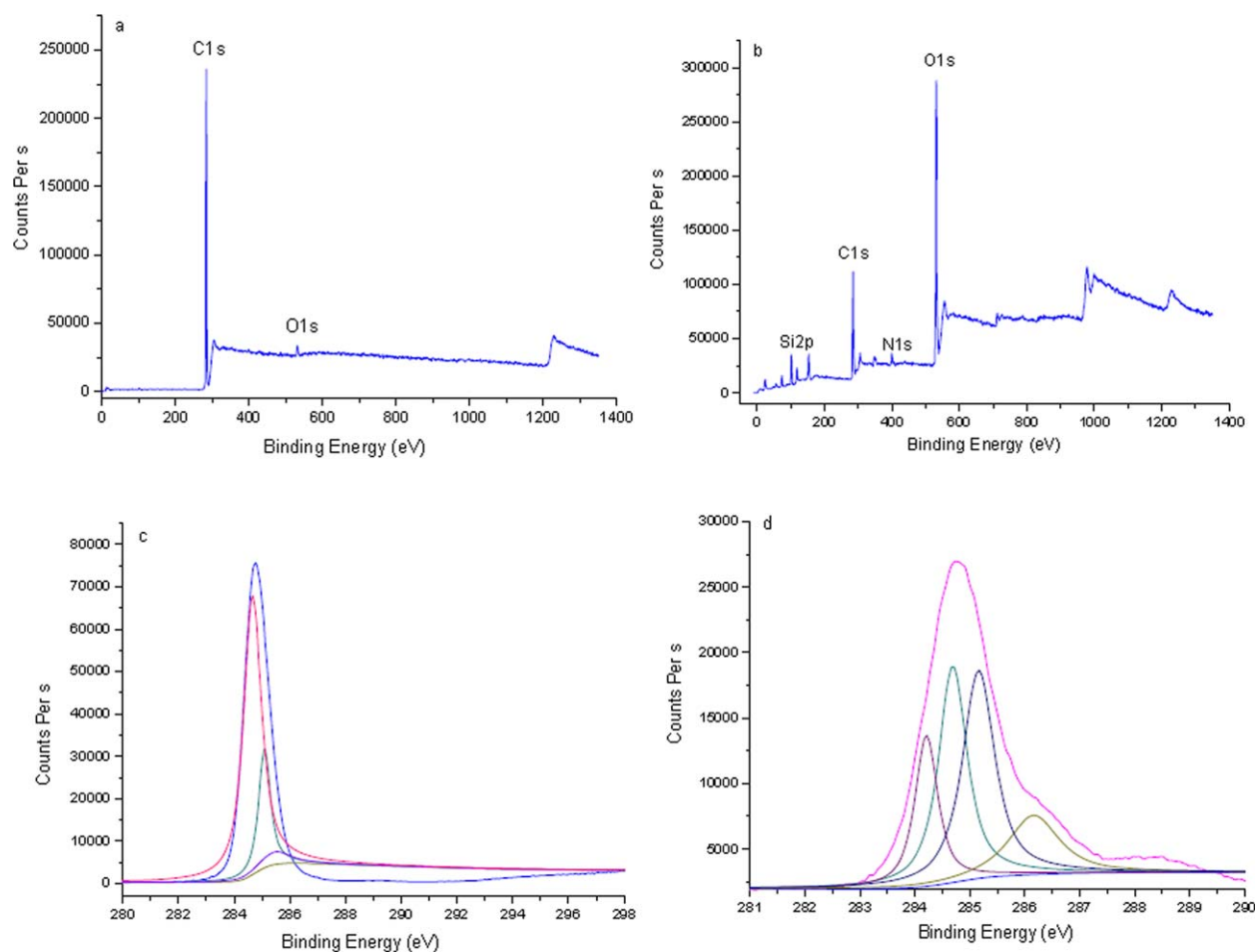
eroded by microorganisms resulting in breakage of polymer molecules, and producing many micropores and smaller molecular mass chips on the surface of PU coating materials as shown in Figure 3(a). With increasing of burial time, the micropores and breakages on the surface of PU coating materials were larger and larger. Furthermore, the enzymes produced by mobile micro-organisms eroded the nature polymer compounds and easily attacked the groups in the interior of PU along micropores and breakages, enabling holes to become larger and deeper as evident in stereovision holes of Figure 3(c). And those relatively low molecular mass chips produced during the degradation process could be absorbed and digested by those enzymes because the chips were not observed in Figure 3(c).

The SEM images of section surface of PU buried for various months had great changes in contrast of that of PU0. There are many debris and some micropores on the section surface of PU6 [Figure 3(b)]. The delamination phenomenon is observed on the section surface of PU6 and PU12 [Figure 3(d)]. And the trend is further obvious with prolonging of buried time. However, the degradation extent of section surface is obviously slower than that of surface. This is because the section surface of coating materials has much less opportunity to contact with the substance, such as water, oxygen, and micro-organisms in the environmental medium, in contrast to the coating surface. To sum up, the PU coating materials had obvious trend of degradation after buried in soil.

#### FTIR Analysis

Figure 4 shows the FTIR spectra of PU0, PU6 and PU12. The IR spectrum of PU0 [Figure 4(a)] shows a strong and broad N-H stretching vibration band around 3385  $\text{cm}^{-1}$  and the bands in the range of 2932–2800  $\text{cm}^{-1}$  arising from C-H stretching vibration in methyl, methine, and methylene. Sharp absorption peaks at 1594  $\text{cm}^{-1}$  and 1632  $\text{cm}^{-1}$  are ascribed to C=C stretching vibration of aromatic compounds and C=O stretching vibration of urethane, respectively. The 1347  $\text{cm}^{-1}$  prominent peak is associated with CH<sub>2</sub> twisting, wagging, scissoring vibrations in polyols. Several weak peaks near 1230  $\text{cm}^{-1}$  and 1057  $\text{cm}^{-1}$  related to C-O stretching vibration from N-CO-O are also observed.

The IR spectrum of PU6 coating material has some changes compared with that of PU0. However, the IR spectrum of PU12 coating material has great changes compared with PU0 and PU6. The intensity of band at 3385  $\text{cm}^{-1}$  is reduced suggesting the loose structure of the hard segments of PU12. The isocyanates has been reported to exhibit a cumulated double bond stretch in the region of 2200–1900  $\text{cm}^{-1}$ .<sup>11</sup> A prominent peak at 2123  $\text{cm}^{-1}$  belonging to isocyanates monomers appears in the PU12 coating materials, which is not observed in the IR spectra of PU0 and PU6, and the peak at 1632  $\text{cm}^{-1}$  related with C=O stretching vibration of urethane is strengthened on the IR spectrum of PU12. A new weak peak appears at 1744  $\text{cm}^{-1}$  related to the C=O stretching vibration of ester in the soft segments. This illustrates the degradation of PU. The intensity of peaks in the region of 2932–2800  $\text{cm}^{-1}$  for soft segments biomass polyols increase, demonstrating that C-H stretching vibration is strengthened. Several small peaks near



**Figure 6.** Survey XPS of PU0 (a) and PU12 (b) and multiplex scans of carbon 1s region of PU0 (c) and PU12 (d). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

856–767  $\text{cm}^{-1}$  corresponding to out-of-plane bending vibration of C–H in benzene ring are strengthened. These strengthened peaks could be caused by the increase on freedom degree of molecular chains and the decrease on intermolecular interaction forces in the decomposed PU12. Moreover, the sharp peak at 1594  $\text{cm}^{-1}$  related with C=C stretching vibration of aromatic compounds weakens obviously suggesting the instability of benzene ring, which easily attacked by micro-organisms. It is attrib-

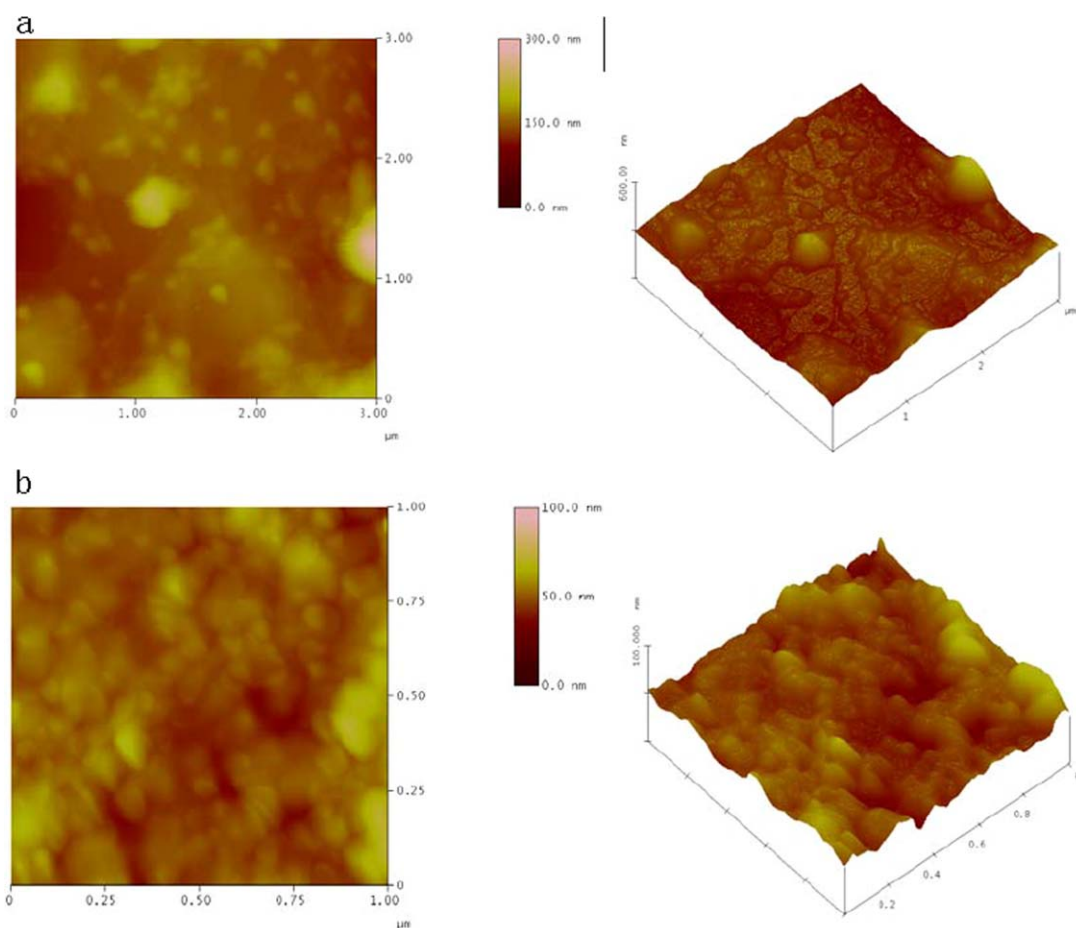
uted to the oxidative degradation of PU12, forming the carboxylic acid and alcohol due to the peak appearing at 1744  $\text{cm}^{-1}$  related to C=O stretching vibration of ester.

### Thermal Properties

Thermal analysis, including DSC and TGA, was used to investigate the thermal properties of PU0, PU6 and PU12. The glass transition temperature ( $T_g$ ) occurs at 13.6, 8.4, and 6.8 °C for

**Table II.** XPS Analysis of PU0 and PU12

PU0			PU12		
Linkage	Binding energy (eV)	Atomic %	Linkage	Binding energy (eV)	Atomic %
O=C–O	532.86	0.31	O–C	532.59	7.87
N–C–O	531.74	0.55	O–Si	531.92	12.80
N 1s	400.67	0.41	O–N	531.34	16.30
	399.83	0.31	N 1s	401.38	1.23
C–H	285.09	19.64	C–N	286.16	7.08
	284.66	73.38		C–H	285.16
C–O	284.47	5.3	C–C	284.69	14.68
			C–O	284.21	8.27



**Figure 7.** The AFM images of PU0 (a) and PU12 (b): the plane (left) and 3D (right). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

PU0, PU6, and PU12, respectively. The gradual reduction of  $T_g$  in the PU with the burial time could be caused by the decrease of polymer molecular weight and the increase of free volume attributed by hydrolytic and oxidative degradation of PU polymer.

TGA and derivative thermogravimetric analysis (DTG) were performed in order to obtain further information. According to the literature,<sup>10</sup> the degradation of hard segments in PU is at 150–300 °C, which would produce isocyanate, alcohol, primary or secondary amine, olefin and CO<sub>2</sub>, whereas the degradation of the soft segments is at the range 300–380 °C. Figure 5 shows the TGA and DTG curves of PU0, PU6, and PU12. Two main thermal decomposition events were obviously observed in the DTG curves. The first one is a strong peak between 150 and 380 °C, due to the disintegrations of PU polymer. The obvious difference for the initial decomposition events are observed among PU0, PU6, and PU12. PU6 decompose at 150 °C similar to PU0, but the highlight changes are observable in the stages at 150–250 °C. The breakage of urethane bond groups in the PU are accelerated due to the weak interaction force of molecules after buried in soil. And the CO<sub>2</sub> produced by thermal decomposition may escape from the breakage of chips or micropores as shown in SEM of Figure 3(a). However, the thermal decomposition temperature of PU12 begins at about 200 °C. It

is because the urethane groups with the low thermal stability have been degraded when buried in soil, which was demonstrated by the FTIR results. Sui *et al.*<sup>9</sup> studied in detail the products and mechanism of PU thermal degradation at 175 °C with the time-dependent IR spectra, and the results demonstrated that the PU break up into isocyanate and polyols and simultaneously degrade to produce secondary amine and CO<sub>2</sub> at this temperature. The second one is a weak peak at 480 °C, due to the further decomposition of residues. It is seen from the TGA curves that beyond the temperature of 380 °C, PU6 and PU12 are higher weight loss rate than PU0 because the PU materials decompose completely and produce more volatile products at this temperature. The dense char hinders from the volatilization of CO<sub>2</sub> and other gases in the PU0, which hinders the sample from further thermal degradation. So, more residues of PU0 was left about 34 wt % at 600 °C, while PU6 and PU12 after decomposition at 600 °C left about 21 and 25 wt % residues, respectively.

#### XPS Analysis

Survey analysis of PU0 and PU12 are shown in Figure 6(a,b). The multiplex carbon 1s scan of PU0 and PU12 are portrayed in Figure 6(c,d) and Table II. A pass energy of 100 eV is used for survey spectra of PU0, which indicates peaks at 532 and 285 eV due to oxygen (1s), and carbon (1s), and for survey spectra

**Table III.** Effects of Different Fertilizers Treatments on Soil Quality

Treatments	pH value	NH <sub>4</sub> <sup>+</sup> -N content (mg kg <sup>-1</sup> )	Available P content (mg kg <sup>-1</sup> )	Available K content (mg kg <sup>-1</sup> )	Organic matter content (g kg <sup>-1</sup> )
CK	7.65ab	15.62b	2.75bc	55.94c	10.85bcd
Urea	7.57bc	1.78d	2.59c	73.34b	10.25cd
PU-CRF	7.47bc	2.71cd	3.50b	76.45b	12.19bc
PU-CRF1	7.39c	2.10d	3.16c	86.39a	10.29d
PU-CRF5	7.65ab	12.44bc	2.99bc	78.00ab	10.41cd
PU-CRF10	7.80a	11.00bcd	5.37a	76.46b	10.94bcd
PU-CRF50	7.55bc	41.73a	5.02a	78.93ab	12.81b
PU-CRF100	7.68ab	10.93bcd	2.34c	57.21c	20.15a

Note: Means followed by the same lowercase letters in the row do not differ according to Dunca's test ( $p < 0.05$ ).

of PU12, which indicates peaks at 529, 400, 283, and 100 eV due to oxygen (1s), nitrogen (1s), carbon (1s), and silicon (1s), respectively. It is obviously noted that carbon atomic concentration was decreased and oxygen atomic concentration was increased significantly in the PU12 coating material compared with PU0 as shown in Figure 6(a,b). The reason is related to the oxidative degradation of PU, resulting in the increase of oxygen atomic content. Si is suspected to be derived from clay mineral as reported earlier.<sup>14</sup> Survey analysis of PU0 exhibits no nitrogen due to very little content (0.72%). However, PU12 after 12 months burial time is observed to contain a nitrogen peak with atomic concentration of 3.77%. The core of PU-CRF is urea and nitrogen-based compounds also are existed in the soil, but the amount adsorbed on the PU would be very small and not influence the nitrogen atomic concentration change. Moreover, it is noted that the C—N atomic concentration increased from 0.55% for PU0 to 7.08% for PU12. The increase in nitrogen-based compounds and nitrogen atom may be attributed to biofilm attachment on the surface of buried samples, and indicate that microorganisms are involved in environmental degradation of PU coating materials.<sup>14</sup> This is suggestive of PU biodegradation. Furthermore, it was seen from Table I that the C—C linkage is the major band for PU0. However, the C—C content sharply dropped from 73.38% to 14.68%, and conversely the C—O content increased from 5.3% to 8.27% after 12 months burial time, providing evidence of an oxidative degradation mechanism, which was consistent with FTIR results.

#### AFM Analysis

The plane and height topography of PU0 and PU12 surface was observed by the AFM analysis. As Figure 7(a) shows, there are smooth surface in the most of area and several white spots on the PU0 film surface. After 12 months burial, PU12 surface changes significantly. There are a lot of swelling particles on the surface and no smooth region appeared on the surface of PU12. These swelling particles parts are the solid region of PU12 in Figure 3(c) suggesting that the solid region firstly swell due to hydrolytic degradation in the PU materials.

#### Effects of Fertilizers Treatments on Soil Quality

The effects of different fertilizers treatments on soil quality are listed in Table III. The organic matter contents in treatments were reduced compared with the initial value (14.8 g kg<sup>-1</sup>),

except for the PU-CRF100. In comparison with CK, no prominent differences were found among other treatments after the harvest of oilseed rape, except for the PU-CRF100. The NH<sub>4</sub><sup>+</sup>-N contents in all treatments were increased compared with the initial value (0.1 mg kg<sup>-1</sup>), but N fertilization treatments were lower than the CK treatment after the harvest of oilseed rape, except for the PU-CRF50. The contents of NH<sub>4</sub><sup>+</sup>-N and organic matter in PU-CRF treatments were higher than urea treatment. The reason was that PU-CRF achieved more yield and biomass, and also increased residues, including roots, returned to the soil, and as a result, increased NH<sub>4</sub><sup>+</sup>-N and organic matter.<sup>16</sup> Moreover, it was observed that the addition of resin residual coatings increase these two values. It was explained that the biodegradability of residual coating affects the activity of microorganism, then resulting in the increase of NH<sub>4</sub><sup>+</sup>-N and organic matter. The pH value in soil was declined slightly in all treatments compared with initial value (pH 7.74), and no remarkable differences were found between PU-CRF treatments and urea treatment. The pH values in PU-CRF5, PU-CRF10, PU-CRF50, and PU-CRF100 treatments were increased by 0.08–0.33 compared with PU-CRF. This suggested that the acidification of soil was decelerated by the addition of resin residual coating. Potassium (K) is an essential nutrient element and involved in many important physiological processes in plants.<sup>18</sup> The soil available K content in all treatments displayed a clear decrease compared with initial value in the pot experiment. This result could be explained that the oilseed rape removed enormous amounts of K, resulting in a significant negative K balance in soils regardless of whether K fertilizers were applied.<sup>16</sup> The available K content in PU-CRF1, PU-CRF5, PU-CRF10, and PU-CRF50 treatments were higher than PU-CRF. This indicated that the addition of residual coating increased the available K content. For the soil available P, it has a similar effect on soil quality. All the above results indicated that the resin residual coating has a positive effect on soil quality.

#### CONCLUSIONS

1. SEM images of PU after buried in soil show many small chips or stereovision holes, exhibiting excellent degradability of PU in soil and more obvious degraded tendency of PU with the burial time. The height topography of AFM depicts



the swelling morphology in the solid region of PU12 compared with the smooth surface of PU0 suggesting that the solid region was hydrolyzed.

2. Thermal degradation of the buried PU coating materials follows a different weight loss curves than that of PU0 probably indicating the different structure among PU0, PU6, and PU12.
3. Pot experiment indicated the resin residual coating has a positive effect on soil quality.
4. The FTIR analysis demonstrated the urethane bond groups of PU break up into isocyanates and biomass polyols after buried for 12 months. At the meantime, the biomass polyols segments are decomposed and oxidized to carboxylic acid and alcohol because of the sharp decrease in the C—C content and the increase in the C—O content of PU12. XPS results also revealed an accumulation of biofilm on the surface of buried samples, providing evidence of a biodegradation mechanism.
5. On the basis of all the results, the mechanism of PU environmental degradation has been evaluated. The hydrolytic, oxidative degradation, and biodegradation effects are presented in the PU materials after burial time.

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#### REFERENCES

1. Shavit, U.; Shaviv, A.; Shalit, G.; Zaslavsky, D. *J. Control. Release* **1997**, *43*, 131.
2. Ge, J.; Wu, R.; Shi, X.; Yu, H.; Wang, M.; Li, W. *J. Appl. Polym. Sci.* **2002**, *86*, 2948.
3. Kurimoto, Y.; Takeda, M.; Doi, S.; Tamura, Y.; Ono, H. *Bioresour. Technol.* **2001**, *77*, 33.
4. Kurimoto, Y.; Takeda, M.; Koizumi, A.; Yamauchi, S.; Doi, S.; Tamura, Y. *Bioresour. Technol.* **2000**, *74*, 151.
5. Lee, S. H.; Teramoto, Y.; Shiraiishi, N. *J. Appl. Polym. Sci.* **2002**, *84*, 468.
6. Wang, T.; Zhang, L.; Li, D.; Yin, J.; Wu, S.; Mao, Z. *Biore-sour. Technol.* **2008**, *99*, 2265.
7. Kunaver, M.; Medved, S.; Čuk, N.; Jasiukaitytė, E.; Poljanšek, I.; Strnad, T. *Bioresour. Technol.* **2010**, *101*, 1361.
8. Zhang, M.; Lu, P. Crop Straw as Coating Material to Make Controlled Release Fertilizers and Processing Methods, **2013**, Chinese Pat. ZL 201210261735.0 (in Chinese).
9. Sui, H.; Ju, X.; Liu, X.; Cheng, K.; Luo, Y.; Zhong, F. *Polym. Degrad. Stab.* **2014**, *101*, 109.
10. Chattopadhyay, D. K.; Webster, D. C. *Prog. Polym. Sci.* **2009**, *34*, 1068.
11. Jiao, L.; Xiao, H.; Wang, Q.; Sun, J. *Polym. Degrad. Stab.* **2013**, *98*, 2687.
12. Pellizzi, E.; Lattuati-Derieux, A.; Lavédrine, B.; Cheradame, H. *Polym. Degrad. Stab.* **2013**, *102*, 1.
13. Shima, M. *Curr. Opin. Biotechnol.* **2001**, *12*, 242.
14. Mousavioun, P.; George, G. A.; Doherty, W. O. S. *Polym. Degrad. Stab.* **2012**, *97*, 1114.
15. Nelson, D.M.; Sommer, L.E. *Proceeding Indiana Academic Science* **1975**, *84*, 456.
16. Geng, J.; Sun, Y.; Zhang, M.; Li, C.; Yang, Y.; Liu, Z.; Li, S. *Field Crops Res.* **2015**, *184*, 65.
17. Lu, P.; Zhang, Y.; Jia, C.; Wang, C.; Li, X.; Zhang, M. *BioRe-sources* **2015**, *10*, 7877.
18. Duan, Y. H.; Shi, X. J.; Li, S. L.; Sun, X. F.; He, X. H. *J. Integr. Agric.* **2014**, *13*, 588.