Morphology and Properties of a New Biodegradable Material Prepared from Zein and Poly(butylene adipate-terephthalate) by Reactive Blending

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ABSTRACT: In this study, zein, a renewable natural biopolymer from corn, was used to prepare a new biodegradable material with poly(butylene adipate-terephthalate) (PBAT) by reactive blending in the presence of poly(ethylene glycol diglycidyl ether) (PEGDGE). The effects of blending temperature and zein content on the morphology and mechanical and thermal properties of PBAT/zein blends with or without PEGDGE were investigated. Because of the high reactivity of the epoxy group in PEGDGE, the interfacial compatibility between zein and PBAT was improved greatly, and zein exhibited as a spherical phase with smaller size and finer dispersion in the PBAT matrix after the introduction of PEGDGE. Therefore, PEGDGE served as a plasticizer and reactive compatibilizer in the PBAT/zein blending system. Both the tensile strength and elongation at break of the blends with PEGDGE were improved greatly compared with those of the blends without PEGDGE but decreased gradually with the increase of zein content. These findings may provide a feasible way to utilize zein widely, and the new biodegradable blends with excellent stretchability could be used as packing materials in the future.

INTRODUCTION

In the past 70 years, the commercial products from synthetic polymers have been widely used, covering almost all fields of human life and activities, and have made tremendous contributions to the development of human civilization. However, the most initial sources of them are from the nonrenewable fossil resources. With the rapid developing economy and the increasing population, fossil resources are quickly depleted, which may limit the development of the traditional polymer industry in the future. In addition, the worst thing is that most synthetic polymers are difficult to be degraded in the natural environment. The debris formed by discarded plastics have resulted in serious environmental pollution; even the accumulation of small plastic particles has been found in marine animal bodies. Therefore, the design and development of environmental-friendly biodegradable polymer materials to replace the petroleum-based polymers may be the effective way to solve the above problems.

Corn, one of the world’s highest yield crops, is an important food and mainly used to produce corn starch in industry. Thus, a large amount of zein, the main component in the industrial scraps, is produced. However, the scraps were often sold as a low-value feed protein resource for animals because zein lacks the essential amino acids of human body, such as lysine and tryptophan, or even discharged into the river, which has caused serious environmental pollution. Therefore, exploring more efficient utilization for zein, a renewable natural biopolymer, will have great significance for promoting the development of corn industry and protecting the environment with remarkable economic and social benefits.

However, the pure zein is difficult to be manufactured into a certain material because it is not thermoplastic and has very poor mechanical properties. Therefore, we used zein as a filler to prepare a new material with good mechanical properties by reactive blending with poly(butylene adipate-terephthalate) (PBAT). PBAT is a synthetic, biodegradable aliphatic-aromatic copolyester with excellent stretchability. It is obtained by condensation polymerization of adipic acid, butanedioi, and terephthalic acid, wherein the aromatic structure unit provides good thermal stability and mechanical properties and the aliphatic structure unit contributes to its excellent flexibility and good biodegradability. However, the low mechanical properties and high price of PBAT have hindered its wide application. Therefore, many biopolymers or synthetic polymers, such as soy protein, starch, cellulose, and poly(lactic acid), were introduced into PBAT by blending. However, the mechanical properties of blends often decreased significantly, or the high toxic cross-linkers (such as methylene diphenyl disocyanate) were used.

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Figure 1. Effects of blending temperature on the mechanical properties of PBAT/zein blends with PEGDGE (90/10/5, mass ratio). (a) Molding temperature was the same as the blending temperature. (b) Molding temperature was fixed at 175 °C. Blending temperature: (1) 130; (2) 145; (3) 160; (4) 175; and (5) 190 °C.

Figure 2. Effects of content of zein and PEGDGE on the mechanical properties of the blends (the molding and blending temperature was 175 °C). (a) Stress–strain curve without PEGDGE. (b) Stress–strain curve with 5 phr (parts per hundreds of PBAT and zein mixture) PEGDGE. Zein content in the mixture of PBAT and zein: (1) 0; (2) 5; (3) 10; (4) 15; (5) 20; (6) 25; and (7) 30%. (c) Tensile strength; (d) tensile modulus; and (e) elongation at break.
In this work, zein was introduced into PBAT by reactive blending in the presence of poly(ethylene glycol diglycidyl ether) (PEGDGE). The effects of blending condition and content of zein on the mechanical properties of the resulting blends were investigated. It was found that PEGDGE has played an important role in improving the interfacial compatibility between zein and PBAT and mechanical properties of blends. Morphology, thermal properties, water absorption, and degradability of PBAT/zein blends were also studied. The new biodegradable material with excellent stretchability could be used as the packing material.

## RESULTS AND DISCUSSION

### Mechanical Properties

#### Effects of Blending Temperature on the Mechanical Properties of the Blends.

To explore the suitable blending and molding temperature for the preparing process of PBAT/zein blend with good mechanical properties, the mixtures of PBAT, zein, and PEGDGE with a fixed feed mass ratio (90/10/5) were blended under various blending temperatures in the range from 130 to 190 °C and then compressed to form a sheet under the same temperature as their corresponding blending process, respectively. The stress–strain curves of the samples obtained from different blending temperatures (as the melting temperature is equal to the blending temperature) are shown in Figure 1a. With the increase of the blending and molding process temperature from 130 to 175 °C, the tensile strength of the blends increased from 20 to 29 MPa, whereas the elongation at break increased from 20 to 30 MPa (that of the blend without PEGDGE was kept under a partially melting condition with poor fluidity, which resulted in the rather low mechanical properties of the blending sample. With the increase of process temperature, the blending mixture had better fluidity, which led to the blend sample with higher mechanical properties. However, if the process temperature was too high, it could cause a large range of decomposition of zein, which resulted in a decrease of mechanical properties. Furthermore, the molding temperature was fixed at 175 °C and just the blending temperature was changed to manufacture the PBAT/zein blends with mass ratio 90/10/5, and the stress–strain curves of these blends are shown in Figure 1b. Similar results could be learnt from Figure 1b to those in Figure 1a. Therefore, the temperature of the blending and molding process was fixed at 175 °C in the following research studies.

#### Effects of Content of Zein and PEGDGE on the Mechanical Properties of the Blends.

By fixing the blending temperature and molding temperature at 175 °C, a series of PBAT/zein blends with various zein contents with or without PEGDGE addition was prepared. The typical stress–strain curves of the blend samples containing different zein contents with or without PEGDGE are shown in Figure 2a,b, respectively. Moreover, the variations in the relevant tensile properties as a function of different zein contents are displayed in Figure 2c–e.

As shown in Figure 2a, in PBAT/zein blend without PEGDGE, the elongation at break of the blend sample containing 5% zein was 1300% (line 2), which was close to that of the pure PBAT sample (1220%, line 1). As the content of zein increased from 10 to 30%, the tensile strength and elongation at break of the resulted material decreased rapidly. When 30% zein was added, the tensile strength dropped to 3.7 MPa and the elongation at break reduced to 30%. It may be due to the poor compatibility between PBAT and zein. Thus, by considering the availability of the resulted materials, the maximum addition of zein was limited within 25% in the subsequent experiments.

With the addition of PEGDGE, the overall performance of the blending material has been greatly improved. For example, when 5% zein was added, the tensile strength of the blend with PEGDGE increased from 28.2 MPa (that of the blend without PEGDGE) to 34.3 MPa, whereas the elongation at break...
increased from 1300 to 1430%. When the zein content was 20%, the tensile strength of the blend was 18.2 MPa and the elongation at break was 860% with the addition of PEGDGE. Guo et al. reported that the mixture of PBAT and 20% soy protein has a tensile strength of 9 MPa and an elongation at break of 530%. Compared with PBAT/soy protein blends, the PBAT/zein blends modified by PEGDGE had the better mechanical properties. In all cases, the tensile strength and elongation at break of blends with PEGDGE were better than that of the blend without PEGDGE.

With the increase of zein content, both tensile strength and elongation at break of the blends with PEGDGE were decreased, which is similar to that of the blends without PEGDGE as discussed above. This can be attributed to the bifunction of PEGDGE in the PBAT/zein blend system. First, PEGDGE acts as a plasticizer, which can increase the mobility of the polymer molecular chain and reduce the crystallizability, and thus improves the elongation of the blending samples. On the other hand, PEGDGE serves as a reactive compatibilizer in the PBAT/zein blend system. PEGDGE has two epoxy groups, which are ready to react with the amino, carboxyl, or hydroxyl group of zein and the terminal carboxyl group or hydroxyl group of PBAT under the blending condition. The reaction of epoxy group with PBAT and zein will improve the interfacial compatibility between PBAT and zein, which is more helpful to improve the mechanical properties of PBAT/zein blend and the stability of zein in the PBAT matrix.

In addition, as learnt from Figure 2d, the tensile modulus of the PBAT/zein blends increased with the increase of zein content, which means that zein can increase the stiffness of the blend material. It may help to eliminate the intrinsic shortcomings of PBAT (soft and low tensile modulus). With the same zein content, the addition of PEGDGE resulted in a decrease in the tensile modulus of the blends, which is due to the plasticizing effect of PEGDGE.

**Morphology.** For pure PBAT and PBAT with only PEGDGE (Figure 3a,b) sample, the fractured surface is smooth with the same ripples which are caused by deformation during the fracturing in liquid nitrogen. When 10% zein (Figure 3c) was added, the fracture surface of the blend becomes rough. It can be clearly seen that the zein particles are discontinuously embedded in the PBAT matrix phase, which is similar to that in the PBAT/starch blend system. With the addition of PEGDGE (Figure 3d, 90/10/5), the zein particles with a smaller size dispersed in the PBAT phase and the phase interface between zein and PBAT becomes unclear. It means that the interfacial compatibility between PBAT and zein in the blend is improved with the introduction of PEGDGE.

As the zein content increases to over 20% (Figure 3e,g), many pores, which are formed by the loss of zein particles after fracturing, can be observed in the fractured surface of the blends without PEGDGE. Because of the poor interaction force of the two phases, a large phase separation occurs in the blends, which leads to the poor mechanical properties of the blends. When 5 phr of PEGDGE was added (Figure 3f,h), the pores can also be seen on the fractured surface, but becomes smaller apparently.

To better understand the function of PEGDGE in the blends, the fractured blend sheets were immersed in dimethyl sulfoxide (DMSO) for 24 h and the scanning electron microscopy (SEM) images of the fracture surface of blends after DMSO treatment are shown in Figure 3i–p. Because zein is soluble in DMSO, zein that was not attached to PBAT by chemical reaction will be removed after being treated with DMSO. As can be seen in Figure 3k–p, many pores on the fractured surface of those blends containing zein can be found. However, the pore size of the blends with PEGDGE is smaller than that of blends with the same zein content but without PEGDGE but larger than their corresponding sample before DMSO treatment apparently. These findings confirm that the zein particles with smaller size are dispersed in the PBAT matrix after introduction of PEGDGE, compared to that of samples without PEGDGE. The better mechanical properties of PBAT/zein blends with PEGDGE could be attributed to the finer zein dispersion in the PBAT matrix and the improved interfacial compatibility between PBAT and zein.

**Fourier Transform Infrared Analysis.** To detect the chemical reaction of epoxy with zein and PBAT, the PBAT/zein blends with and without PEGDGE were immersed in DMSO to remove the unboned zein from the blends. The Fourier transform infrared (FT-IR) spectra of PBAT and PBAT/zein blends before and after being treated with DMSO are displayed in Figure 4 (Figure 4a is the enlarged portion of Figure 4a at a wavelength of 1700−1300 cm⁻¹). By comparing with the spectra of PBAT (spectrum 1) and PBAT/zein blend (80/20/0, spectrum 5), the two peaks at 1680−1630 and 1570−1520 cm⁻¹ can be found in the FT-IR spectrum of the PBAT/zein blend, which are assigned to the characteristic peaks of amide I and amide II of zein. It confirms the introduction of zein in the blend sample by blending. After being treated with DMSO, the two characteristic peaks of zein...
are disappeared in the spectrum of the PBAT/zein blend without PEGDGE (80/20/0, spectrum 2), which meant that the free zein particles which physically encapsulated in the PBAT matrix had been removed completely after being immersed in DMSO. However, the characteristic peaks of zein could still be seen in the spectra of the DMSO-treated PBAT/zein blends with PEGDGE (90/10/5, spectrum 3; 80/20/5, spectrum 4). These results from FT-IR analysis have provided clear evidence for the occurrence of chemical reaction of epoxy with PBAT and zein during the blending process, which led to the improvement of interfacial compatibility between PBAT and zein. It is consistent with the observation by SEM.

**Differential Scanning Calorimetry and Dynamic Mechanical Properties.** The glass-transition temperature ($T_g$), melting temperature ($T_m$), and crystallization temperature ($T_c$) of PBAT and PBAT/zein blends are obtained with differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) and summarized in Table 1. From Table 1 and Figure 5, when 5 phr of PEGDGE was added to pure PBAT, the glass-transition temperature of PBAT decreases from $-27 \, ^\circ C$ to about $-36 \, ^\circ C$. PEGDGE mainly acts as a plasticizer to reduce the entanglement between the PBAT molecular chains. As the content of zein increases from 0 to 25%, the $T_g$ of PBAT in the blends with PEGDGE increases from $-35.9 \, ^\circ C$ to $-31.2 \, ^\circ C$ (DSC). Because the $T_g$ of zein is higher than that of PBAT, and the addition of PEGDGE causes the PBAT segment react with the zein segment to hinder the mobility of PBAT chain, which led to the increase of $T_g$ of PBAT.

Figure 6 shows the relationship between the storage modulus of the material and the loss factor to temperature. It can be seen from Figure 6a that all blend sheets exhibit high storage modulus at low temperatures and have a sharp drop in the storage modulus around $-25 \, ^\circ C$, which corresponds to the glass-transition process of PBAT in the blend. During the rubbery plateau period, the storage modulus of the material remained stable. With the addition of zein, the storage modulus of the samples increases, which is attributed to the reinforcing effect provided by zein. It is consistent with the results from mechanical testing. As can be seen from Figure 6b, the addition of zein causes the peak temperature of loss factor to increase, which represents an increase in the glass-transition temperature. Therefore, the effects of zein content on the glass-transition temperature of PBAT/zein blends are similar to that obtained from DSC analysis.

**Thermogravimetric Analysis.** The thermogravimetric analysis (TGA) curves of pure PBAT, zein, and PBAT/zein blends with 5 phr of PEGDGE are shown in Figure 7. Zein begins to decompose at about $200 \, ^\circ C$ and has over 20% weight loss at $300 \, ^\circ C$ (line 6). The blends with 20% zein begins to decompose at $290 \, ^\circ C$ (line 4), which is caused by dehydration, depolymerization, and decomposition of thermally unstable proteins and carbohydrate units. In addition, the weight of the blend containing 20% zein is reduced by 20% until the temperature reaches $360 \, ^\circ C$. This indicates that the thermal stability of zein in the blends is greatly improved by blending with PBAT; thus, the PBAT/zein blend has a good thermal stability.

**Water Absorption and Weight Loss.** The effects of zein content and PEGDGE on the water absorption and weight loss in the water of the blends are displayed in Figure 8. Pure PBAT had the lowest water absorption because of its high hydrophobicity. As the content of zein increases from 5 to 25%, the water absorption of the blend material increases gradually from around 2 to 12%, which may be attributed to the plenty of hydrophilic groups in zein, although zein is insoluble in water. With the addition of PEGDGE (5 phr), the water absorption of the blend material increases slightly (about 1%), compared with that of the sample with the same zein content. Moreover, the water absorption of polyblend samples is rather low ($<0.6\%$). It means that most of PEGDGE was bonded tightly in those blend materials by the chemical reaction of epoxy group with zein and PBAT, though PEGDGE is a water-soluble compound. Therefore, these findings may guarantee for the application of PBAT/zein blends in a humid and watery environment.

**Biodegradability.** The biodegradability of PBAT/zein blends was tested by burying the samples in natural soil. As shown in Figure 9a–d, the surfaces of all samples are smooth with some ripples before degradation. For pure PBAT, no significant change can be found in the surface of the sample before 15 d and only a tiny crack (Figure 9m) can be seen and about 2% weight loss can be detected after 30 d, which indicate the low degradation rate of PBAT. With the addition of zein, after 3 d degradation, the small crack (Figure 9f) can be found on the surface of the blend sample with 10% zein, while many holes appear on the surface of those blend samples with 20% (Figure 9g) and 25% (Figure 9h) zein. The degradation rate of the blend samples increases with the increase of zein in the blend. After burying in soil for 30 days, the blend sheet with...
25% zein was broken to debris, and the weight loss of the blend samples with 10 and 25% zein had reached to over 26 and 53%, respectively. Therefore, the introduction of zein can greatly enhance the biodegradability of the PBAT/zein blend materials.

**CONCLUSIONS**

A new biodegradable material was prepared by reactive blending of zein and PBAT. By the addition of the reactive plasticizer PEGDGE, the tensile strength and elongation at break of the blends were greatly improved compared with that of PBAT/zein without PEGDGE but did not reduce too much when compared with that of pure PBAT. For example, when the mass ratio of PBAT/zein was fixed to 95/5, the tensile strength of the material increased by 22% and the elongation at break increased by 10% with the addition of 5 phr of PEGDGE. Meanwhile, zein has shown a reinforcing effect in the PBAT matrix, which led to the increase of the storage modulus and glass-transition temperature of the blends. Considering the mechanical performance of the blends, the addition of zein may be controlled within 20%. This flexible blending strategy can be easily extended to other polymer/natural macromolecule systems, such as wheat protein, keratin, and so on. The biodegradable PBAT/zein blend materials with good thermal stability and low water absorption can adapt to the application in different environments. The introduction of zein in PBAT may increase the competitiveness of PBAT in cost as a degradable material in the market.

**MATERIALS AND METHODS**

**Materials.** Zein (Z3625, moisture ca. 8 wt %) and DMSO were purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd. (Shanghai, China). PBAT (TH801T, \( M_w = 24,350 \)) was purchased from Xinjiang Blue Ridge Tunhe Chemical Industry Joint Stock Co., Ltd. (Xinjiang, China), having a density of 1.26 g/cm³. Zein and PBAT were dried in a vacuum oven at 40 °C for 24 h before blending, to remove moisture for avoiding hydrolytic degradation. PEGDGE (S65149, >99%, molar mass: 400 g/mol) was obtained from Shanghai Yuanye Biological Technology Co., Ltd. (Shanghai, China) and used as received without further purification.

**Methods.** Preparation of PBAT/Zein Blends. The blends of PBAT and zein were prepared in an intensive mixer with the following typical process. The predried 6 g of zein and 54 g of PBAT were premixed at room temperature using a mixer and then stirred in an intensive mixer (HAAKE PolyLab OS, Thermo Fisher, USA) at a certain temperature for 10 min. For the PBAT/zein blends with PEGDGE, 3 g of PEGDGE was poured into the intensive mixer with zein and PBAT mixture. Finally, the obtained sample was compression-molded on a vulcanizing machine (GT-7014-H30C, Taiwan High Speed Rail Testing Instrument Co., Ltd. Taiwan, China) under 30 MPa for 10 min.

![Figure 6](https://example.com/figure6.png)

Figure 6. Storage modulus (a) and tan δ (b) of pure PBAT and PBAT/zein blends. PBAT/zein/PEGDGE ratio: (1) 100/0/0; (2) 100/0/5; (3) 90/10/5; (4) 80/20/5; and (5) 75/25/5.

![Figure 7](https://example.com/figure7.png)

Figure 7. TGA curves of pure PBAT, zein, and PBAT/zein blends with PEGDGE. PBAT/zein/PEGDGE ratio: (1) 100/0/0; (2) 100/0/5; (3) 90/10/5; (4) 80/20/5; (5) 75/25/5; and (6) 0/100/0.

![Figure 8](https://example.com/figure8.png)

Figure 8. Water absorption (1,2) and weight loss (3,4) of PBAT/zein/PEGDGE blends with different contents of zein. Without PEGDGE: 1,3; with 5 phr PEGDGE: 2,4.
MPa molding pressure for 3 min at a certain temperature to form a sheet. The obtained PBAT/zein blends with and without PEGDGE were labeled PBAT/zein/PEGDGE: 90/10/5 (mass ratio) and 90/10/0, respectively. The addition of PEGDGE was shown as parts per hundreds (phr) of resin (the mixture of PBAT and zein), for example, 5 phr of PEGDGE.

**Characterization. Mechanical Testing.** According to the Standard Test Method for Tensile Properties of Plastics (ASTM D638-14), dumbbell samples for tensile testing were prepared using a cutter from the blend sheets and placed under 55% relative humidity for 48 h before testing. Tensile tests were carried out using universal testing machine (Instron 5966, Instron, USA) with a crosshead speed of 20 mm/min. At least five individual replicates were tested for each sample to get the average value.

**Scanning Electron Microscope.** The morphology of the cross section of PBAT/zein blends with or without PEGDGE was observed using a scanning electron microscope (Ultra 55, Zeiss, Germany) at an accelerating voltage of 1.0 kV. The blend sheet was fractured in liquid nitrogen and sputtered with 60 s gold before observation.

**FT-IR Spectroscopy.** To check the reaction between zein and PBAT with PEGDGE, the blend sheets (10 mm × 10 mm × 0.8 mm) were placed in 300 mL of DMSO for 12 h, then washed with distilled water thoroughly, and dried at 70 °C for 12 h. The FT-IR spectra of the blend sheets before and after being immersed in DMSO were obtained by a Nicolet 6700 FT-IR spectrometer (Thermo Fisher, USA) with the attenuated total reflectance mode at 4 cm⁻¹ resolution using 64 scans in the range of 4000–500 cm⁻¹.

**Differential Scanning Calorimetry.** The thermal properties of the blends were investigated using DSC (Q2000, TA Instruments, USA). The sample was first heated to 150 °C at 50 °C/min and held for 6 min to eliminate the thermal history of the sample, then cooled to −80 °C at 10 °C/min and stayed for 10 min, and then reheated to 150 °C at a rate of 10 °C/min.

**Dynamic Mechanical Analysis.** The dynamic mechanical properties of the blends were studied using a dynamic mechanical analyzer (SDTA861e, Mettler Toledo, Switzerland). The sample (10.5 mm × 4 mm × 0.8 mm, 8–12 mg) was first equilibrated at −60 °C for 3 min and then scanned from −60 to 90 °C at a heating rate of 3 °C/min with a frequency of 1 Hz in a stretching mode, thereby obtaining the storage modulus and the loss factor. The peak temperature of the loss factor is determined to be the glass-transition temperature (Tg).

**Thermal Analysis.** The thermal stability of the blends was investigated using a thermogravimetric analyzer (TGA 1, Mettler Toledo, Switzerland). Samples (5–7 mg) were heated in a range of 50–600 °C at a rate of 10 °C/min under a nitrogen atmosphere. All TGA were repeated three times.

**Water Absorption Tests.** The water absorption and the weight loss of the PBAT/zein blends in water were evaluated in accordance with ASTM D570-98 (2018, Standard Test Method for Water Absorption of Plastics). First, all samples (20 mm × 20 mm × 1 mm) were dried in a vacuum oven at 40 °C for 24 h until constant weight (W1). The dried samples were placed in distilled water, submerged for 24 h at room temperature, then taken out from water, and immediately weighed (W2) after wiping off the surface water. The wet samples were again dried in a vacuum oven at 40 °C for 24 h until constant weight and weighed (W3). Five replicates were tested for each sample to get the average value. Then, the weight loss rate and water absorption rate are calculated by eqs 1 and 2, respectively,

\[
\text{Weight loss rate } (\%) = \left(\frac{W_1 - W_2}{W_1}\right) \times 100 \quad (1)
\]

\[
\text{Water absorption rate } (\%) = \left(\frac{W_2 - W_3}{W_1}\right) \times 100 \quad (2)
\]

**Biodegradability Test.** The biodegradability of the PBAT/zein blends was evaluated by burying the samples in natural soil according to GBT 19275-2003 (evaluation of the potential biodegradability and disintegration of plastic materials by the action of specific microorganisms). First, all blend sheets (30 mm × 30 mm × 1 mm) were dried in a vacuum oven at 40 °C for 24 h until constant weight. Then, three individual groups of the blend sheets were buried in the soil with plants at a depth of 20 cm. The moisture content and pH of soil were kept at about 35 wt % and 6.0–7.0, respectively. After 3, 15, and 30 days, one group of the degraded sample was taken out, washed.

**Figure 9.** SEM images (a–p) of the surfaces of pure PBAT and PBAT/zein/PEGDGE blends after burying in soil for various degradation times.
with distilled water, and dried in a vacuum oven. The surface morphology of the degraded blend sheet was observed by SEM.

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Notes

The authors declare no competing financial interest.

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