Ultrafast Bulk Degradation of Polylactic Acid by Artificially Cultured Diatom Frustules

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Abstract

In the field of governing our “Plastic Planet”, polylactic acid (PLA) has been considered to be a promising and ecologically friendlier alternative to traditional petroleum-based plastics. However, PLA-based products degrade slowly in the natural environment, likely resulting in a large accumulation of PLA waste worldwide in the near future. Herein, we have incorporated artificially cultured diatom frustules (DFs) into PLA, and found an improvement of more than eightfold on the degradation rate, from more than 24 months to 3 months or even less, as compared with the pure PLA. Mechanistic investigations illustrate that DFs change the degradation behavior of PLA from surface erosion to bulk erosion by the induced microfibril crystals. Simulation analysis verifies that the unstable crack propagation inside the PLA matrix greatly accelerates the degradation. The method developed in this work provides an efficient way to achieve rapid and controllable degradation of biodegradable polymers for the urgent and widespread usage of green plastic productions.

Introduction

Plastics are, apparently causing a global environmental and health crisis. By the end of 2015, 8,300 million tons of petroleum-based plastics were produced, and roughly two-thirds were emitted into the environment, causing air, water and soil pollution^{1–3}. Recently, a shocking report showed that plastics have emerged into food chains in the form of microplastics and toxic chemicals^{4,5}. Prompted by environmental protection and human health, many researchers have focused on investigating natural and biodegradable polymers to curb carbon emissions on our plastic planet^{6–8}.

A biodegradable polymer is defined as a material that can be fully degraded into carbon dioxide, methane and water, among which polylactic acid (PLA) is appealing in this regard due to its easy processing, green pathways and good biocompatibility^{9,10}. However, its inherently slow and uncontrollable degradation rate remains today a serious shortcoming for widespread adoption^{11–13}. Based on previous research, PLA will take at least two years or even longer to be fully degraded. Some papers report that the degradation rate can be improved by virtue of the specific sample size (thin film/porous structure) and degradation environment (acid/alkali degradation, photodegradation and enzymatic degradation)^{14–16}; however, these approaches are pretty impractical, in addition to high cost^{17–19}. Given its rapid market growth, there is a bold prediction that mountainous PLA-based products may ultimately threaten the eco-environment again if the problem of slow degradation is not solved. Therefore, the investigation of rapid degradation mechanisms in natural soil should not be ignored^{20,21}.

Biomass, an organism formed by photosynthesis, is identified as a promising energy and modifier due to its renewability and non-pollution process^{22,23}. The diatom is a widely existing natural biomass, that accounts for approximately one-fifth of global primary production. The assimilation products of diatoms are mainly oil and frustules, The former have been applied to biodiesel, while the diatom frustules (DFs) have not been thoroughly explored. As a biomass silica, DFs have the advantages of high purity, high

surface activity and a hierarchically porous structure, which can be applied in catalyst carriers and enhancing additives^{24,25}. Additionally, DFs open up a vast range of prospects in the field of biodegradable materials due to their bioactivity and renewable characteristics.

In this study, diatoms are harvested in large quantities by artificially cultured techniques, and then the diatoms are oxidized and purified to obtain DFs²⁶. The degradation behavior of the PLA/DF composites is investigated with respect to their mechanical properties, morphological structure, porosity and crystallinity. Compared with pure PLA, the PLA/DF composites exhibit an ultrafast degradation rate in natural soil. The results demonstrate that DFs can induce the formation of microfibril crystals during degradation and transform the degradation behavior from surface erosion to bulk erosion. Moreover, the propagation of cracks inside PLA is simulated by the extended finite element method (XFEM), and the obtained stress field and strength factor at the crack tip show that stress concentration occurs inside the PLA matrix, causing unstable crack propagation and a rapid decomposition rate. In short, both experimental results and theoretical analyses uncover the degradation mechanism; i.e., microfibril crystals induced by DFs drive unstable crack propagation to further accelerate the degradation of the PLA matrix.

Results And Discussion

Degradable characterization of PLA/DF composites. A fully-biodegradable material was prepared by blending cultured DFs and PLA extracted from starch, and then the PLA/DF composites were degraded into carbon dioxide and water by being buried in soil (Fig. 1). Then CO₂ and H₂O will be absorbed again through photosynthesis. Therefore, PLA/DF composites can be incorporated into the natural cycle to achieve carbon neutrality. The artificially cultured diatoms were oxidized, pickled and sintered successively to remove diatom oil and obtain DFs. DFs show a multilevel pore structure ranging from 50-100 nm (Fig. 1b). After melt blending, DFs can be dispersed well in the PLA matrix (Fig. 1c), indicating good compatibility between them. Infrared spectroscopy (Fig. 1d) was performed to investigate the interactions in-between the DFs and PLA matrix. DFs show an absorption band at $\sim 3490\text{ cm}^{-1}$, representing Si-OH stretching vibrations. Pure PLA exhibits sharp absorption bands at $\sim 3500\text{ cm}^{-1}$ and $\sim 3600\text{ cm}^{-1}$, indicating C-OH stretching vibrations. However, after mixing the PLA and DFs, the PLA/DF composites show weak absorption bands at $\sim 3480\text{ cm}^{-1}$ and $\sim 3585\text{ cm}^{-1}$. In addition, the infrared absorption band of Si-OH cannot be found for PLA/DF. These changes are attributed to the formed hydrogen bonds between Si-OH and C-OH. Moreover, X-ray photoelectron spectroscopy (XPS) results show that the component ratio of C=O decreases from 56% to 47% (Fig. 1e-1f). It is suggested that the Si-OH of DFs can form hydrogen bonds with the C-OH of PLA. In short, the hydrogen bonds increase the interaction between DFs and PLA.

The good compatibility can affect the crystallization behavior of PLA. X-ray diffraction (XRD) results (Fig. 1g) show that DFs can promote the formation of a crystals in PLA. Generally, a crystals are considered as a more stable crystal form than a α crystals in PLA, so the addition of DFs can increase the crystallinity

and stability of PLA. In addition, due to the heterogeneous nucleation effect of DFs, more nucleation sites are formed and the spherulites become smaller and more regular in PLA, as observed by using polarizing microscopy (Supplementary Fig. 1).

Table 1. Tensile results for pure PLA and the PLA/DF composites.

	E (GPa)		s_y (MPa)		e (%)	
	Pure PLA	PLA/DF	Pure PLA	PLA/DF	Pure PLA	PLA/DF
W_0	7.35 ± 0.15	7.74 ± 0.14	71.7 ± 1.1	71.4 ± 1.2	2.6 ± 0.2	2.9 ± 0.2
W_4	7.22 ± 0.16	6.51 ± 0.28	71.2 ± 1.5	59.9 ± 1.9	2.3 ± 0.1	2.1 ± 0.3
W_8	7.12 ± 0.15	4.62 ± 0.40	67.2 ± 1.7	30.2 ± 4.3	2.2 ± 0.1	1.3 ± 0.4
W_{12}	6.40 ± 0.33	-	59.1 ± 2.0	-	2.1 ± 0.3	-

Mechanical properties are a significant criterion for the degradation rate of polymeric materials (Fig. 2a, Table 1). Before degradation, the strength and ductility are enhanced simultaneously by adding DFs into PLA compared with pure PLA. This is because that PLA forms interpenetrating networks with DFs, and the enhancement mechanisms are discussed in a previous report²⁶. For pure PLA, there is no significant decrease in its tensile performance and only a slight loss in the yield strength (s_y) after 8 weeks. After 12 weeks of degradation in soil, the tensile modulus (E) of pure PLA decreases from 7.35 to 6.40 GPa, s_y is reduced from 71.7 MPa to 59.1 MPa, and the elongation at break (e) decrease from 2.6% to 2.2%. Slight changes in mechanical properties indicate that the degradation rate of pure PLA is very low in natural soil.

However, the tensile properties of PLA/DF composites significantly decrease in a short period of time. After 4 weeks of degradation, the E of the PLA/DF composites is 6.51 GPa, which is reduced by ~16% compared with that before degradation. The corresponding s_y and e decrease by ~16% and ~27%, respectively. Furthermore, the mechanical performance of the PLA/DF composites has gone down dramatically after 8 weeks. The corresponding E, s_y and e, decrease by ~40%, ~58% and ~55%, respectively. At the 12th week, the sample of PLA/DF composites is disintegrated into granules and powders, making it impossible to perform tensile tests. These phenomena show that the degradation rate of PLA/DF composites is higher than that of pure PLA.

Morphology analysis of samples subjected to degradation is performed to investigate the degradation mechanism (Fig. 2b). It is worth mentioning that the color change in pure PLA is not obvious, while the PLA/DF samples gradually became white and opaque with degradation. Moreover, pure PLA shows a smooth surface during degradation. However, the surface of the PLA/DF composites becomes rough with time. In addition to the surface morphology of the samples, the internal fracture surface is analyzed by scanning electron microscopy (SEM) (Fig. 2c). In the first 8 weeks, the fracture surface of pure PLA does not basically change, and only a few micro-nanopores (<1 mm) are found after 12 weeks. However, some

small pores appear in the PLA/DF composites in the fourth week. After wards, the pores inside the PLA/DF composites grow larger in size, i.e., greater than 50 μm .

Furthermore, the degree of hydrolysis can be considered a critical parameter of the degradation rate. This is because the PLA chains are first hydrolyzed into small segments or monomers and then are absorbed by microbes to transform into CO_2 , H_2O and CH_4 (Fig. 3a). The degree of hydrolysis can be characterized by the Fourier transform infrared (FT-IR) spectrum of PLA (Fig. 3b). The band at 1750 cm^{-1} corresponds to the stretching vibrations of the ester carbonyl group $\text{C}=\text{O}$. Within the $1280\text{--}1030\text{ cm}^{-1}$ range, the bands are assigned to symmetric and asymmetric vibrations of the $-\text{C}-\text{O}-$ groups. The band at 1180 cm^{-1} associated with the $\text{C}-\text{O}-\text{C}$ bending vibrations. For pure PLA, the absorbance values of the characteristic $\text{C}-\text{O}-\text{C}$ and $\text{C}=\text{O}$ peaks barely change with degradation, indicating that pure PLA degrades slowly. However, both $\text{C}-\text{O}-\text{C}$ and $\text{C}=\text{O}$ characteristic peak intensities of the PLA/DF composites decrease gradually, proving that the PLA chains have been broken and the number of ester segments is decreasing. In other words, the degradation rate of the PLA/DF composites is faster than that of pure PLA.

The differences between the morphology and microstructure elucidate two degradation pathways, namely, surface erosion and bulk erosion (Fig. 4). When the rate of hydrolysis is greater than that of water diffusion into the polymer, the polymer is eroded from the surface and the core polymeric material remains intact²⁷. Otherwise, when the rate of water diffusion is faster than that of hydrolysis, the pathway of degradation shifts to bulk erosion, and the polymer becomes porous. Moreover, the accumulation of byproducts ($-\text{OH}$, $-\text{COOH}$) can induce internal autocatalysis, which accelerates the bulk erosion compared with surface erosion²⁸. Based on the SEM and FTIR analysis, bulk erosion occurs in the PLA/DF composites, and the degradation rate increases rapidly after 8 weeks. However, pure PLA degrades slowly through surface erosion.

The variation difference in the porosity and pore size between the pure PLA and PLA/DF composites is quantified by microtomography (M-CT) for statistics (Fig. 5). The pores inside pure PLA are under $10\text{ }\mu\text{m}$ in size even after 12 weeks of degradation (Fig. 5a), and the porosity of pure PLA increases slightly from $\sim 0.8\%$ to $\sim 5.2\%$ (Fig. 5b). However, a large number of pores at approximately $50\text{ }\mu\text{m}$ are formed inside the PLA/DF composites at the eighth week. Furthermore, the PLA/DF composites have become porous, and the pores continue to grow through holes after 12 weeks. Moreover, the porosity of the PLA/DF composites increases significantly from $\sim 3\%$ to $\sim 60\%$, and the corresponding weight loss shows the same growing tendency. The above statistics demonstrate that pure PLA mainly degrades by surface erosion, and its degradation rate is slower than that of the PLA/DF composites, which degrade by bulk degradation.

Analysis of the Degradation Mechanism. Some new crystals are formed around DFs after 4 weeks of degradation (Fig. 6a). Based on energy dispersive spectroscopy (EDS) analysis, the microfibril crystals come from PLA (Supplementary Fig. 2). Generally, the crystallization process of PLA by melt cooling is divided into two stages: nucleation and crystal growth. After nucleation, microfibril crystals are formed and then grow to form spherulites through three dimensions. With the degradation from W_0 to W_{12} , the

microfibril crystals grow gradually (~10 mm), similar to a sprout from the ground. Furthermore, many cracks appear along the direction of crystal growth. This phenomenon is referred to as stress corrosion cracking, and has been studied in many materials, such as metals and rubber²⁹⁻³¹. Usually, the stress comes from external stress imposed by the external environment³². The stress corrosion cracks induced by internal crystals, however, have not yet been investigated in degradable polymers. In this study, the new formation of microfibril crystals induced by DFs during degradation causes internal stress around them, and the stress will lead to the propagation of cracks and unexpected decomposition in the PLA matrix.

Table 2 DSC results for pure PLA and the PLA/DF (P/D) composites.

	T_g (°C)		T_{cc} (°C)		T_{m1} (°C)		T_{m2} (°C)		X_c (%)	
Time	PLA	P/D	PLA	P/D	PLA	P/D	PLA	P/D	PLA	P/D
W_0	63.3	65.1	109.4	107.1	155.1	156.8	168.7	170.1	10.1	31.4
W_4	62.9	65.6	107.5	96.2	154.5	154.3	168.2	168.5	9.5	37.8
W_8	62.9	64.3	107.2	94.3	154.6	152.1	167.8	166.9	9.3	33.5
W_{12}	62.7	62.4	103.3	87.8	154.8	147.7	167.5	152.4	8.9	28.4

Furthermore, the effect of DFs on crystallization behavior of PLA is explored by non-isothermal differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD). DSC thermographs of the PLA/DF composites were analyzed and compared to pure PLA after 0, 4, 8, and 12 weeks of degradation (Fig. 6b). The corresponding results in terms of glass transition temperature (T_g), cold crystallization temperature (T_{cc}), melting temperature range (T_m) and the degree of crystallinity (X_c) are summarized in Table 2. Before degradation, the addition of DFs increases the T_g to ~65.1 °C, and T_{m1} to ~156.8 °C owing to the hydrogen bonds formed between PLA (C=O) and DFs (Si-OH), which restrict the movement of the chains and segments. Moreover, the reduced T_c and increased X_c of the PLA/DF composites are attributed to the heterogeneous nucleation effect of DFs, which promotes the crystallization of PLA by reducing the nucleation surface energy. During degradation, pure PLA exhibits a slight decrease in T_g , T_m and X_c . In addition, pure PLA shows low (T_{m1}) and high (T_{m2}) melting peaks, representing two crystal forms of α and α' by virtue of incomplete crystallization (Fig. 6b)³³. After 12 weeks of degradation, the melting peak of the α' crystal becomes slightly weak, and the corresponding X_c only decreases from 10.1% to 8.9%. These phenomena show that the crystal region in pure PLA degrades slowly. However, for the PLA/DF composites, both the T_g and T_m drop greatly. Moreover, the melting peak of α crystals tends to weaken, while the melting peak of the α' crystal appears and becomes stronger. This suggests that the α crystals in the PLA/DF composites decompose with time. Different from pure PLA, the crystalline region in PLA/DF composites is broken off and changes from a stable state to an unstable state. Moreover, it can be observed that the degree of crystallization of the PLA/DF composites first increased and then decreased. The increase in crystallinity is responsible for the preferential degradation of the amorphous phase, in addition to the formation of microfibril crystals.

Generally, PLA is capable of forming the α crystal (200/110) and $\alpha\zeta$ crystal (203) due to the polymorphism of PLA (Fig. 6c). The α crystal and $\alpha\zeta$ crystal have the same conformation (10/3 helical conformation), while the intermolecular forces in the $\alpha\zeta$ crystal are weak, causing a disordered arrangement of the unit cell^{34, 35}. Therefore, the $\alpha\zeta$ crystal is unstable compared with the α crystal^{36, 37}. Degradation occurs from the amorphous region to the crystal region due to density differences. Pure PLA shows a broad diffraction peak at 16.8° , indicating a low degree of crystallinity. With time, the α diffraction peak changes little. However, the PLA/DF composites show a sharp diffraction peak of a crystals, and the peak gradually widens after degradation. At 12 weeks, the diffraction shows two peaks, including α and $\alpha\zeta$ crystals, indicating the crystal transformation of solid-solid^{38, 39}.

Both DSC and XRD results illustrate that the addition of DFs accelerates the decomposition of crystalline regions during degradation. This can be due to the porous structure of DFs, which provides a pathway for water molecules to enter the crystal region. Water can cause the expansion of the crystal region and accelerate hydrolysis degradation.

The above experimental results propose that during the sample preparation process, crystals (mainly α crystals) are preferentially generated around the DFs due to the heteronucleation effect of DFs. After degradation, DFs promote the formation of new microfibril crystals, giving rise to internal stress at the interface between DFs and the PLA matrix. The internal stress leads to crack development and accelerates the degradation near the crystal region. Therefore, the PLA/DF composites degrade faster than pure PLA.

Stress Field and Crack Tip Intensity Factor Analysis. G. R. Irwin established the stress intensity factor (SIF, K_I) criterion in the field of linear elastic fracture mechanics by combining the energy release rate with the SIF at the crack tip^{40, 41}. The criterion describes that a crack will propagate unsteadily when the SIF at the crack tip is greater than the fracture toughness (K_{IC})⁴². In this study, the cracks induced by the growth of microfibril crystals can be simulated by built-in cracks. The initiation and growth of cracks can be simulated by using the XFEM without the definition of a location and path a priori⁴³.

Based on the geometrical diagram of the I type crack (opening mode) and the coordinate system of the crack tip (Fig. 7), the formula for displacement fields at the crack tip can be obtained according to the linear elastic fracture mechanics:

$$U_x = \frac{K_I}{E} (1+\nu) \sqrt{\frac{r}{2\pi}} \cos \frac{\theta}{2} (k - \cos \theta) \quad (1)$$

$$U_y = \frac{K_I}{E} (1+\nu) \sqrt{\frac{r}{2\pi}} \sin \frac{\theta}{2} (k - \cos \theta) \quad (2)$$

$$k = \begin{cases} 3 - 4\nu, & \text{plane strain} \\ \frac{3 - \nu}{1 + \nu}, & \text{plane stress} \end{cases} \quad (3)$$

where K_I represents the SIF, E is the elastic modulus, ν is Poisson's ratio, r is the length of the crack, U_y is the normal displacement of the crack face at the distance r behind the crack front (length of the element along the quarter point side), $q=p$ for plane strain, $k= (3-4\nu)$ for plane strain, and $k= (3-\nu)/(1+\nu)$ for plane stress. In the case of cracks under plane strain, the formula of K_I can be found:

$$U_x = 0 \quad (4)$$

$$U_y = \frac{4K_I}{E} (1-\nu^2) \sqrt{\frac{r}{2\pi}} \quad (5)$$

$$K_I = \sqrt{\frac{2\pi}{r}} \frac{EU_y}{4(1-\nu^2)} \quad (6)$$

Extended Finite element model. A finite element model of built-in crack based on the actual microstructure is established by node-by-node modeling (Fig. 8a). A pre-crack is incorporated into the model, and the crack size is 1~5 mm (L) × 1 mm (W). Plane #a182# in ANSYS is used as a plane element for crack analysis. The corresponding mesh size of the body is 0.6 mm, and the mesh at the crack tip is locally compacted to 0.1 mm. For PLA/DF composites, it is assumed that the elastic moduli, tensile strength and Poisson's ratios in the model are 7 GPa, 70 MPa and 0.28, respectively. After setting properly assigned boundary conditions, the stress field and crack tip intensity factor are then analyzed by ANSYS.

Fig. 8b is a stress nephogram around the crack tip after applying an internal stress of 10MPa. The stress concentration occurs at the tip of the crack, where the internal stress is more than 1000 MPa. Because the existing stress strength is far beyond the tensile strength of the PLA itself, unstable fracture occurs locally in the material. Therefore, the cracks induced by microfibril crystals can advance rapidly.

To study the influence of the crack length on the K_I , a set of lengths are selected between 0.001 mm and 0.005 mm. (Fig. 8c and Supplementary Fig. 3). It has been stated that stress concentration occurs in the initiation of cracks, leading to unstable crack development. When the crack length reaches 0.002 mm, the

obtained K_I value is over the K_{IC} of PLA itself ($\sim 100 \text{ MPa}\cdot\text{mm}^{1/2}$)⁴⁴; as a result, unstable fracture occurs locally in the PLA matrix. Moreover, the internal stress improves rapidly with increasing crack length, and the strength factor is positively correlated with the crack length (Fig 8c). These phenomena elucidate that the formation of microfibril crystals caused internal stress, contributing to the propagation of cracks. With the growth of microfibril crystals, the stress around the tip of microfibril crystals further increases beyond its extreme strength, which accelerates unstable crack propagation. In brief, the microfibril crystals induced by DFs can promote the degradation of PLA. Based on the simulation by the XFEM, it is believed that DFs can regulate the PLA degradation rate by controlling the formation of microfibril crystals.

Discussion. In this study, biomass DFs were applied to regulate the degradation rate of the PLA. The experimental results indicate that pure PLA is mainly degraded by surface erosion, showing only slight changes in the morphology, mechanical properties and porosity. However, the PLA/DF composites achieve sharp degradation by the bulk erosion induced by DFs. Further analysis proposes a major degradation mechanism in which DFs can promote the formation of microfibril crystals during degradation, and the ever-forming crystals drive crack propagation, causing high heterogeneity inside the PLA matrix. Additionally, the XFEM shows that the crack can be highly develop and that, subject to a small internal load, the stress field of the crack tip is orders of magnitude higher than the tensile strength of the material itself. Therefore, the PLA/DF composites degrade faster than pure PLA under the action of DFs. In summary, both the test data and simulated results prove that DFs can greatly regulate the degradation behavior. Rapid degradation solves the problem of recycling PLA products and makes them quickly return to nature. The newly found mechanism provides a method to regulate the degradation rate for other degradable polymers.

Methods

Sample preparation. Polylactic acid (PLA) was provided by NatureWorks LLC. (Ingeo™ Biopolymer 4032D), with a melt flow index (MFI) of 12 g/10 min and a density of 1.24 g/cm^3 . Diatom frustules (DFs) were extracted from artificially cultured diatoms in the South China Sea (114.5°E, 22.3°N). First, diatoms were oxidized by hydrogen peroxide (H_2O_2 , Aldrich Chemical Co.) with 99% purity for 12 h, pickled in hydrochloride (HCl, Aldrich Chemical Co.) with 37 wt% for 24 h, and then sintered at 600°C for 2 h. Afterwards, the sintered DFs were added for planetary ball milling to obtain DF powder. (200 r, 2 h). PLA and DFs were dried at 50°C in an air-dry oven for 24 h before use. PLA and DFs were mixed by melt blending in an internal mixer (Rheomix 300, Haake) operated at 180°C and 50 rpm for 15 min. The samples for tests were prepared by an injection molding machine (Minijet II, Haake) at a plasticizing temperature of 175°C , mold temperature of 50°C , injection pressure of 550 bar, packing pressure of 500 bar, injection time of 2 s and packing time of 8 s.

Degradation test. Pure PLA and PLA/DF composites were buried in soil. The soil was taken from the natural environment (114.5°E, 22.3°N). The degradation test was carried at $\sim 30^\circ\text{C}$ and $\sim 60\%$ humidity. Samples were degraded for 0, 4, 8 and 12 weeks before being removed for testing, including mechanical

properties, morphological structure and crystallization behavior. All samples were first washed in alcohol three times before testing.

Field emission scanning electron microscopy (SEM). Fractured surfaces and damaged surfaces were imaged using a scanning electron microscope (Tescan, VEGA 3) at an accelerating voltage of 5 kV. The specimens were coated via gold film sputtering before testing (20 mA, 90 s).

Fourier Transform Infrared spectroscopy (FT-IR). Infrared spectroscopy was performed by a spectrometer (Thermo Scientific, Nicolet iS5) with 32 scans and a resolution of 2 cm^{-1} by means of the attenuated total reflection mode in the region of $400\text{--}4000\text{ cm}^{-1}$.

X-ray photoelectron spectroscopy (XPS). The study of chemical changes after incorporating DFs into PLA was performed using XPS (Thermo Fisher Scientific, ESCALAB 250Xi). The following settings were used as follows: monochromatic Al K α radiation, X-ray emission at 9 kV and 19 mA, and measuring spot sizes of 300 μm .

Wide-angle X-ray diffraction (WAXD). WAXD patterns were measured on a multipurpose diffractometer (Smartlab). X-ray were generated by a Cu K α radiation source ($\lambda=1.5418\text{ \AA}$). The intensity was recorded at 45 kV and 40 mA within 2θ range from 5° to 90° with a step interval of 0.02° .

Tensile tests. The mechanical properties were determined according to ASTM D638 using an Instron 2367 material testing system at a 2 mm/min crosshead speed. Samples were kept in a vacuum oven at 50°C for 24 h before the tensile tests. Dried samples were covered with a gold-palladium film by sputter coating. All results presented were the average values of at least five measurements.

Differential scanning calorimetry (DSC). The melting and crystallization behavior of the PLA/DF composites was determined on a scanning calorimeter (METTLER DSC1) under flowing nitrogen from 25°C to 190°C at a rate of $10^\circ\text{C}/\text{min}$, kept at 190°C for 10 min and then cooled to 25°C at a rate of $10^\circ\text{C}/\text{min}$. The degree of crystallinity (X_c) was calculated from the ratio of the melting enthalpy (ΔH_m)⁴⁵. X_c was calculated by the following eq. (1):

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0(1 - \omega_f)} \times 100\% \quad (1)$$

where ΔH_m is the melting enthalpy, ΔH_{cc} is the cold crystallization enthalpy, and ΔH_m^0 is the melting enthalpy of 100% crystalline PLA, which is considered 93 J/g ^{26, 46}. The enthalpy values for the composites were normalized according to the amount (ω_f) of DFs, as the DFs are not involved in melting/crystallization processes.

Extended finite element method (XFEM). To understand crack propagation during the degradation of PLA, analogue simulations were performed by the XFEM. ANSYS software was used for modeling, and Plane

#182# was selected as the plane stress element for crack analysis. A step-by-step procedure for the XFEM simulation of crack growth is developed.

Declarations

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Competing interests

The authors declare no competing interests.

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Figures

Figure 1

Preparation and properties of DFs and PLA/DF composites. a Carbon cycle diagram: I-marine culture, II-production, III-application and IV-degradation in soil. b-c SEM images of the DFs and PLA/DF composites. d FT-IR spectra of pure PLA (blue), DFs (gray) and PLA/DF composites (red). e-f XPS spectra of pure PLA and PLA/DF composites. Insert: component ratio of functional groups by the ratio of oxygen atoms from different functional groups. g XRD pattern of pure PLA (blue), DFs and PLA/DF composites.

Figure 2

Performance of pure PLA and PLA/DF composites. a Tensile stress-strain curves. The PLA/DF composites exhibit only three curves due to failure in the 12th week. b Sample photos (above) and optical micrographs (below). c SEM images of pure PLA and PLA/DF composites after 0, 4, 8, and 12 weeks of degradation.

Figure 3

Schematic of the degradation mechanism of PLA. b FT-IR spectra of pure PLA and the PLA/DF composites after 0, 4, 8, and 12 weeks of degradation.

Figure 4

Steps of degradation in the biodegradable polymer. Under a bulk erosion mechanism, the polymer is eroded inside the material and becomes porous. Under a surface erosion mechanism, the polymer is mainly eroded from the surface and remains intact.

Figure 5

Evolution in the microporosity. a Layer fitting results by microtomography (M-CT). b Statistical results of the porosity. The evolution of the internal porosity (bars) is compared to the evolution of the weight loss (dots).

Figure 6

Analysis of degradation mechanism. a SEM micrographs of brittle fracture surface. Blue indicates the newly formed microfibril crystals. b Non-isothermal DSC thermograms. c WAXD patterns of the pure PLA and PLA/DF composites after 0, 4, 8, and 12 weeks of degradation.

Figure 7

Geometric diagram of the type I crack (left) and the coordinate system of the crack tip (right). L and W represent the crack length and width, respectively. σ is the applied stress.

Figure 8

Stress field and crack tip intensity factor analysis. a Grid diagram of the plane model with built-in crack. b Stress nephogram under an inter-stress of 10 MPa. c Curve of the stress intensity factor (K_I) with crack length (L).

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