**The physical properties of poly(L-lactide) and functionalized eggshell powder
composites**

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1. Introduction

Because poly(L-lactide) (PLLA) is biomass-derived, biocompatible, biodegradable, and nontoxic to both human body and the environment, it has been paid much attention. It has been widely applied to the medical, agricultural, and general-purpose plastics fields [1-4]. However, its slow crystallization rate, relatively poor mechanical properties, and poor thermal stability have limited its further wide application. In order to overcome these disadvantages, copolymer synthesis, polymer blending, and reinforced composite methods have been introduced and developed extensively [5,6]. The crystallization rate of PLLA could be enhanced by incorporation of nucleating agents. Up to now, many kinds of nucleating agents have been developed both in the scientific community and industry toward the improvement of PLLA crystallization rates [7,8]. A detailed overview on the developed nucleating agents for PLLA has been provided by Huneault et al. recently [8]. Among various nucleating agents for PLLA, layered metal phosphonates based on inorganic–organic hybrids have exhibited pronounced nucleating ability on PLLA [9-12]. The nucleation effect of zinc phenylphosphonate (PPZn) to that of talc and poly(D-lactide) was compared by Pan et al. [9]. The isothermal crystallization kinetics tests showed that PPZn was more effective than talc and PDLA in enhancing the crystallization rate of PLLA. The effect of metal type on the nucleating ability of PLLA was also investigated by comparing zinc phosphonates (PPZn), calcium phosphonates (PPCa) and barium phosphonates (PPBa) previously [10]. The nucleating ability increased in the order of $PPBa < PPCa < PPZn$ has been observed as a result of the different dispersion and

interfacial interactions of these nucleating agents in the PLLA matrix. Moreover, PPCa supported onto the surface of nano- CaCO_3 or clay could further improve its dispersion and nucleating efficiency in the PLLA matrix [11, 12]. In addition, metal phosphonates can find applications in the field of biomaterials because phosphate is a naturally occurring functional group. It has been suggested that the metal phosphonates are potential materials for developing oligonucleotide microarrays, protein binding, and drug-delivery systems [13].

Of particular interest is the recently developed composite technology consisting of biopolymer and many natural and biobased fillers like starch, soy protein, lignocellulosic agricultural residues like soy stalk, and many other plant fibers [14-17]. Mechanical and thermal properties of these green composite with comparable properties have been extensively investigated and employed in a wide range of engineering applications due to their sustainable, economic and environmental advantages compared to petroleum-based composite. A widely used strategy to tailor the crystallization and mechanical properties of polymer composites is via the incorporation of various hard fillers into polymer matrix [18]. Exploring sustainable green resources for the development of novel environment-friendly and biobased hard fillers is also important and has been paid great interest from both academy and industry [19-24].

Eggshell, a natural bioceramic composite, represents great source of biobased calcium carbonate [25]. Eggshell mainly contains 94% calcium carbonate, 1% magnesium carbonate, 1% calcium phosphate and an 4% organic matrix of sulfated

polysaccharides, collagen, and other polypeptides [26]. Approximate 11 wt% of a chicken egg is eggshell and most of the eggshell is treated as waste residue in food industries [27]. However, the unique chemical structure and compositions and abundant resource of the eggshell make itself a versatile and free available resource of biobased calcium carbonate. The application of calcium carbonate based on eggshell has been extensively studied as additives for human nutrition, natural absorbent of heavy metals and dyes, and low-cost precursor for efficient synthesis of nitrogen-doped fluorescent carbon nanodots [28-30]. One of its most useful applications is as nano/micro fillers for polymer composites. Various contents of chicken eggshell have been added into polypropylene (PP) and the mechanical properties of the composites have been characterized [31]. The Young's modulus was obviously enhanced with increasing eggshell content. Hassan and co-workers prepared the bionanocomposites by infusing three different weight percentages (1%, 2%, and 3%) of the eggshell nanoparticles in Bioplast GS 2189 thermoplastic polymer [32]. Thermal and mechanical properties of these nanocomposites could be greatly improved over the pristine bioplast GS 2189 polymer. A bioderived and ecofriendly hybrid nanocomposite based on soy protein and eggshell nanopowder was developed by Rahman et al. [27]. Important enhancement in mechanical properties and thermal stability of the nanocomposite were obtained due to addition of well-dispersed eggshell nanoparticles. Moreover, the effect of the eggshell particles on the biodegradation properties of thermoplastic starch was investigated and compared with the effect of commercial calcium carbonate [33]. The thermoplastic starch/eggshell

composites showed more rapid biodegradation rates than that of the TPS/commercial calcium carbonate composites. Moreover, the eggshell particle also increased the thermal stability and water resistance of the thermoplastic starch.

Herein, a new eggshell powder functionalized with a nucleating surface (NES) to enhance the crystallization rate of PLLA was first prepared through the chemical reaction between phenylphosphonic acid and the calcium carbonate on the surface of eggshell powder. Then the NES was incorporated into PLLA matrix to form PLLA/NES composites by a melt blending method. The structure of eggshell powder decorated with a PPCa surface was proved by DSC and FTIR spectroscopy. The isothermal melt crystallization behavior of PLLA/NES composites was investigated. Then the thermal stability of these composites was characterized. The effects of the addition of NES on the static and dynamic mechanical properties of PLLA were further studied. Finally, the enzymatic hydrolysis of these composites was evaluated. The prepared NES can not only disperse the nucleating agent active component effectively, and enhance the overall isothermal crystallization rates, but also increase the thermal stability, mechanical properties and enzymatic hydrolysis of PLLA. To the best of our knowledge, this is the first report on improved crystallization performance and simultaneously enhanced solid-state properties such as mechanical properties and enzymatic hydrolysis through melt blending with biobased NES. This work could give access to design and develop advanced PLLA-based composites, completely derived from sustainable biomass resource, with high performance on matrix crystallization ability and outstanding solid-state properties through

constructing functional nucleating surface structures at the interface.

2.Experimental

2.1.Materials and samples preparation

PLLA (4032D) was purchased from NatureWorks LLC. Its M_w and polydispersity were $2.1 \times 10^5 \text{ g mol}^{-1}$ and 1.73, respectively. The chicken eggshell was obtained from waste at a local restaurant. Eggshells were first washed in deionized water to get rid of any impurities, dried in an oven at 110 °C for 4 hours and then ground by a ball milling machine. After milling, the eggshell powder (ES) was dried in an oven at 110 °C for 4 hours and kept in a desiccator before use. The particle size of the eggshell powder was approximately 2 μm (SEM observation). Phenylphosphonic acid (PPOA) was obtained from Jiaxing Alpharm Fine Chemical Co. Ltd., China, which was used as received.

ES and PPOA were first mixed at ambient temperature. Then, the mixture was placed in an oven at 180 °C to react for 3 min. The NES was synthesized by fixing the eggshell powder/PPOA mass ratio at 5/1.

PLLA and NES were dried in an oven at 110 °C for 4 hours prior to melt blending. PLLA/NES composites were fabricated by using a Haake Rheomix 600 internal mixer at 60 rpm. The melt-mixing temperature was set to be 180 °C. Neat PLLA and PLLA/eggshell powder were prepared as control samples following the same process. Then, to attain the various samples with different thickness for characterization, the samples were prepared by compression molding at 180 °C and

subsequently quenching in liquid nitrogen. Composites filled with NES or ES were denoted as PLLA/NESX or PLLA/ESX, where X represents the content of NES or eggshell powder (wt%) in the composite.

2.2. Characterizations

The molecular weight of various samples was characterized in CHCl_3 at 25 °C with a Waters instrument (515 HPLC) equipped with a Wyatt interferometric refractometer. GPC columns were calibrated using polystyrene as a standard. After melt blending, the molecular weight parameters of neat PLLA and PLLA/NES20 were characterized. The M_w values of neat PLLA and PLLA/NES20 were 1.86×10^5 and $1.80 \times 10^5 \text{ g mol}^{-1}$ with M_w/M_n values of 1.78 and 1.80, respectively. The molecular weight parameter characterization indicated that during melt blending process NES did not induce any dramatic drop of the M_w of PLLA from thermal degradation or hydrolysis of the polyester chains.

The morphology of the PLLA/NES composites was observed using a field emission scanning electron microscopy (SEM) (FEI Co., Eindhoven, Netherlands). All specimens were coated with gold before examination.

FTIR spectra were recorded on a BIO-Rad Win-IR spectrometer with a resolution of 4 cm^{-1} over a spectral range from 4000 to 500 cm^{-1} .

The isothermal crystallization behavior of various samples was investigated using a TA Instruments Q20 differential scanning calorimeter (DSC). Temperature and enthalpy calibration was performed using an Indium standard. The measurements were conducted in a dry nitrogen atmosphere. The sample was first heated and

equilibrated at 190 °C for 3 min to remove any thermal history. Then the sample was cooled from 190 °C to crystallization temperatures (T_c) selected between 125 and 135 °C at 45 °C min⁻¹ and held isothermally until the isothermal crystallization process was complete.

WAXD measurements were performed with a Rigaku model Dmax 2500 X-ray diffractometer with Cu K α radiation ($\lambda = 0.154$ nm) with a voltage of 40 kV and a current of 200 mA. Radial scans of the intensity versus the diffraction angle (2θ) were recorded in a range of 10–30° with a speed of 3° min⁻¹.

The spherulitic morphologies of various samples were observed with a Leica DM2500 P polarized optical microscope (POM) with hot stage and digital camera. The samples for POM observation were first heated and equilibrated at 190 °C for 3 min. Then samples were rapidly cooled to 130 °C and maintained until the completion of crystallization to observe the spherulite morphologies.

To evaluate the thermal stability properties of the composites, thermogravimetric analysis (TGA) of all samples was carried out under a nitrogen gas atmosphere on a Perkin Elmer TGA7 thermal analyzer from 50 to 600 °C at a heating rate of 10 °C min⁻¹. The samples were precisely cut into small pieces (~10–20 mg) and kept in an aluminium oxide sample pan.

Dynamic mechanical analysis (DMA) tests were carried out on various samples with thickness, width, and height of 1 mm, 4 mm, and 9 mm, respectively, using a dynamic mechanical analyzer from Rheometric Scientific. The specimens were tested in the tension mode at a frequency of 1 Hz, and a heating rate of 3 °C min⁻¹ under a

nitrogen atmosphere.

Tensile tests were conducted on an Instron-1121 tensile tester at a crosshead rate of 2 mm min^{-1} according to the ISO 527-93 standard [34].

The enzymatic hydrolysis experiments of the composites films was carried out in phosphate buffer (pH = 8) containing proteinase K at 37°C with shaking at 140 rpm. Sample films (approximately $10 \times 10 \times 0.25 \text{ mm}^3$) were placed in vials filled the buffer and proteinase K. The films were periodically removed, washed with distilled water, and dried to constant weight in a vacuum, and then the weights of the films were measured. For comparison, neat PLLA was treated with the same procedure. The degraded surfaces and cross-section of the samples were coated with a thin layer of gold and then were observed with SEM. Control tests for all samples in buffer solution free from the proteinase K were also carried out, and the result showed no appreciable weight losses over the time scale of the experiments.

3. Results and discussion

3.1. Structure of NES

To identify the structure of NES, neat PPOA and NES were qualitatively characterized by DSC, shown in Fig. 1(a). It can be clearly seen from Fig. 1(a) that PPOA has a melting peak at 166°C with a melt enthalpy around 139.9 J g^{-1} . For NES, the melting peak at 166°C of PPOA disappears during the heating process, indicating a chemical reaction took place between ES and PPOA to form PPCa on the surface of ES. Then, FTIR spectroscopy was used to further characterize the structure

of the samples. The NES sample was washed in acetone for three times prior to FTIR testing to get rid of possible unreacted PPOA. As shown in Fig. 1(b), for PPOA, the C–H out-of-plane deformation bands of the monosubstituted benzene ring can be seen at 757 and 697 cm^{-1} [35]. FTIR result of ES exhibited typical characteristic absorption peaks at 713, 875, and 1424 cm^{-1} wavenumbers which were assigned to in-plane bending, out-of-plane bending, and asymmetric stretching modes of CO_3^{2-} in the ES, respectively, associated with calcite. In addition, the peak at 1798 cm^{-1} was assigned to the combination vibrations of C=O stretching and –NH– in-plane bending owing to small contents of organic component [27]. These observations are in good agreement with the results reported previously [27]. Compared to the spectrum of PPOA and ES, the prepared NES showed characteristic bands at 757 and 697 cm^{-1} , which were assigned to the C–H out-of-plane deformation bands of the monosubstituted benzene ring. These result indicated that the chemical reaction between PPOA and calcium ion on the surface of eggshell powder to form effective nucleating surface for poly(L-lactide).

3.2. Morphology and Dispersion of NES in the PLLA Matrix

SEM micrographs of the fractured surfaces of neat PLLA and PLLA/NES composites are presented in Fig. 2. Neat PLLA exhibited a clear and smooth surface (Fig. 2(b)). For the fractured surfaces of the composites, coarse surfaces were observed from Fig. 2(c)–(f). It should be noted that most of NES were well dispersed in the PLLA matrix. Even with 20 wt% NES, there was no obvious agglomeration of NES in the PLLA matrix. These characteristics of fractured surface of the composites clearly indicated

that the PLLA/NES composites showed good dispersion, and the NES demonstrated a better adhesion to the PLLA matrix owing to the organic components in the NES. The organic components in the NES can act as coupling agents to improve the dispersion and interfacial interactions between the PLLA matrix and the NES [33]. This result is in agreement with the results of infrared spectrum that confirmed the organic compounds on the surface of the ES.

3.3. Effect of NES on the Isothermal Melt Crystallization of PLLA

The completion of isothermal crystallization inside the preheated mold within a short interval plays an important role in develop PLLA injection articles with high performance. Therefore, the isothermal crystallization characteristic of neat PLLA and the composites was investigated in a temperature range of 125-135 °C. Fig. 3 demonstrates the DSC curves of neat PLLA, PLLA/ES10 and various PLLA/NES composites crystallized at 130 °C as an example. As seen from Fig.3, the crystallization rate of neat PLLA is very slow. Moreover, it is observed that loadings of ES caused an increase in the crystallization rate compared to the neat PLLA. The increase in the crystallization rate of the PLLA/ES composite is attributed to the incorporation of the ES. The ES may serve as nucleating agents in the PLLA melts; however, the nucleating ability of the ES is still very limited. With the addition of NES and an increase in its content, the exothermal peak sharpens and increases in amplitude, indicating that NES, serving as effective nucleating agents in the polymer melts, dramatically enhanced the crystallization rate of PLLA.

The relative crystallinity as a function of time was determined and it is presented

in Fig. 4(a). As can be seen from Fig. 4(a) that the crystallization time of the PLLA/NES composites becomes shorter with an increase in the NES loading. For example, it took neat PLLA and PLLA/ES10 almost 70 and 35 min to complete crystallization at 130 °C, respectively; however, for the PLLA/NES5, PLLA/NES10, PLLA/NES15, and PLLA/NES20 composites, the time required to finish crystallization became only around 4.1, 3.0, 2.5, and 1.9 min, respectively. Thus, NES enhanced the isothermal melt crystallization of PLLA much greater than that of neat PLLA or PLLA/ES composite; moreover, the crystallization rate is increased with increasing the NES loadings.

The most widely used analysis of isothermal crystallization experimental data is based on the well-known Avrami equation. It was written as follows [36,37]:

$$1 - X(t) = \exp(-k t^n) \quad (1)$$

where $X(t)$ is the crystalline conversion at time t , n is the Avrami exponent related to the type of nucleation and to the geometry of the growing crystals, and k is the overall rate constant. The Avrami plots for various samples crystallized at 130 °C are shown in Fig. 4(b), where the solid lines are linear fits of equation (1) to the experimental data. In all cases, the isothermal crystallization data can be well described by the Avrami equation. The values of n , obtained from the slope of the Avrami plot, are summarized and listed in Table 1 for comparison. For all the samples, including the neat PLLA sample, and different T_c s used, n values are in the range of 2.3-2.9. The almost unchanged n values indicate that the crystallization mechanism of PLLA was not changed by the addition of NES into PLLA matrix. The k values, calculated from

the Avrami plots in Fig. 4 are also listed in Table 1 for comparison. For each sample, k value increased with decreasing T_c , which is in agreement with faster crystallization kinetics as the undercooling was increased. This indicates that the free surface energy, not the diffusional transport, dominates the crystallization rate in the range of T_c s used in this study. In addition, at a given T_c , k value also increased after incorporation of NES and it further increased with increasing the content of NES, indicating faster crystallization kinetics of PLLA after incorporation of NES.

Moreover, the half-life crystallization time $t_{0.5}$, which was defined as the time to achieve 50% of the final crystallinity of the samples, is an important parameter for the discussion of crystallization kinetics. The value of $t_{0.5}$ of the samples is calculated by the following equation:

$$t_{0.5} = (\ln 2 / k)^{1/n} \quad (2)$$

The calculated $t_{0.5}$ values are also listed in Table 1. It can be seen that $t_{0.5}$ values of PLLA are influenced by the incorporation of NES and the NES content. As an example, neat PLLA presented a $t_{0.5}$ of around 34.87 min for T_c of 135 °C; in the case of the PLLA/NES nanocomposites, the $t_{0.5}$ values at the same temperature change with the NES concentration as follows: 1.94 min for 5 wt %, 1.78 min for 10 wt %, 1.37 min for 15 wt % and 1.22 min for 20 wt %. The crystallization rate of PLLA/NES nanocomposites increased pronouncedly with composition indicating that the well-dispersed NES have a remarkable contribution to enhance the nucleation of PLLA. As suggested in previous work [12], as a result of excellent matching of lattice parameters between PLLA and PPCa, an epitaxial crystallization mechanism was

proposed for the improved crystallization of PLLA after incorporation of PPCa. From DSC and FTIR results as aforementioned, the formation of PPCa chemically supported on the surface of ES has been identified. Then the PPCa decorated on the surface of ES, acting as an effective nucleating component played the important role in enhancing the crystallization process of these composites.

POM photographs of neat PLLA and its composites crystallized at 130 °C were shown in Fig. 5. In pure PLLA, black and white spherulites were formed and their boundary was obvious. The spherulites were formed mainly by homogeneous nucleation. Fig. 5(b, c, and d) demonstrated the spherulitic morphology of the composites with the NES loading from 5 to 20 wt%. It can be clearly seen that the size of PLLA spherulites became smaller, and the spherulites boundaries are obscurer. The nucleation density of PLLA spherulites greatly increased in the presence of NES in the PLLA/NES composites because of their effective nucleation ability. These results indicate that the well-dispersed NES exhibits a remarkable nucleation ability to enhance the nucleation of PLLA, which is in consistent with the aforementioned DSC results.

To further investigate the effect of the addition of NES on the crystal structure of PLLA in the PLLA/NES composites, WAXD experiments were carried out. PLLA can crystallize in α , β , and γ forms [8]. Crystallization from the melt usually results in α form. Recently, a new crystal modification α' has also been observed for the PLLA samples cold- or melt-crystallized at low crystallization temperature ($T_c < 100$ °C) [38]. In the current case, the isothermal crystallization kinetics of neat PLLA and its

composites was studied in the temperature range of 125-135 °C; thus, they all may crystallize in α form. Moreover, in this work, the samples for the WAXD measurements were crystallized at 125 °C; hence, neat PLLA and its composites should still crystallize in α form. As shown in Fig. 6, two main diffraction peaks at 16.3 and 18.6° of neat PLLA can be observed, corresponding to (200)/(110) and (203) planes, respectively [8]. In addition, the composites illustrate almost the same diffraction peaks at 16.3 and 18.6°, suggesting that the crystal structure of PLLA was not changed after addition of NES.

3.4. Thermal Stability

Fig. 7 shows the TGA curves of neat PLLA and the composites at a heating rate of 10 °C min⁻¹. Thermal degradation of both neat PLLA and the composites through a one-step process was observed, and the thermal stability of the composites was obviously better than that of neat PLLA. The main thermal parameters are summarized and listed in Table 2. It can be seen from Table 2, with increasing the NES contents, the initial decomposition temperature (T_0) enhanced from 285.3 °C for pure PLLA to the maximum of 310.0 °C for PLLA/NES15 and then slightly decreased to 308.6 °C for PLLA/NES20. The similar effect can be also found for decomposition temperature at 5% weight loss ($T_{5\%}$) and decomposition temperature at 50% weight loss ($T_{50\%}$). Compared with those for neat PLLA, the T_0 , $T_{5\%}$, and $T_{50\%}$ for PLLA/NES15 with the best thermal stability increased by about 24.7, 19.3, and 13.5 °C, respectively. The improved thermal stability of the composites is attributed to the strong adhesion between NES and the PLLA matrix, which stabilizes the

composite against thermal decomposition. In addition, the T_0-T_m values of neat PLLA and the composites, reflecting the melt-processing window [39], are also obtained and showed in Table 2. The larger the T_0-T_m value of the polymer is, the wider the melt-processing window achieves. As shown in Table 2, the T_0-T_m values of the composites were higher than that for neat PLLA, indicating the composites demonstrated the wider melt-processing windows. In addition, among all the composites, the PLLA/NES15 composite showed the widest melt-processing window.

3.5. Mechanical properties

Dynamic mechanical properties of the composites are greatly affected by phase structure. Fig. 8 compares the DMA results of neat PLLA and its composites. As seen from Fig. 8(a) that the storage moduli (E') of neat PLLA and its composites show sharply decreases in the temperature ranges of 60 to 80 °C, owing to the glass transitions of PLLA matrix. After glass transition, a cold crystallization of PLLA occurred at 90 °C, resulting in an increasing of E' . It can be clearly seen from Fig. 8(a) the E' values were obviously enhanced by incorporation of NES in the temperature range of 0-140 °C. In addition, the E' values also increased with an increasing of NES level at a given temperature. These results clearly indicated that NES had critical influence on the enhancement of modulus of PLLA. The measured E' values at 20 °C, 80 °C and 130 °C were summarized and listed in Table 3. At 20 °C and 130 °C, the E' s were increased from 2882 MPa and 158MPa for pure PLLA to 3686 MPa and 199 MPa for the PLLA/NES20 composite, respectively. The increase in E' was 27.9% and 25.9% compared with pure PLLA. Moreover, it should be noted that the E' value was

only approximate 4.7 MPa for neat PLLA at 80 °C. However, it increased to 22.8 MPa for the PLLA/NES20 composite. A pronounced increase of 385% was obtained as compared to that of pure PLLA. These results indicated that NES can act as effective reinforcing fillers to improve the modulus of PLLA, especially in the rubbery state. The improvement in E' of PLLA/NES composites can be due to the high modulus of the NES which can introduce rigid interface into the composites and strong interfacial interaction with polymer matrix, which provided better stress transfer ability and increase in E' of the PLLA matrix. Moreover, above T_g , when materials became soft, reinforcement effect of the NES became prominent and hence strong enhancement of modulus appeared. From Fig. 8(b), the T_g for all samples are approximate 68 °C, which indicated that the incorporation of NES did not significantly affect the segmental motion of PLLA.

The effects of incorporating with different NES content on the tensile properties of PLLA were further evaluated. The stress–strain curves of all samples are demonstrated in Fig. 9. The corresponding data are given in Table 4. Neat PLLA showed high tensile modulus and tensile strength, but low elongation at break. With the addition of NES, the moduli were enhanced obviously; while the tensile strength and elongation at break decreased. The tensile modulus increased from 1880 MPa for neat PLLA to 2460 MPa for the PLLA/NES20 composite, an increase of 30.9%. This result was in good agreement with the result of dynamic mechanical properties. The enhanced modulus of the composites may be due to the fact that the high modulus NES act as carriers of the load and stress which are transferred from the matrix to the

NES giving rise to effective and uniform stress distribution, resulting in an increase in tensile modulus of the composites [40]. It should be noted that even with 20 wt% NES, the composite still exhibited good mechanical properties with tensile strength of 53.4 MPa, tensile modulus of 2460 MPa and elongation at break of 2.5%, respectively. The improved mechanical properties of the composites may be attributed to the fine dispersion of NES and the strong interfacial interaction between NES and the PLLA matrix as observed in SEM, indicating that NES is an effective filler to enhance the mechanical properties of polymer.

3.6. Enzymatic Hydrolysis Properties

From the discussion above, it is clear that the crystallization, thermal stability and mechanical properties of PLLA could be improved simultaneously through melt blending with biobased and sustainable NES. For ideal biodegradable plastics or composites, superior performance during their entire use processes is required. However, it is necessary to trigger off biodegradation immediately after usage and disposal. Thus, the enzymatic hydrolysis behaviors of the composites are attractive and worth to be investigated.

Fig. 10 shows the variation of weight loss of neat PLLA and the composites with exposed time during hydrolysis test. The values of weight loss increase with prolonging exposed time for both neat PLLA and the composites. As illustrated in Fig. 10, mass loss versus the exposed time shows almost linear variation. Thus, the hydrolytic degradation rates of neat PLLA and the PLLA/NES composite were obtained from the slopes of the plots of variation of weight loss with hydrolytic

degradation time. For neat PLLA, the hydrolytic degradation rate was about 0.416 mg per cm² per day; however, the hydrolytic degradation rates were enhanced to be about 0.568, 0.745, 1.134, and 1.891 mg per cm² per day for the PLLA/NES composites with increasing the NES loading from 5 to 20 wt%. Obviously, the composites degraded faster than neat PLLA, indicating the incorporation of NES accelerated the hydrolytic degradation of PLLA in the composites; in addition, the hydrolytic degradation rate increased with increasing the NES level. The results that polymer degraded faster in the polymer composites than in neat polymer had also been recently reported in other literatures [41,42]. Cotton et al. have reported that the in vitro degradation of the poly(DL-lactide-co-glycolide) and calcium carbonate composites were faster than that of parent polymer [42]. The weight-average molecular weight (M_w) of neat PLLA and the composites were also studied during the hydrolytic degradation process. M_w s of neat PLLA and PLLA/NES20 after a hydrolytic degradation of 5 days were 1.60×10^5 g mol⁻¹, and 1.65×10^5 g mol⁻¹. The slightly decreased M_w indicated that no significant chain scission occurred for both neat PLLA and the PLLA/NES composite during the hydrolytic degradation process. It is well-established that degradation process of polymers can be mainly classified into two typical types, i.e., surface eroding process and bulk eroding process. As for ideal bulk erosion process, polymer is lost from the entire polymer volume. While in the case of surface erosion process, polymer is lost from the exterior surface of polymer matrix; moreover, the erosion rate is directly proportional to external surface area and remains constant as the sample becomes progressively thinner [43,44].

Hence, to further explore the hydrolysis mechanism, the surface and cross-section morphology of various samples were observed. Fig. 11(a-d) demonstrates the surface and cross-section morphology of neat PLLA prior to hydrolytic degradation and after a hydrolytic degradation of 5 days. It can be obviously seen that before degradation the surface of neat PLLA showed a smooth surface. However, the surface of degraded sample became clearly blemished. In contrast, cross-section morphology of neat PLLA still showed a smooth surface as shown in Fig. 11(b and d). A clear decrease in film thickness can be observed after degradation, indicating that the degradation mechanism of PLLA may be surface erosion mechanism. Moreover, the surface and cross-section morphology for the PLLA/NES composites were also observed. Fig. 11(e-f) illustrates the surface and cross-section morphology of the PLLA/NES5 composite after a hydrolytic degradation of 5 days. The surface of the PLLA/NES5 composite shown in Fig. 11(e) is rougher than that of neat PLLA shown in Fig. 11(c). Moreover, compared with the cross-section images given in Fig. 11(d) and (f), the thickness of the films became thinner in the PLLA/NES5 composite. The film thickness change indicated that the composite may still proceed through surface erosion mechanism; furthermore, increasing the NES loading enhances the hydrolytic process. Similar results are also found in other samples as shown in Fig. 12.

Deduced from these results, the hydrolytic degradation of both neat PLLA and the PLLA/NES composites proceeded via surface erosion mechanism, which is in good agreement with the previous research work [45]. During the hydrolytic degradation, both the weight and thickness of the films decreased with time. The hydrolytic

degradation rates are faster in the PLLA/NES composites than in neat PLLA and increase with the NES loading. The incorporation of NES may result in an easy attack of the enzyme molecule to PLLA chains, since the small amounts of organic materials in NES are completely biocompatible. Moreover, the PLLA surface continues to increase during the hydrolysis process as a result of the release of NES particles, which increase the interface between enzyme molecule and PLLA matrix. This factor can also lead to an increase in hydrolysis rate. However, the exact reason is still unknown and needs further investigation.

4. Conclusions

A novel functionalized eggshell powder with effective nucleating surface for poly(L-lactide) (NES) was successfully prepared. Then the NES was added into PLLA matrix by a melt blending approach to prepare green composites. The filled NES was finely dispersed into PLLA matrix with the NES content in the range of 5-20 wt%. Simultaneous enhancements on the thermal and mechanical property, and enzymatic hydrolysis of green composites were achieved. The overall crystallization rates were increased greatly for the PLLA/NES composites compared with neat PLLA and PLLA/ES composite; however, the crystal structure and crystallization mechanism of PLLA has not been altered despite the incorporation of NES. At the same time, T_0 , $T_{5\%}$, and $T_{50\%}$ increased by 24.7, 19.3, and 13.5 °C, respectively. The composites also exhibited wider melt processing windows than neat PLLA. NES showed good reinforcing effects on the PLLA matrix. Both the tensile and storage

moduli of composites improved with increasing NES content. The intriguing result of this work was that the enzymatic hydrolytic degradation rates had been increased pronouncedly in the PLLA/NES composites when compared with neat PLLA. The enzymatic hydrolytic degradation of neat PLLA and its composites may proceed through surface erosion mechanism. These sustainable PLLA/NES composite with high performance can be considered as potential biomaterials or green plastics as replacements for traditional petrochemical plastics.

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Tables and figures caption

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Table 2. Thermal analysis parameters for neat PLLA and its composites.

Table.3. Storage modulus values of neat PLLA and its composites at various temperatures

Table.4. Static mechanical properties of neat PLLA and its composites.

Figure.1. (a) DSC heating curves of PPOA, ES and NES at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$; (b) FTIR spectrum of PPOA, ES and NES at room temperature.

Figure.2. The fracture surfaces of ES, neat PLLA and composites with various NES concentrations: (a) ES, (b) neat PLLA, (c) PLLA/NES5, (d) PLLA/NES10, (e) PLLA/NES15, and (f) PLLA/NES20.

Figure.3. DSC exotherms of isothermal crystallization at $130\text{ }^{\circ}\text{C}$ for various samples.

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Figure.6. WAXD patterns of neat PLLA and its composites.

Figure.7. TGA curves for neat PLLA and its composites.

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Figure.11. SEM photographs of surface and cross section for neat PLLA and PLLA/NES5 samples: (a) surface of neat PLLA before hydrolysis; (b) cross section of neat PLLA before hydrolysis; (c) surface of neat PLLA after a hydrolysis degradation of 5 days; (d) cross section of neat PLLA after a hydrolysis degradation of 5 days; (e) surface of PLLA/NES5 after a hydrolysis degradation of 5 days; (f) cross section of

PLLA/NES5 after a hydrolysis degradation of 5 days.

Figure.12. SEM images showing the morphology of surface and cross section for the composites after a hydrolysis degradation of 5 days: (a) surface of PLLA/NES10; (b) cross section of PLLA/NES10; (c) surface of PLLA/NES15; (d) cross section of PLLA/NES15; (e) surface of PLLA/NES20; (f) cross section of PLLA/NES20.

Table 1. Kinetic parameters of neat PLLA and its composites isothermally crystallized at different temperatures.

Simple	$T_c (^{\circ}\text{C})$	n	$K (\text{min}^{-n})$	$t_{0.5} (\text{min})$
PLLA	135	2.4	1.43×10^{-4}	34.87
	130	2.6	1.21×10^{-4}	27.09
	125	2.6	1.90×10^{-4}	22.47
PLLA/ES10	135	2.3	2.27×10^{-4}	33.83
	130	2.4	1.84×10^{-3}	12.09
	125	2.4	4.24×10^{-3}	8.47
PLLA/NES5	135	2.3	0.16	1.94
	130	2.4	0.43	1.22
	125	2.7	0.76	0.96
PLLA/NES10	135	2.8	0.14	1.78
	130	2.7	0.55	1.09
	125	2.9	1.68	0.74
PLLA/NES15	135	2.7	0.30	1.37
	130	2.6	1.20	0.81
	125	2.9	3.69	0.57
PLLA/NES20	135	2.4	0.43	1.22
	130	2.6	1.84	0.69
	125	2.9	4.03	0.54

Table 2. Thermal analysis parameters for neat PLLA and its composites.

Sample	T_0 (°C)	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	T_0-T_m (°C) ^a
Neat PLLA	285.3	310.1	337.5	113.7
PLLA/NES5	304.9	324.1	345.9	137.7
PLLA/NES10	306.7	326.7	347.6	139.4
PLLA/NES15	310.0	329.4	351.0	142.2
PLLA/NES20	308.6	328.9	350.6	142.0

^a T_m of the composites was determined from the DSC curves at a heating rate of 10 °C min⁻¹.

Table 3. Storage modulus values of neat PLLA and its composites at various temperatures.

Sample	Storage modulus (MPa)		
	at 20 °C	at 80 °C	at 130 °C
Neat PLLA	2882	4.7	158
PLLA/NES5	3000	4.8	165
PLLA/NES10	3022	8.8	173
PLLA/NES15	3513	13.8	182
PLLA/NES20	3686	22.8	199

Table 4. Static mechanical properties of neat PLLA and its composites.

Samples	Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
Neat PLLA	1880 ± 20	58.5 ± 3.3	4.5 ± 0.5
PLLA/NES5	2020 ± 55	56.7 ± 4.0	4.6 ± 0.6
PLLA/NES10	2200 ± 45	55.6 ± 5.2	3.5 ± 0.6
PLLA/NES15	2320 ± 72	53.9 ± 4.3	3.2 ± 0.4
PLLA/NES20	2460 ± 90	53.4 ± 6.3	2.5 ± 0.3

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