Phase Morphology and Performance of Supertough PLA/EMA−GMA/ZrP Nanocomposites Prepared through Reactive Melt-Blending
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ABSTRACT: Nano filler zirconium phosphate (ZrP) and ethylene-methyl acrylate−glycidyl methacrylate copolymer (EMA−GMA) were introduced into poly(lactic acid) (PLA) through reactive melt-blending method to improve its toughness. The impact strength of PLA/EMA−GMA/ZrP (82/15/3) nanocomposites was improved about 22 times that of pure PLA to 65.5 kJ/m². Fourier transform infrared spectroscopy (FTIR) analysis indicated there were compatibilization reactions between the components. The miscibility and thermal behavior of the blends were investigated by dynamic mechanical analysis (DMA), differential scanning calorimetric (DSC), and thermogravimetric analysis (TGA). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were applied to observe the fractured surface and phase morphology to study the toughness mechanism. A typical core−shell morphology, ZrP wrapped by EMA−GMA phase, was observed in the nanocomposites, which can cause plastic deformations. The supertough effect of the compound was mainly confirmed by effective interfacial compatibilization and massive shear-yielding deformation achieved by the synergy of EMA−GMA with ZrP in the PLA matrix.

1. INTRODUCTION
Poly(lactic acid) (PLA) is a biodegradable polymer that can be completely obtained from renewable resources. It has been widely used recently due to its good biodegradability, biocompatibility, transparency, high mechanical strength, and excellent processability.1−8 Because the problem of pollution is becoming more and more serious, PLA has become a potential replacement for petroleum-based plastics in many applications, such as packaging, fiber and biomedical materials.14−15 However, its deficiencies such as brittleness and bad ductility have limited its commercial application greatly. Therefore, a large number of strategies such as physical blending,8−15 copolymerization,16−18 and plasticization19 have been used to toughen PLA to improve its physical performance. Particularly, among the effective methods, reactive melt-blending with elastomer−ethylene−methyl acrylate−glycidyl methacrylate (EMA−GMA) can obtain excellent toughness. Recently, many studies13,20,21 have reported supertough PLA-based compounds. EMA−GMA can react with PLA, and the interfacial adhesion can be promoted. The formation of special phase morphologies also plays a key role in improving the impact strength of PLA blends drastically.

Polymer/montmorillonite (MMT) nanocomposites have better physical and mechanical properties than either pure polymers or microcomposites.22 Similar to MMT clay, synthetic α-zirconium phosphate (ZrP) (Zr(HPO₄)₂·H₂O) has the same layered structure. However, the difference with MMT clay is that the layers of ZrP are formed by zirconium atoms and the oxygen atoms of phosphate groups are connected with them. The layers are also formed by three oxygen atoms, which are contributed by each phosphate molecule and the phosphate molecule also donating one hydroxyl group pointing into the interlayer space.23 Due to the remarkable structure, ZrP has many excellent features, such as good chemical and thermal stability, high mechanical strength, perfect particle size, ease of surface functionality control, and high purity, aspect ratio, and ion-exchange capacity.24−27 A strong interaction of interfacial between ZrP and polymer composites can be achieved by miscibility reaction, and the nanofiller ZrP can evenly disperse in a polymer matrix. Through ionic bond, hydrogen bond, van der Waals forces, and other actions, polymer molecules can be inserted into the spaces between layers of nanolayered zirconium phosphate, thus the compound of polymer matrix with a nanofiller ZrP can be achieved on a nanoscale. Then, the thermal stability, electrical conductivity, and mechanical properties of the

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nanocomposites material are improved.\textsuperscript{28–30} So, the addition of nano filler ZrP can promote the physical properties and broaden the application field of polymers.

In this study, we filled nano filler ZrP and elastomer EMA–GMA into the PLA matrix through reactive melt-blending to fabricate supertough nanocomposites. The attention was focused on the improvement of toughness and thermal stability of the composition, and the synergetic toughening mechanism of EMA–GMA and ZrP on PLA was also studied. To the best of our knowledge, there is no study on this so far. The toughening mechanism was analyzed by various characterization studies, such as Fourier transformation infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). The relationship between the mechanical properties, thermal behavior, and phase morphology of the nanocomposites was also established.

2. EXPERIMENTAL SECTION
2.1. Materials. The poly(lactic acid) (PLA) (commercially labeled as 4032D, had a high optical purity with about 98% l-lactide content) was supplied by Nature Works Co. Ltd. Its density, molecular weight ($M_w$), and polydispersity index are 1.24 g/cm$^3$, 1.7 $\times$ 10$^5$ g/mol, and 1.74 respectively. The ethylene–methyl acrylate–glycidyl methacrylate (EMA–GMA) is a random terpolymer of 68% ethylene, 24% acrylic ester, and 8% glycidyl methacrylate purchased from Arkema Company with a commercial name of Lotader AX 8900. ZrP was purchased from Mianzhu Yaolong Chemical Co. Ltd. (China). The content of ZrO$_2$ is greater than or equal to 40%, and its density is 1.6 g/cm$^3$. Figure 1 shows the SEM micrograph of ZrP and its average lamellar thickness and particle size are about 83.5 nm and 1.7 $\mu$m, respectively. Chemical structure of PLA, EMA–GMA, and ZrP used for the blends are shown in Figure 2.

2.2. Sample Preparation. PLA pellets and ZrP powder were dried at 80 °C in an oven to remove the moisture for 12 h. Afterward, the mixed PLA/EMA–GMA (15 wt %) samples with different contents (1, 3, and 5 wt %) of ZrP were melt-blended by an internal mixer (Brabender W50E) at 200 °C for 6 min with a rotor speed of 60 rpm. Subsequently, the samples were compressed by a compression molding machine (QBL-350, Wuxi No. 1 Rubber and Plastic Machinery Co., Ltd., China). The process parameters of temperature and pressure for compression molding were 200 °C and 100 bar, respectively. The tensile and impact samples were prepared by cutting standard sizes.

2.4. Characterization. 2.4.1. Mechanical Properties. Tensile specimens of a dumbbell shape with a gauge length of 35 mm, width of 4 mm, and thickness of 1 mm were machined and tested by an Instron 5566-type universal testing machine with a crosshead speed of 50 mm/min according to the ASTM D882 standard. All values were repeated five times, and the average values were obtained.

A Zwick impact tester (model 5117, Germany) was used to conduct impact testing according to the GB/T 1843 (2008) standard. All data were the average of 5 determinations. All tests were performed at room temperature.

2.4.2. Fourier Transform Infrared Spectroscopy (FTIR). FTIR absorption spectra of PLA, EMA–GMA, ZrP, and PLA/EMA–GMA binary blends with 15 wt % EMA–GMA and PLA/EMA–GMA/ZrP nanocomposites (with 3 wt % ZrP) were recorded using Perkin–Elmer Spectrum 2000 instrument in the wave number range of 400–4000 cm$^{-1}$. All specimens but ZrP were compressed into slices of 120 $\mu$m thickness at 200 °C before test. A small amount of dried ZrP powder was ground with dried KBr powder and then compressed into disks for the FTIR test at room temperature.

2.4.3. Scanning Electron Microscopy (SEM). The fractured surface morphology of PLA/EMA–GMA binary blend and PLA/EMA–GMA/ZrP nanocomposites with 3 wt % content of nano filler ZrP was studied by using scanning electron microscopy (FEI-SEM). The SEM was operated at the condition of 5 kV accelerating voltage to characterize the phase morphology of the impact-fractured and cryofracture surfaces. The fractured surface was gold coated for 0.1 nm in thickness before SEM imaging to avoid electrostatic charging during inspection.

2.4.4. Transmission Electron Microscopy (TEM). The morphologies of the dispersed phases were observed by a transmission electron microscope (JEOL 1200EX) with an acceleration voltage of 100 kV. Prior to TEM imaging, the samples were cryo-microtomed at −60 °C and then stained by ruthenium tetroxide (RuO$_4$) vapor.

2.4.5. Dynamic Mechanical Analysis (DMA). DMA was conducted on a NETZSCH DMA 204C analyzer in a three-point bending mode at temperatures ranging from −100 to 120 °C with the heating rate of 3 °C/min under nitrogen atmosphere. The scanning frequency was 1 Hz, and the strain amplitude was 0.05%. The shape of the samples was rectangular strip with dimensions of 10 $\times$ 4 $\times$ 40 mm$^3$.

2.4.6. Differential Scanning Calorimetry (DSC). Differential scanning calorimetry of samples was conducted on a DSC instrument (Netzsch 204F1 Phoenix, Germany). All the samples (5–7 mg) were first heated from 30 to 200 °C at a heating rate of 10 °C/min and held for 5 min to eliminate the thermal history. They were then cooled to 30 °C at a constant rate of 10 °C/min and finally heated to 200 °C at 10 °C/min.

The glass transition temperature ($T_g$), cold crystallization temperature ($T_{cc}$), melting temperature ($T_m$), cold crystallization enthalpy ($\Delta H_{cc}$), and melting enthalpy ($\Delta H_m$) were determined in the second heating scan. The degree of crystallinity ($\chi_c$) was calculated by the following formula

![Figure 1. SEM micrographs of ZrP.](image1)

![Figure 2. Chemical structures of PLA, EMA–GMA, and ZrP.](image2)
\[
\chi_c = \frac{\Delta H_m - \Delta H_c}{w_f \Delta H_m^0} \times 100\%
\]

where \(\Delta H_m\) and \(\Delta H_c\) are the enthalpies of the melting and cold crystallizations during the heating, respectively; \(\Delta H_m^0\) is the theoretical melting enthalpy of 100% crystalline PLA (\(\Delta H_m^0 = 93.7\) J/g),\(^{10}\) and \(w_f\) is the weight fraction of PLA component in the blend.

2.4.7. Thermogravimetric Analysis (TGA). The samples were subjected to thermogravimetric analysis (TGA) using a Netzsch STA-409c thermal analyzer equipment. The mass of sample was approximately 5 mg and all the samples were heated from 30 to 600 °C using a linear heating rate of 20 °C/min under an air flow of 50 cm³/min. All DSC and TGA values were repeated twice and averaged to obtain representative values.

3. RESULTS AND DISCUSSION

3.1. Mechanical Properties. The mechanical properties of pure PLA, PLA/EMA−GMA, and PLA/EMA−GMA/ZrP nanocomposites with different contents of ZrP are presented in Figure 3, and the data of tensile and impact properties of the composites are listed in Table 1. Figure 3a summarizes the tensile strength and elongation at break of the pure PLA, binary blend, and PLA/EMA−GMA/ZrP nanocomposites. The tensile stress−strain curves and impact strength of the compositions are shown in Figure 3b,c, respectively. As we all know, the pure PLA is a typical brittle polymer with a low toughness; as can be seen from Figure 3, the tensile strength was about 67 MPa, while the impact strength and elongation at break were only 2.9 kJ/m² and 10.4%, respectively. The toughness of PLA can be widely improved by the melt-blending with EMA−GMA, which have been reported by literatures.\(^{13,20,31-34}\) The ductility of PLA−EMA−GMA binary blend had been improved effectively by the toughening effect of 15 wt % content EMA−GMA blended into the PLA matrix, its elongation at break was 421%, about 40 times higher than pure PLA, while the impact strength was up to 47.9 kJ/m².

The toughness of the PLA matrix was further enhanced by the addition of a tiny amount of ZrP nano filler. The trend of fracture strain and impact strength of PLA/EMA−GMA/ZrP nanocomposites in Figure 3 shows an increase first and then a decrease with more ZrP loading. When the nanofiller content is 3 wt %, the nanocomposites obtain optimum mechanical performance. Its elongation at break is 450% and the impact strength is 65.5 kJ/m², enhanced almost 37.6% than PLA/EMA−GMA binary blend. The tensile strength and tensile modulus of PLA/EMA−GMA/ZrP composite also reach the maximum value. From the tensile stress−strain curves in Figure 3b, we can also see that there is a shoulder after yielding in the curves of ZrP-containing blends, which does not appear in PLA/EMA−GMA blend. The possible explanation for this phenomenon can be explained, as there is a reaction between EMA−GMA and ZrP, and new chemical bonds are produced, which absorbed the energy during the process of drawing. As a result, the shoulder appeared.

Table 1. Mechanical Properties of PLA, PLA/EMA−GMA Blend, and PLA/EMA−GMA/ZrP Nanocomposites

| compositions          | tensile strength (MPa) | tensile modulus (MPa) | impact strength (kJ/m²) | elongation (%) |
|-----------------------|------------------------|-----------------------|-------------------------|---------------|
| pure PLA              | 67.3 ± 0.1             | 1590 ± 21             | 2.9 ± 0.4               | 10.4 ± 2.8    |
| PLA/EMA−GMA (85/15)  | 41.9 ± 1.6             | 893 ± 65              | 47.9 ± 3.4              | 421.1 ± 53.9  |
| PLA/EMA−GMA/ZrP (84/15/1) | 38.9 ± 2.1           | 776 ± 55              | 59.9 ± 3.0              | 409.8 ± 36.8  |
| PLA/EMA−GMA/ZrP (82/15/3) | 38.8 ± 1.1           | 852 ± 42              | 65.5 ± 2.5              | 450.8 ± 22.9  |
| PLA/EMA−GMA/ZrP (80/15/5) | 36.9 ± 0.9            | 811 ± 59              | 58.3 ± 7.4              | 326.4 ± 61.7  |

The mechanical properties of PLA, PLA/EMA−GMA, and PLA/EMA−GMA/ZrP blends as prepared: (a) tensile strength, (b) tensile stress−strain curve, and (c) impact strength.
It can be concluded from the results of mechanical properties that the PLA matrix changed from brittle fracture to ductile fracture due to the synergistic effect of EMA−GMA and ZrP on PLA. A toughening reaction was supposedly between PLA matrix, EMA−GMA phase, and ZrP nanofiller, which will be verified by the analysis of FTIR, DMA, micromorphology, and thermal property below.

3.2. Fourier Transform Infrared Spectroscopy (FTIR). To verify the relative reaction between PLA, EMA−GMA, and ZrP, FTIR spectra of the polymers and compounds were recorded in the range of 500−4000 cm^{−1}, which is shown in Figure 4. The stretching vibration peaks of hydroxyl group for PLA are around 3650 and 3504 cm^{−1}, and the hydroxyl group’s peaks of ZrP appear at 3510 and 3594 cm^{−1}. The characteristic peak of the −CH_{3} appears at 2850 cm^{−1} and the peaks of epoxy group locate in 844 and 911 cm^{−1} for EMA−GMA.35,36

The absorption peaks disappeared at 844 and 911 cm^{−1}, and characteristic peaks of −CH_{3} at around 2850 and 2920 cm^{−1} corresponding to the symmetrical and asymmetrical stretching vibrations were found in PLA/EMA−GMA and PLA/EMA−GMA/ZrP blends, which indicated that there was chemical reaction between the end hydroxyl groups and end carboxyl groups of PLA and epoxy groups of EMA−GMA. The result has also been confirmed by literatures.33,34,37,38 The intensity of the peak at 3594 cm^{−1} correspond to the stretching vibration of the hydroxyl group for PLA/EMA−GMA/ZrP nanocomposites was absolutely much lower than that of nanofiller ZrP, indicating the hydroxyl groups of ZrP reacted with the epoxy groups of EMA−GMA and the nanofiller ZrP grafted in the molecular chain of EMA−GMA. The reaction mechanism between PLA, ZrP, and EMA−GMA is illustrated below.

3.3. Reaction Mechanism. From the illustration of the chemical structure in Figure 2, we can see that PLA has hydroxyl (−OH) and carboxyl (−COOH) groups at both ends of the molecular chain, the characteristic structure of EMA−GMA is the epoxy group, and hydroxyl groups are at the periphery of ZrP. So, during the process of melt-mixing in the mixer chamber, there would be a chemical reaction between the polymers of PLA, EMA−GMA, and inorganic filler ZrP, which is verified by the analysis the FTIR spectra of the polymer and compounds. Figure 5 illustrates the possible reaction between PLA, EMA−GMA, and ZrP. The epoxy groups incorporated in EMA−GMA reacted with both hydroxyl groups and carboxyl groups located at the end of PLA chains, and the epoxy groups of EMA−GMA reacted with hydroxyl groups located around the ZrP chains as well. So, the EMA−GMA will react with PLA and ZrP, respectively, by in situ grafting reaction. Consequently, graft copolymers are formed at the interface21 and the reaction will certainly promote the compatibility between the ternary components; the tests of DMA, SEM, and TEM were conducted to characterize the compatibility of the blends as follows.

3.4. Morphological Analysis. The phase morphologies formed during the melt-blending process plays a decisive role in the mechanical properties for multiphase compounds. SEM and TEM were applied to further investigate the mechanism of toughness and phase structure of the PLA matrix incorporated with EMA−GMA and ZrP.

The micrographs shown in Figure 6 are the impact-fractured surfaces of the PLA/EMA−GMA blend and PLA/EMA−GMA/ZrP nanocomposites with 1, 3, and 5 wt % ZrP. The impact-fractured surface of pure PLA was smooth and featureless without much deformation, and the value of impact strength was quite low, showing a typical brittle fracture behavior.39 The fracture surface of the binary blend became rough, while the elastomer of EMA−GMA was incorporated, which can be seen from Figure 6A, and some plastic deformations in the fracture surface can be seen. In Figure 6A, the EMA−GMA phases (marked in red circles) dispersed well in the PLA matrix and there was no interface observed between the binary phase, indicating the good compatibility between PLA and EMA−GMA. Compared with that of the PLA/EMA−GMA binary blend, there were more and much larger plastic deformations in the impact-fractured surface of PLA/EMA−GMA/ZrP nanocomposites, and also some fibrils were observed in Figure 6B, which indicated that the fracture form of the compounds transformed from brittle to ductile fracture due to the synergistic effect of EMA−GMA and ZrP on PLA.
fracture to plastic deformation. From Figure 6b−d and the cryofracture surface of PLA/EMA−GMA/ZrP blend in Figure 7, we can see that the nano filler ZrP was well-wrapped by the soft phase of EMA−GMA, which seems like a core−shell structure in the fracture surface, and there was no obvious interface between nanofiller ZrP and EMA−GMA phase; this is because the −OH groups of ZrP reacted with the epoxy groups of the EMA−GMA during the melt-blending process at high temperature and the lamellar structure of ZrP has a large specific surface area, which can facilitate its full contact with EMA−GMA. When the composite is impacted, the wrapped nanofillers act as stress concentration points that distribute the impact stress to the soft phase of EMA−GMA, which absorbs lots of energy and then the buffered stress was conducted into the PLA matrix evenly. As a result, the impact strength would be improved obviously by the addition of the nanofiller ZrP into the PLA/EMA−GMA compound.

We can also see from Figure 6B−D that with the increase in the content of ZrP there is an increase in plastic deformation points on the impact section of the PLA/EMA−GMA/ZrP compound and the plastic deformation also increases. So, the toughness of PLA/EMA−GMA−GMA/ZrP compound increases with the increase of the ZrP content. This is consistent with the impact strength of PLA/EMA−GMA and PLA/EMA−GMA/ZrP compounds. A comparison of Figure 6C with D shows more and larger plastic deformations in the impact section of PLA/EMA−GMA−GMA/ZrP compound than that of PLA/EMA−GMA/3 wt % ZrP compound. This can explain why the impact strength of PLA/EMA−GMA/3 wt % ZrP is higher than that of PLA/EMA−GMA/3 wt % ZrP.

The phase structures of the PLA/EMA−GMA blend and PLA/EMA−GMA/ZrP composition, which were observed by SEM, were further verified by TEM in Figure 8. Figure 8A shows the EMA−GMA phase dispersed in the PLA matrix, which corresponds to Figure 6a. A typical mixture of core−shell morphology is clearly seen in Figure 8B, the lamellar structure of nanofiller ZrP was wholly wrapped by the EMA−GMA phase during the PLA matrix, which verified the dispersion mode of ZrP in the PLA/EMA−GMA compound discussed above.

3.5. Miscibility Analysis. The mechanical properties of the compound are influenced greatly by the miscibility of the components, for it can not only determine the phase behavior but also the interfacial compatibility of the blends.13 The miscibility of the blends was assessed by the dynamic mechanical analysis. The tan δ curves of pure PLA, PLA/EMA−GMA binary blend, and PLA/EMA−GMA/ZrP nanocomposites are shown in Figure 9.

In the PLA/EMA−GMA (85/15) blend, there are two peaks of tan δ at −31 and 81 °C, corresponding to the glass transition temperature (Tg) of EMA−GMA and PLA, respectively. It has been proved that EMA−GMA has great

Figure 6. SEM micrographs of the impact-fractured surface of PLA/EMA−GMA/ZrP (w/w/w) blends: (A) 85/15/0; (B) 84/15/1; (C) 82/15/3; and (D) 80/15/5. (a), (b), (c), and (d) Local enlarged maps of (A), (B), (C), and (D), respectively.

Figure 7. SEM micrograph of cryofracture surface of PLA/EMA−GMA/ZrP (82/15/3 w/w/w) blend.

Figure 8. TEM images of PLA/EMA−GMA/ZrP (wt/wt/wt) blends of different compositions: (A) 85/15/0 and (B) 82/15/3.
miscibility with PLA after the compatibilization reaction during the melt-blending process by Zhang et al.,33,34 Li et al.,37 and Wei et al.38 and the FTIR analysis above. From Figure 9, we can see that, with the increase in the content of ZrP in PLA/EMA–GMA/ZrP compounds, the $T_g$ peaks of EMA–GMA shift toward higher temperature, while there is only a tiny change in $T_g$ of the PLA matrix with respect to pure PLA. The $T_g$ value was improved by 6 to $\pm$25 °C when the content of ZrP was 5 wt %, indicating the miscibility between PLA and EMA–GMA was promoted by the addition of the nanofiller ZrP. This is because the hydroxyl groups of ZrP can react with the epoxy groups of EMA

$\Delta H_m$, and degree of crystallinity ($\chi_c$) calculated from the thermograms, are summarized in Table 2.

The $T_g$ values of PLA in the PLA/EMA–GMA binary blend and PLA/EMA–GMA/ZrP nanocomposites almost did not change compared with that of pure PLA, which is consistent with the result of DMA. For PLA/EMA–GMA binary blend, the value of $T_g$ was increased 5.9 from 105.8 °C of pure PLA to 111.7 °C, indicated the crystallization of PLA was restricted by the presence of the EMA–GMA phase. Accordingly, the degree of crystallinity of the PLA/EMA–GMA blend decreased and the melting temperature shifted to a lower temperature. As for PLA/EMA–GMA/ZrP nanocomposites with only 1 wt % content of ZrP, the $T_g$ can be further increased by 8.7–120.4 °C than that of PLA/EMA–GMA blend. With increase in the content of ZrP within the nanocomposites, $T_g$ is improved slightly and the melting peaks shift to a lower temperature to 165.3 °C when the content of ZrP was 3 wt %, which is 5 °C lower than that of pure PLA. From Table 2, we can also see that the $\chi_c$ of nanocomposites decreased with the increasing ZrP content. When the presence of ZrP was 5 wt % within the nanocomposites, the $\chi_c$ was only 3.6%, far below that of pure PLA, which indicated that the crystallization of the PLA matrix at a relative low level (0 to ca. 8%)40 did not appear to play a significant role in improving the toughness. The trend that the crystallization decreased as the content of ZrP increased can be explained, as there were compatibilization reactions between the ZrP nanofiller, EMA–GMA phase, and PLA matrix, and the resulting strong interfacial interaction between the three components limited the mobility of the PLA segments. Therefore, the incorporation of ZrP can improve the cold crystallization temperature and reduce the melting temperature and the degree of crystallinity of the PLA matrix.

3.6.2. Thermogravimetric Analysis (TGA). The influence of ZrP on the thermal degradation of PLA was investigated by TGA. The TGA thermograms of pure PLA, PLA/EMA–GMA blend, and PLA/EMA–GMA/ZrP nanocomposites with different ZrP contents are shown in Figure 11, and the TGA data, including the initial decomposed temperature ($T_i$), temperature of the maximum rate of weight loss ($T_{fl}$), the final decomposed temperature ($T_f$), the maximum rate of mass loss ($R_{max}$), and the fraction of the residue remaining at 590 °C (Char), are presented in Table 3.

It is obvious that the thermal degradation of pure PLA and PLA/EMA–GMA blend started at 319 and 332.6 °C, the values of $T_i$ are 362.4 and 364.9 °C, respectively, the final decomposed temperatures are 373.6 and 483.3 °C, respectively, and the elastomer of EMA–GMA has a better thermal stability than that of pure PLA. Therefore, the presence of 15 wt % EMA–GMA enhanced the thermal stability of PLA for EMA–GMA has great compatibility with PLA and the mobility of the chains is restrained.

Compared with that of the PLA/EMA–GMA blend, the thermal stability of the compatibilized blends incorporated with a nanofiller ZrP is further improved. For example, when the ZrP content was 3 wt %, the onset of thermal degradation was improved about 10–342.9 °C compared with that of the PLA/EMA–GMA blend and 23.9 °C compared with that of pure PLA. The $T_i$ was improved from 364.9 °C of the PLA/EMA–GMA blend to 370.5 °C, and the corresponding $R_{max}$ was decreased from 29.63 to 25.43%/min. One of the important means to improve the thermal stability of polymeric materials is to increase the char formation.41 As the content of...
Table 2. Glass Transition Temperature (T_g), Cold Crystallization Temperature (T_{cc}), Melting Temperature (T_m), Cold Crystallization Enthalpy (\Delta H_{cc}), Melting Enthalpy (\Delta H_m), and Degree of Crystallinity (\chi_c) of Pure PLA and PLA/EMA–GMA/ZrP Blends

| compositions                  | T_g (°C) | T_{cc} (°C) | T_m (°C) | \Delta H_{cc} (J/g) | \Delta H_m (J/g) | \chi_c (%) |
|-------------------------------|----------|-------------|----------|--------------------|-----------------|------------|
| pure PLA                      | 60.3     | 105.8       | 170.3    | 32.4               | 40.6            | 8.8        |
| PLA/EMA–GMA (85/15)           | 61.0     | 111.7       | 168.5    | 25.4               | 30.9            | 6.9        |
| PLA/EMA–GMA/ZrP (84/15/1)     | 60.9     | 120.4       | 165.4    | 28.5               | 32.5            | 5.1        |
| PLA/EMA–GMA/ZrP (82/15/3)     | 60.9     | 120.5       | 165.3    | 28.1               | 31.1            | 3.9        |
| PLA/EMA–GMA/ZrP (80/15/5)     | 60.8     | 123.2       | 165.8    | 28.4               | 31.1            | 3.6        |

Figure 11. TGA curves of pure PLA, EMA–GMA, PLA/EMA–GMA blend, and PLA/EMA–GMA/ZrP nanocomposites.

In this study, supertough PLA matrix compound materials were prepared through the method of melt-blending by the addition of 15 wt % EMA with a small quantity of ZrP. The interfacial reaction between PLA matrix, EMA–GMA phase, and ZrP nanofiller, verified by the analysis of FTIR, promoted the compatibility of the nanocomposites and changed the brittle fracture of PLA to ductile fracture. The impact strength was improved about 22 times that of pure PLA for the nanocomposites with 3 wt % content of ZrP, and its elongation at break was nearly 43 times that of pure PLA. The nanofiller ZrP was well-wrapped by EMA–GMA phase to form a typical core–shell morphology and homogeneous dispersal in the PLA matrix was revealed by SEM and TEM. The results of DMA suggested that nanofiller ZrP can promote the compatibility between the PLA matrix and EMA–GMA phase. The DSC and TGA studies indicated that the nanofiller of ZrP can enhance the thermal stability of PLA in synergy with EMA–GMA and reduce the degree of crystallinity of the PLA matrix, which indicated that the crystallization did not appear to play a significant role in improving the toughness within a relative low level. The effective interfacial compatibilization and massive shear-yielding deformation achieved by the synergy of EMA–GMA with ZrP in the PLA matrix played a significant role in the supertough effect of the composition.

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**Notes**

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Table 3. TGA Data of Pure PLA, EMA–GMA, PLA/EMA–GMA Blend, and PLA/EMA–GMA/ZrP Nanocomposites

| compositions               | T_i (°C) | T_p (°C) | T_f (°C) | R_{max} (%/min) | char (%) |
|----------------------------|----------|----------|----------|-----------------|---------|
| pure PLA100/0/0            | 319.0    | 362.4    | 373.6    | 29.63           | 0.82    |
| EMA–GMA                   | 398.4    | 457.5    | 491.5    | 20.37           | 0.23    |
| PLA/EMA–GMA (85/15)       | 332.6    | 364.9    | 483.3    | 26.05           | 0.73    |
| PLA/EMA–GMA/ZrP (84/15/1) | 342.1    | 371.0    | 484.2    | 25.46           | 1.33    |
| PLA/EMA–GMA/ZrP (82/15/3) | 342.9    | 370.5    | 484.9    | 25.43           | 2.96    |
| PLA/EMA–GMA/ZrP (80/15/5) | 342.3    | 370.2    | 485.3    | 24.61           | 4.53    |
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