

폴리락틱산/산화아연 기둥구조의 유기사포나이트 나노복합체의 특성, 구조 및 결정화

Weijun Zhen[†] and Jinlu Sun

Key Laboratory of Oil and Gas Fine Chemicals, Ministry of Education and Xinjiang Uygur Region, Xinjiang University, China
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Properties, Structure and Crystallization of Poly Lactic Acid/Zinc Oxide Pillared Organic Saponite Nanocomposites

Weijun Zhen[†] and Jinlu Sun

Key Laboratory of Oil and Gas Fine Chemicals, Ministry of Education and Xinjiang Uygur Region,
Xinjiang University, Urumqi 830046, China

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Abstract: ZnO pillared saponite was synthesized via a microwave hydrolysis method. To enhance interfacial compatibility between zinc oxide (ZnO) pillared saponite and poly lactic acid (PLA), ZnO pillared organic saponite was prepared by intercalation modification of cetyltrimethylammonium bromide. Moreover, PLA/ZnO pillared organic saponite nanocomposites were prepared by melting processing. The microstructure analysis of PLA/ZnO pillared organic saponite nanocomposites showed that ZnO pillared organic saponite was exfoliated and homogeneously dispersed in PLA matrix. The property results showed that ZnO pillared organic saponite improved the mechanical properties and thermal stabilities of PLA/ZnO pillared organic saponite nanocomposites. Differential scanning calorimetry (DSC) demonstrated that ZnO pillared organic saponite restrained the appearance of cold crystallization, lowered the glass transition temperature and melting temperature of PLA, and improved the crystallinity of PLA. The results demonstrated that ZnO pillared organic saponite had a good interfacial compatibility and heterogeneous nucleation effect in PLA matrix, and also played an active role in accelerating the crystallization process of PLA.

Keywords: poly lactic acid, ZnO pillared organic saponite, nanocomposites, properties, crystallization.

Introduction

Poly lactic acid (PLA) is a typical crystalline polymer with excellent biocompatibility and biodegradability owing to its synthetic source from renewable crops.^{1,2} So PLA has become one new kind of polymer material with a wide application prospect.^{3,4} But in the process of practical production, PLA always has a low degree of crystallinity and crystallization rate, which influenced its biodegradation, mechanical properties and thermostability.^{5,6} Therefore, it is very important to improve the crystallinity and properties of PLA for developing and application of PLA composite materials by modification⁷ and blending.^{8,9} Furthermore, nucleators¹⁰ which were often used in productive process had a good promotion to the pro-

cess of crystallization of PLA. Layered silicate clay particles have a heterogeneous nucleation effect in PLA matrix, increasing the crystallization rate of PLA and promoting the cold crystallization process at low temperatures.¹¹⁻¹³

Saponite is a specific layered silicate minerals from Xinjiang of China which has trioctahedron structure and excellent properties.¹⁴ Moreover, because ZnO also has many outstanding integrated performance, such as magnetic, optical and electrical properties and so on,¹⁵⁻¹⁷ ZnO pillared saponite was prepared via microwave hydrolysis method and improved the mechanical and thermostability of PLA materials.¹⁸ In this work, cetyltrimethyl ammonium bromide (CTAB) was used to organically modify the ZnO pillared saponite to enhance the interfacial compatibility of ZnO pillared saponite with PLA matrix to improve the comprehensive performance of PLA materials. On the basis, effects of ZnO pillared organic saponite on the crystallization and properties on PLA materials were studied.

[†]To whom correspondence should be addressed.
E-mail: zhenweijun6900@163.com

Experimental

Materials. PLA (injection grade, $M_v=80000$), Shenzhen Guanghuaweiye Industrial Co., China. Nature saponite powder (mean grain size was about 60–70 μm) was purchased from Xinjiang Tuogema Colloid Co., China. Acetyl tributyl citrate (ATBC) (industrial grade) was provided by Changzhou Tianzheng Chemical Technology Co., China. TMC-328 (nucleator, industrial grade) was provided by Institute of Shanxi Chemical Industry, China. Analytically pure ZnCl_2 and cetyltrimethyl ammonium bromide (CTAB) were purchased from Tianjin Fuchen Chemical Reagent Factory, China. Analytically pure NaOH was provided by Tianjin Zhiyuan Chemical Reagent Factory, China.

Preparation of ZnO Pillared Organic Saponite. Firstly, 10 g ZnO pillared saponite¹⁸ was made into 10 wt% suspensions. After that, 4.37 g CTAB was dissolved in 300 mL deionized water and added into ZnO pillared saponite water suspensions to yield precipitates with a separating funnel under vigorous stirring in a water bath at 70 °C for 2 h. After filtration, the precipitates were washed with deionized water until no Br^- ion (examined by 0.1 M AgNO_3) was tested and then dried to yield ZnO pillared organic saponite.

Preparation of PLA/ZnO Pillared Organic Saponite Nanocomposites. PLA, ZnO pillared organic saponite, ATBC were mixed in a high speed mixer (1000 rpm) at room temperature for 20 min. The mixing composition and name of all composites in this paper were shown in Table 1. PA0, PAZ1, PAZ3, PAZ5, PAZ7 and PAZ9 indicated that the content of PLA and ATBC in PLA materials was 150 and 15 g, respectively, and the content of ZnO pillared organic saponite in PLA matrix was 0, 0.1, 0.3, 0.5, 0.7, 0.9%, respectively. Moreover, PAT0, PATZ1, PATZ3, PATZ5, PATZ7, PATZ9 indicated that the content of PLA, ATBC and TMC-328 in PLA materials was 150, 15, 0.45 g, respectively, and the content of ZnO pillared organic saponite in PLA matrix was 0, 0.1, 0.3, 0.5, 0.7, 0.9%, respectively. These mixtures were manually fed into the single screw extruder (HAAKE RHEOMEX 254, diameter 19 mm and $L/D=25:1$, Germany) with a speed of 30 rpm, and the temperature profile along the extruder barrel was 170, 180, 180 and 180 °C (from feed zone to die), respectively. After these mixtures were extruded and pelletized, all samples were molded on the HAAKE Mini Jet injection molding machine under a pressure of 80 MPa at 190 °C, mold temperature was 60 °C and pressure-holding time was 10 s.

Characterization. X-ray diffraction (XRD) pattern were

Table 1. Mixing Composition of PLA/ZnO Pillared Organic Saponite Nanocomposites

Compound code	Mixing composition			
	PLA (g)	ATBC (g)	TMC-328 (g)	ZnO pillared organic saponite (g)
PA0	150	15	-	-
PAZ1	150	15	-	0.15
PAZ3	150	15	-	0.45
PAZ5	150	15	-	0.75
PAZ7	150	15	-	1.05
PAZ9	150	15	-	1.35
PAT0	150	15	0.45	-
PATZ1	150	15	0.45	0.15
PATZ3	150	15	0.45	0.45
PATZ5	150	15	0.45	0.75
ATZ7	150	15	0.45	1.05
PATZ9	150	15	0.45	1.35

Note: PA0, PAZ1, PAZ3, PAZ5, PAZ7 and PAZ9 indicated that the content of PLA and ATBC in PLA materials was 150, 15 g, respectively, and the content of ZnO pillared organic saponite in PLA matrix was 0, 0.1, 0.3, 0.5, 0.7, 0.9%, respectively. Moreover, PAT0, PATZ1, PATZ3, PATZ5, PATZ7, PATZ9 indicated that the content of PLA, ATBC and TMC-328 in PLA materials was 150, 15, 0.45 g, respectively, and the content of ZnO pillared organic saponite in PLA matrix was 0, 0.1, 0.3, 0.5, 0.7, 0.9%, respectively.

recorded with a Philips X' Pert X-diffractometer (Netherlands), using $\text{CuK}\alpha$ radiation at $\lambda = 0.1540$ nm (50 kV, 35 mA). Diffraction spectra were obtained over 2θ range of 1.5–60° with a scanning speed of 0.1 °/s. ZnO pillared organic saponite was tested as powders. Samples of PLA/ZnO pillared organic saponite nanocomposites were from the injection mold.

Fourier transform infrared spectroscopy (FTIR) was performed by means of a EQUINOX55 FTIR spectrometer, KBr pellets of samples were prepared. The spectra were collected from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} .

The impact fracture morphology was observed by a scanning electron microscope (SEM, Inspect F, FEI Instrument Co., Ltd, Netherlands) at 20 kV of acceleration voltage and the liquid nitrogen fractured surface of composite samples prepared. Prior to SEM evaluation, the samples were sputter-coated with gold to avoid charging during the tests.

The morphology of PLA/ZnO pillared organic saponite nanocomposites was observed by a transmission electron microscope (TEM), TECNAI G2-F20 (FEI Co., Netherlands). Specimen was observed at an acceleration voltage of 75 kV.

Thermal gravimetric analysis (TG-DTA) was conducted on TA-Q600 analyzer (USA). Samples of about 5-10 mg were placed in an open alumina crucible. Temperature programs for dynamic were carried out at a heating rate of 10 °C/min from room temperature to 450 °C. The measurements were operated under a nitrogen purge (100 mL/min).

Differential scanning calorimetry (DSC) was conducted on a NETZSH 204 DSC differential scanning calorimeter (Germany). Samples of about 5-8 mg were performed by heating from room temperature to 250 °C at a heating rate of 10 °C/min under a nitrogen flow (40 mL/min).

Complex modulus of the sample was obtained on a rotational rheometer (Bohlin Gemini 200 Marlvern Instrument Company, England), the stress and frequency were 10 Pa and 2 rad/s, respectively. Temperature programs were carried out at a heating rate of 3 °C/min from room temperature to 220 °C, and then constant temperature for 3 min till the sample was completely fused. Furthermore, the complex modulus of the samples was recorded in the cooling period at 3 °C/min. The samples were molded into a small disc (25 mm of diameter and 1.5 mm of thickness) before testing and the whole test process was conducted under N₂ atmosphere.

Dynamic mechanical analysis (DMA) was performed in tensile mode on a DMAQ800 analyzer (USA). Temperature scans at 1 Hz frequency were carried out at a heating rate of 5 °C/min from -30 to 210 °C. Samples were from the injection mold and dried in vacuum oven at 60 °C for 24 h before testing.

Tensile tests were carried out according to ASTM D 412-80 by an Instron 4302 Universal Testing Machine (USA) at a crosshead speed of 5 mm/min. At least five measurements for each composite were performed. Samples of PLA/ZnO pillared organic saponite nanocomposites were from the injection mold.

Results and Discussion

Organic Modification of ZnO Pillared Saponite. Figure 1 showed X-ray diffractograms of the ZnO pillared organic saponite, ZnO pillared saponite and saponite. The first peak (001) in Figure 1 indicated the characteristic XRD reflections of saponite. The XRD patterns of ZnO pillared saponite showed that the diffraction peak (001) has been almost disappeared but the diffraction peak of ZnO (100), (002), (101), (102), (110) were found, which suggested that the layers of saponite were almost exfoliated into nanometer scale layers by ZnO. Comparing with saponite, the intensity and area of first

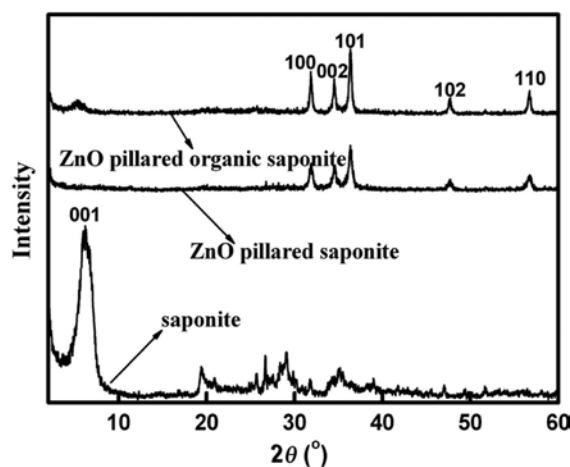


Figure 1. XRD patterns of ZnO pillared organic saponite, ZnO pillared saponite and saponite.

peak (001) of ZnO pillared organic saponite was very weak and shifted towards smaller angle which demonstrated that the ZnO pillared saponite was modified very well by CTAB.

FTIR Analysis of ZnO Pillared Organic Saponite. FTIR can reflect the vibrations of molecular groups and identify the structure of molecular contained in substance. So it can describe the organic groups in modified ZnO pillared saponite and proved whether the organic modification was successful. Figure 2 is the infrared spectra of saponite and ZnO pillared organic saponite. It was shown that the bands at 3632 and 3487 cm⁻¹ indicated -OH group and interlayer water stretching vibration bands of saponite. From the infrared spectra of ZnO pillared organic saponite, the CH₂ stretching vibration band appeared at 1473 and 2854, and 2927 cm⁻¹ was the C-H stretching vibration band, which were characteristic bands of

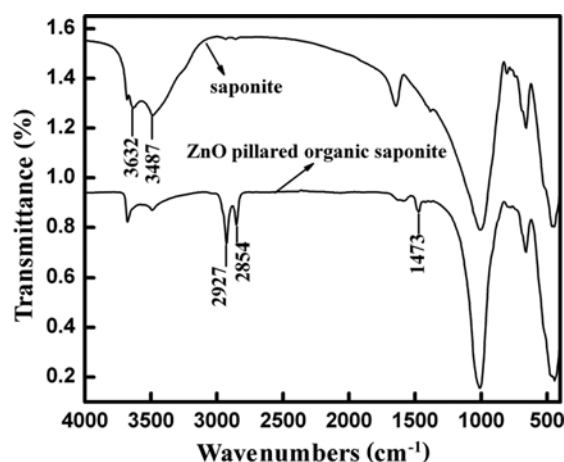


Figure 2. FTIR curves of ZnO pillared organic saponite.

the organic groups of CATB,¹⁹ and suggested that the organic groups of CTAB were successfully intercalated into the structure of saponite.

Mechanical Performance of PLA/ZnO Pillared Organic Saponite Nanocomposites. As shown in Figure 3(a), the elongation at break (EB) of PLA/ZnO pillared organic saponite nanocomposites increased significantly compared with the control samples. The EB of PLA/ZnO pillared organic saponite nanocomposites increased rapidly with the content of ZnO pillared organic saponite increasing, but the trend was less pronounced when the ZnO pillared organic saponite increases beyond 0.1%. From above results, it was clear that there was an optimum amount of ZnO pillared organic saponite required to achieve the greatest improvement in the properties of the nanocomposites. The reason was that a small amount of ZnO pillared organic saponite benefited for the formation of intercalated nanocomposites,^{20,21} and could increase the quantity of crystal nucleus. Furthermore, ZnO pillared organic saponite surface attached many organic cations and made ZnO pillared organic saponite more hydrophobic, which resulted in the organic and inorganic phases being dispersed at the nanometer level under the strong interactions between the polymer and the clay layer. Finally, when the content of ZnO pillared organic saponite was beyond 0.1%, the EB of PLA based nanocomposites was declining. The reasons were that ZnO pillared organic saponite layers stacked or agglomerated in the PLA matrix and had a negative effect on the mechanical properties of PLA composites, moreover the crystal nucleus quantity of PLA declined and the motion and development of PLA molecular chain was blocked.^{14,22} Figure 3(b) also showed that the tensile stress (TS) of PLA based nanocomposites gradually decreased with the content increasing of ZnO pillared

organic saponite. This main reason was that ZnO pillared organic saponite formed aggregation in PLA matrix and formed stress points which would be easy to break under the effect of outside force. In spite of this, the mechanical properties of the PLA based nanocomposites were still held at a high level, which was significant to improve its mechanical properties by adding ZnO pillared organic saponite. On the whole, the PLA based nanocomposites which was mixed with TMC-328 performed a better mechanical properties, which were relevant to the heterogeneous nucleation effect crystallization of TMC-328 for PLA.²³⁻²⁵ Furthermore, TMC-328 and ZnO pillared organic saponite had a synergistic effect and enhanced the mechanical properties of PLA based nanocomposite.

XRD Analysis of PLA/ZnO Pillared Organic Saponite.

As shown in Figure 4, the peaks at $2\theta = 16.4^\circ$ and 19.1° prominently indicated a crystalline PLA matrix.²⁶ Moreover, the peaks observed at $2\theta = 30^\circ\text{--}40^\circ$ were the characteristic peaks from ZnO,²⁷ which indicated that the ZnO pillared organic saponite had been dispersed into the PLA matrix. The patterns of PA0 and PAT0 showed that PLA matrix also exhibited crystalline peaks. This phenomenon was the reason that ATBC increased the mobility of the polymer chains and influenced ordering of PLA molecular chains which was favorable for the crystallization during the melt processing of PLA. In addition, TMC-328 effectively enhanced the crystallization of PLA. It was observed that the diffraction peaks of PAZ1 and PATZ1 were sharper, more single and uniform compared with those of PA0 and PAT0. This phenomenon indicated that addition of ZnO pillared organic saponite really further improved the crystallinity of PLA. Several factors could be responsible for this phenomenon. Firstly, ZnO pillared organic saponite attached

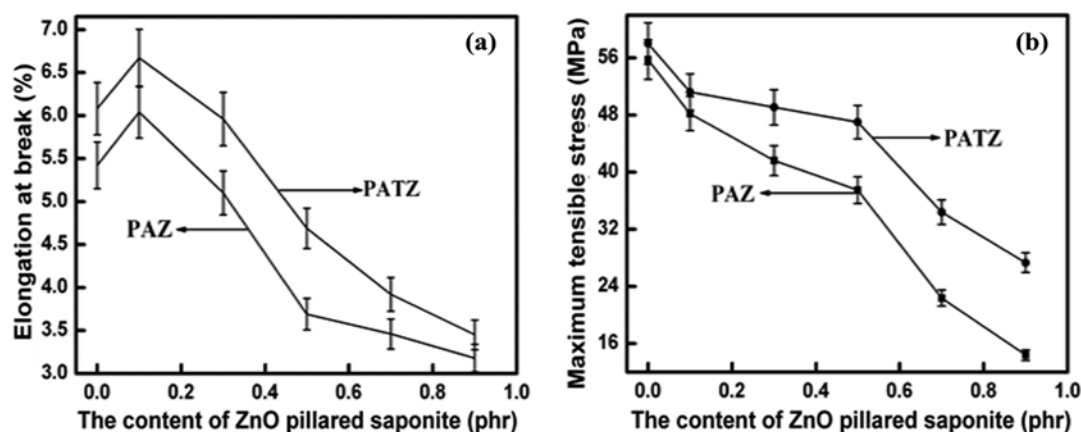


Figure 3. Effects of ZnO pillared organic saponite on mechanical properties of PLA based nanocomposites.

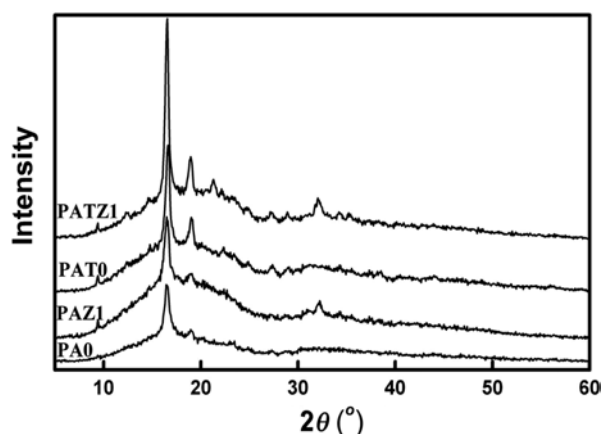


Figure 4. XRD patterns of PLA based nanocomposites.

many organic cations which improved the interfacial compatibility with PLA matrix. Secondly, the increasing in chains mobility due to the plasticizing effect of ATBC increased contact between ZnO pillared organic saponite and PLA molecular chains which improved the heterogeneous nucleation effect and induced the crystallization of PLA. On the other hand, TMC-328 and ZnO pillared organic saponite had a synergistic effect which enhanced the crystallization of PLA more effectively.

Morphological Analysis. To investigate the mechanism of the markedly increased elongation caused by the addition of ZnO pillared organic saponite, the morphology of fractured surface were observed by SEM (Figure 5). It was observed that only a few shear zones had been initiated for the fracture surface of PA0 when submitted to impact, thus it showed low toughness and impact strength (Figure 5(a)). In the fracture surfaces of the blends with ZnO pillared organic saponite (Figure 5(b)), the dispersed phase appeared unsmooth in the matrix and the impact-fractured surfaces performed perceptible plastic deformation. This may be ascribed to the compatibility and heterogeneous nucleation effect of ZnO pillared organic saponite in PLA matrix. In addition, ATBC increased the motion space and the mobility of PLA molecular chains, which was benefit for absorbing more impact energy. Much more shear zones had been observed on their surface in Figure 5(c), which indicated that plastic deformation took place in the matrix of the blends during impact test. Extensive shear yielding of the matrix were shown in Figure 5(d). Fibrillation of the matrix resulted from these observed shear yielding and the two phase interface became blurry, which would absorb more energy during impact test.²⁸ This result may be attributed to the heterogeneous nucleation effect of TMC-328 and ZnO pillared

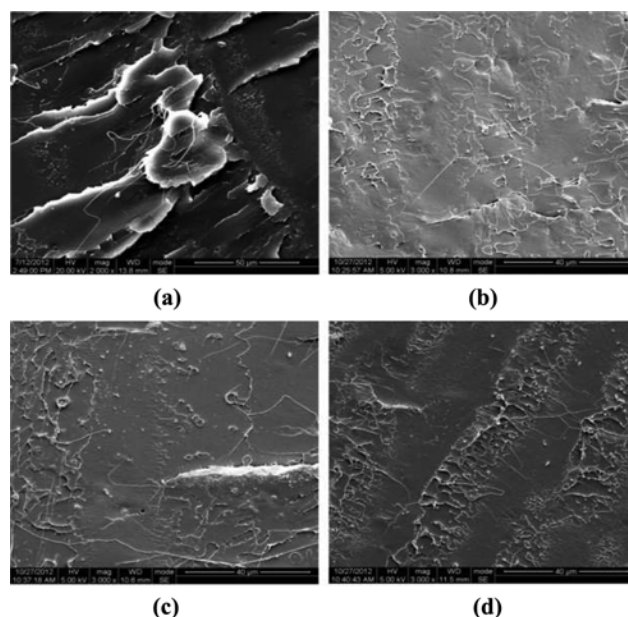


Figure 5. SEM morphology of fracture of PLA based nanocomposites: (a) PA0; (b) PAZ1; (c) PAT0; (d) PATZ1.

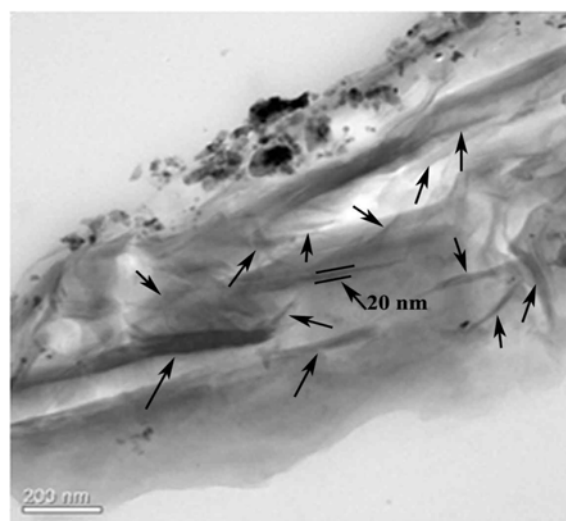


Figure 6. TEM image of PATZ1.

organic saponite which increased the crystallization of PLA with a synergistic effect.

Figure 6 showed a TEM image of PLA/ZnO pillared organic saponite. It was shown that a mixed nano-morphological state of ZnO pillared organic saponite layers had homogeneous dispersion and clear orientation in PLA matrix, and the ZnO pillared organic saponite layers were individualized with dimensions ranging from 90 to 200 nm in length and 15–20 nm in width. This result suggested that the exfoliated nanocomposite had been obtained. Moreover, it was shown in the micrographs that

agglomerated ZnO pillared organic saponite existed in PLA matrix due to the strong electrostatic adsorption effect and non-uniform filler. This phenomenon would have a negative effect on the mechanical properties of PLA based nanocomposites.

DSC Analysis. The crystallization of the PLA based nanocomposites in Figure 7 were given below:

$$X_c = \frac{\Delta H_m - \Delta H_c}{f \times \Delta H_m^0} \times 100\% \quad (1)$$

Where X_c is the degree of crystallinity of the PLA based nanocomposites, ΔH_c is the enthalpy of crystallization, ΔH_m is enthalpy of fusion, f is the weight fraction of PLA in the composite, ΔH_m^0 is enthalpy of fusion of the purely crystalline form of PLA ($\Delta H_m^0 = 93.7 \text{ J/g}$).²⁹ It could be found from Figure 6 that the glass transition temperature (T_g), melting temperature (T_m) of the PLA based nanocomposites were decreased and the

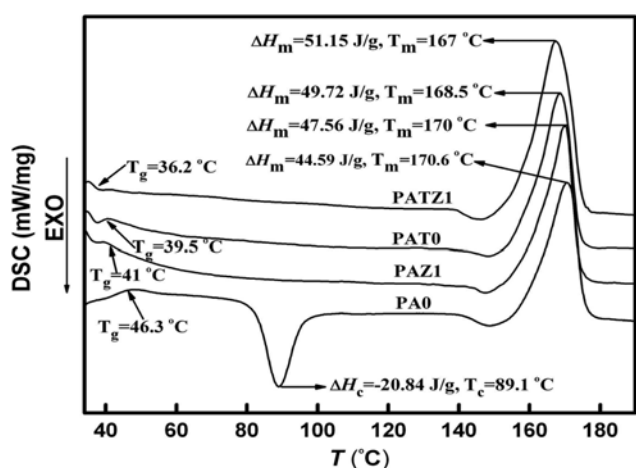


Figure 7. DSC curves of PLA based nanocomposites.

cold crystallization were disappeared after introduction of ZnO pillared organic saponite. The ATBC could induce crystallization of PLA and further melting during heating, so the T_g of PLA shifted towards lower temperature range and restrained its cold crystallization of PLA. This may be ascribed to ATBC which made PLA chains swell or dilute and improved the sliding ability of PLA molecules, moreover decreased its entanglement concentration. The addition of ZnO pillared organic saponite depressed the cold crystallization behavior of PLA. Moreover, T_g and T_m of PLA also shifted towards lower temperature. And the crystallinities of PLA based nanocomposites were 56.4, 59, 60.7%, respectively, which increased by 50, 52.2, 53.5%, respectively, compared to that of PA0. The reason for this phenomenon was that ZnO pillared organic saponite and TMC-328 performed good interfacial compatibility and uniform dispersion in PLA matrix under the effect of ATBC, which benefited for the heterogeneous nucleation effect to improve the crystallization of PLA. It was shown in Figure 7 that the initial temperatures of T_m were migrated to lower temperature region, and all of the sample had only one T_m indicating that the introduction of ZnO pillared organic saponite did not change the crystal structure of PLA.¹⁸

TG Analysis. Figure 8 was the results of TG-DTA analysis of the PLA based nanocomposites. Generally, the addition of ATBC to PLA improved the flexibility and mobility of PLA molecular chains which lowered the energy of thermal decomposition of PLA and decreased the thermal-decomposition temperature of the PLA based nanocomposites. It was shown that when ATBC was used to plastify PLA, and ZnO pillared organic saponite could enhance the thermal-decomposition temperature of PLA nanocomposites. The main reason was

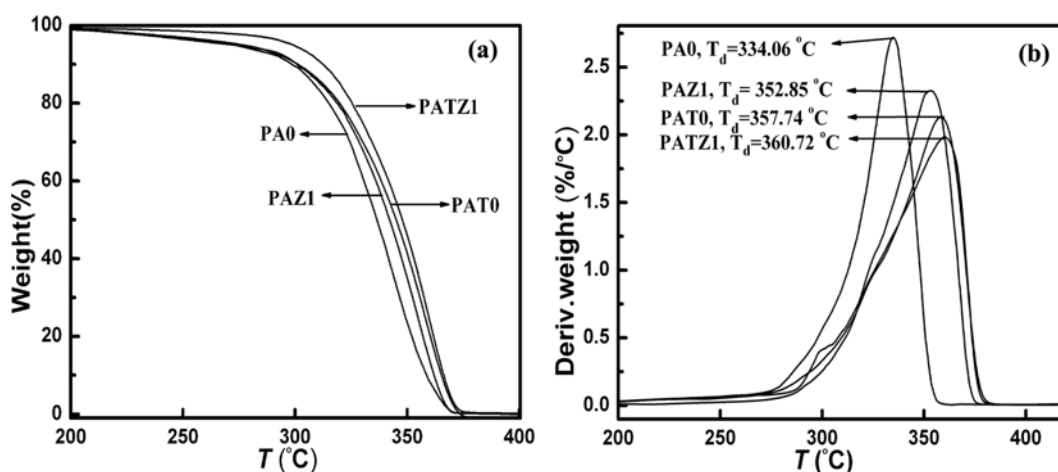


Figure 8. TG curves of PLA based nanocomposites: (a) TG of PLA based nanocomposites; (b) DTG of PLA based nanocomposites.

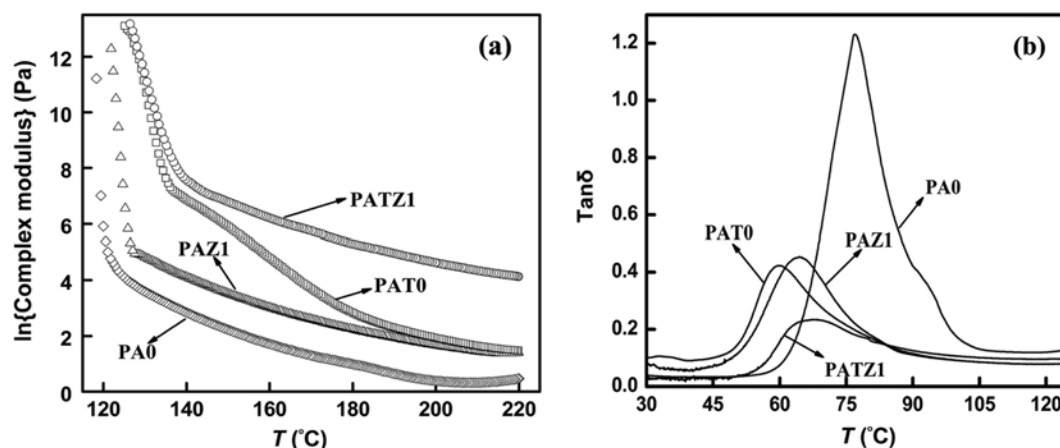


Figure 9. Temperature dependence of (a) $\ln(\text{complex modulus})$; (b) $\tan \delta$ for PLA based nanocomposites.

that the ZnO pillared organic saponite impeded the thermal motion of PLA molecular in PLA matrix, and increased the energy barrier of the thermal decomposition of PLA. So the thermal-decomposition temperature was improved. When TMC-328 was mixed into the matrix, the thermostability of PLA based nanocomposites was improved. Furthermore, when ZnO pillared organic saponite was introduced, the thermostability of PLA nanocomposites was further improved, which also proved that the ZnO pillared organic saponite really enhanced the thermostability of PLA based nanocomposites. At the same time, the thermal stability of PLA based nanocomposites become stronger as the crystallization of PLA based nanocomposites improved. So this could be explained from the combined analysis of DSC and TG-DTA.

Rheological Analysis of PLA/ZnO Pillared Organic Saponite Nanocomposites. Figure 9(a) showed the relation of complex modulus and temperature of the PLA based nanocomposites, the viscosity of PA0 continuously increased from 220 to 110°C, and the complex modulus increased linearly as the temperature decreased. When the temperature reached about 120°C, its complex modulus distinctly increased, which indicated that PLA began to crystallize. Furthermore, the trend of the complex modulus curves of PAZ1 changed very little, but its complex modulus clearly improved because of the addition of ZnO pillared organic saponite fillers. It also enhanced the rigidity of the PLA based nanocomposites as a result of increasing of the complex modulus. TMC-328 had a great influence on the crystallization of PLA. It was shown that showed that the complex modulus of PAT0 began to increase suddenly at 190°C, which could be for the reason that TMC-328 self-assembled into special network structure³⁰ during the cooling process. When the temperature decreased to about

140°C, the special network structure began to induce the PLA crystallization, so the complex modulus increased again. It was found that the complex modulus of PATZ1 slowly increased at the beginning of cooling process, but its complex modulus was further improved, which was because ZnO pillared organic saponite restrained the formation of the special network structure of TMC-328 instead of boosting the rigidity of the PLA based nanocomposites.

To investigate the effect of ZnO pillared organic saponite fillers on the T_g and $\tan \delta$, DMA of PLA based nanocomposites was performed. Figure 9(b) showed that T_g of PLA based nanocomposites shifted towards lower temperature with the introduction of ZnO pillared organic saponite. This was probably because the intercalation of PLA chains into saponite galleries occurred completely and depressed the cold crystallization behavior of PLA when the ZnO pillared organic saponite acted as nucleating agent, which was in accordance with the result of DSC. Furthermore, $\tan \delta$ value of PLA markedly decreased with the addition of ZnO pillared organic saponite. This suggested that the molecular motion of amorphous chains of PLA was largely restricted by introducing of the ZnO pillared organic saponite because the saponite layers were well dispersed in this PLA based nanocomposites.^{31,32}

Conclusions

To improve the crystallization of PLA and to obtain PLA based nanocomposites with excellent performance, a series of PLA/ZnO pillared organic saponite nanocomposites were successfully prepared by melt processing. It was shown that ZnO pillared organic saponite layers homodispersed in PLA matrix and performed a heterogeneous nucleation effect which accel-

erated the crystallization of PLA, so the comprehensive performance of PLA based nanocomposites were improved.

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