

Preparation and performance study of hydrotalcites /PLA composites

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Abstract. 3D printing technology is known as the core technology of "the third industrial revolution". Poly (lactic acid) (PLA) is a new type of biodegradable thermoplastic resin, which is renewable. It has a wide range of raw materials. It also has the properties of high strength, good biocompatibility, excellent mechanical properties, thermoplastic and transparency. Hydrotalcite (HT) was synthesized by coprecipitation method and modified to prepare the HT/PLA composites. The results show that the structure of HT is good. After KH550 surface modification, a large number of OH and Si-O groups are introduced into PLA surface. TG results show that the HT sample has good thermal stability. Compared with pure PLA, the glass transition temperature and crystallization temperature of HT / PLA composites decreases, while the melting temperature increases.

1 Introduction

3D printing refers to the technology of layered discrete processing by 3D printing equipment according to the 3D model files of the product. It accurately stacks certain specific materials layer by layer and rapidly manufactures the required products by laser irradiation. 3D printing is a frontier technology with interdisciplinary [1, 2]. Many technologies such as material technology, information technology, and electromechanical control technology need to be used. Specific structure can be designed according to the model and the precise control of microstructure by computer can be realized. It is known as the core technology of "the third industrial revolution".

At present, 3D printing materials can be divided into two categories: organic polymer materials and inorganic materials. Organic polymer materials are also divided into acrylonitrile styrene butadiene copolymer (ABS), poly (lactic acid) (PLA), polyamide (PA), photosensitive resin and hydrogel. Inorganic materials mainly include metal, ceramics and gypsum. [3]. PLA is a new biodegradable thermoplastic resin, which has renewable properties. Its raw material lactic acid is widely used, which can be obtained by the fermentation of corn, starch and other agricultural products. PLA has high strength and good biocompatibility. Compared with ABS commonly used in FDM process, PLA material is environmentally friendly and has low odor, which is suitable for indoor use. In addition, PLA has excellent mechanical properties, thermoplastic, fiber-forming, transparency and degradation. At the same time, its low shrinkage also makes it impossible to warp even if the

hot bed is not heated when printing large-scale model. However, PLA has disadvantages when it is used as bio plastics. The mechanical properties of the material are poor. The toughness and impact resistance are obviously inferior to ABS. And the melt strength is low. Thus it is not suitable to be made too thin and bear load. It is difficult to form and the printing products are brittle. During printing process of unmodified PLA wire, the leakage phenomenon will occur at the nozzle due to the decrease of melt strength. And the rough edge will be formed by sticking on the modelling part, which will affect the surface quality of the printing part [4].

In recent years, a lot of researches have been carried out on toughening and modifying PLA. The researchers toughened and modified PLA by adding inorganic and organic substances into it. Inorganic materials include montmorillonite, carbon nanotubes, talc powder, titanium dioxide, silica, calcium carbonate and HT. A lot of researches show that [5] HT/PLA layered composites have been improved in gas barrier, heat resistance, flame retardant, mechanical properties and electrical properties compared with pure PLA. This will expand the application of PLA in the field of engineering plastics, packaging materials and electronic electrical gas.

HT compounds have layered structure, and their chemical composition can be expressed by the following general formula: $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} represents bivalent metal cation; M^{3+} represents trivalent metal cation, which are located in octahedral voids on the main layer plate; A^{n-} is anion, located between layers; X is charge density. A large class of anionic layered materials with similar structure are formed due to the types of anions and cations as well

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as the stoichiometric ratio of divalent and trivalent cations can be adjusted in a large range. The structure of HT is shown in Fig. 1.

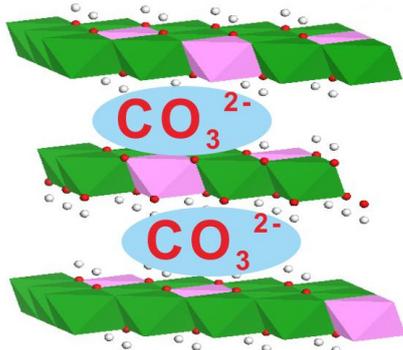


Fig. 1. Structure of HT

In this paper, a series of HT were synthesized by coprecipitation method and modified by KH550. The HT/PLA composites were obtained by melt blending method. The thermal properties of the composites were studied in order to obtain 3D printing materials with excellent performance, so that the PLA materials can obtain better printing effect in practical application.

2 Experimental

2.1. Synthesis of HT

HT with different metal ratios was synthesized by coprecipitation method. The main synthesis steps are as follows: nitrate solution A with a certain stoichiometric ratio and alkali solution B with a certain amount of NaOH and Na₂CO₃ were prepared. The salt solution A was added into the alkali solution B under high speed stirring, and the pH value was controlled at about 9. The slurry C was then transferred to a three-port flask, and stirred vigorously. The mixture was crystallized at 100°C for 6h. The mixture was filtered, washed to neutral with distilled water. The filter cake was dried in a constant temperature drying oven at 70 °C for 24h. The obtained solid was ground into powder.

2.2 Modification of HT

According to ion exchange method, 12.4 g HT and 13.1 g SDS were dissolved in 640 ml CO₂ removal water, and stirred at room temperature for 12 h. The obtained composite was filtered and washed with CO₂ removal water until pH=7. 10 mL KH550 was added into the solution and reacted at 70°C for 10 h. The slurry was filtered, dried and ground to obtain the modified HT.

2.3 Characterization of HT

The X-ray powder diffractometer (XRD) of Shimadzu 6100X was used, with Cu K α radiation ($\lambda=1.5406$ Å), light source wavelength of $\lambda = 0.15406$ nm, working voltage and current of 40 kV and 30 mA respectively, scanning speed of 3 (°) · min⁻¹, scanning range of 5 ~

75 °C. The infrared absorption spectrum (IR) of the sample was determined by the VECTOR22 Fourier transform infrared spectrometer of Bruker Company in Germany. The KBr tablet was pressed in the range of 4000 ~ 600 cm⁻¹. The thermal stability of HT samples was characterized by TA company Q5000 thermogravimetric analyser (TGA). N₂ was used as carrier gas, the flow rate was 50 ml · min⁻¹, the heating rate was 10 °C · min⁻¹, and the temperature range was 25~ 600 °C.

2.4 Preparation of HT / PLA composites

HT/PLA composites were prepared by melt blending method. A certain amount of HT synthesized above was weighed, and was then added to the dried PLA with the amount of 0.5%, 1%, 2%, 4% and 10% (by weigh). After evenly mixed, the mixture was then added to the twin-screw extruder for blending. The temperature of each section from the barrel to the head of the extruder was set as 160 °C, 180 °C, 185 °C, 185 °C, 180 °C and 175 °C, and the screw speed was 20 rad/min. After extrusion and granulation, the HT/PLA materials with different HT contents were prepared.

2.5 Performance test of HT / PLA composites

Shimadzu DSC-60 differential scanning calorimetry (DSC) was used to characterize the thermal properties of HT/PLA samples. N₂ was used as carrier gas, the flow rate was 50 mL · min⁻¹, the heating rate was 10 °C · min⁻¹, and the temperature range was 30~ 200 °C.

3 Results and discussions

3.1. Structure of HT

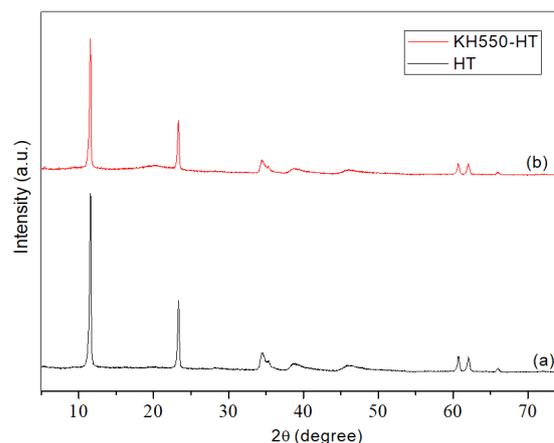


Fig. 2. XRD spectrum of the HT layered materials prepared before and after modification

Fig.2 shows the XRD spectrum of the HT layered materials prepared before and after modification. It can be seen from Fig. 3 that HT shows similar peak patterns. It is found that the peaks are characteristic diffraction peaks of HT by comparing with the standard spectrum. The stable baseline, the sharp peak, and no other

miscellaneous peaks indicating that the prepared HT layered materials have typical HT structure, good crystalline, single crystal phase and complete crystal phase. It can be concluded that the modified samples still keep the good structure of HT layered materials.

3.2 Effect of modification

Fig. 3 shows the IR spectra of HT samples before and after modification. It can be seen from Fig. 3 that the hydrogen oxygen bond stretching vibration peak of -OH in the layer appeared at about 3428 cm^{-1} before modification. Compared with the free state -OH (about 3600 cm^{-1}), the peak shifted to the direction of low wave number, indicating that the water molecules between the layers of the sample had hydrogen bond interaction with CO_3^{2-} and hydroxyl groups on the layer. In addition, the splitting peak of asymmetric stretching vibration of C-O bond in CO_3^{2-} appears at 1366 cm^{-1} , and it is a symmetrical single peak, which indicates that CO_3^{2-} in the sample layer is well arranged, highly symmetrical and well crystallized. The bending vibration peak of O-H in interlayer water appears at 1650 cm^{-1} , and C-O stretching vibration peak appears at 792 cm^{-1} . After modification, two sharp peaks appeared at 2842 and 2919 cm^{-1} , were assigned to -CH₃ and -CH₂ vibration peaks. -NH₂ vibration peak appeared at 1467 cm^{-1} . At 1222 and 1134 cm^{-1} obvious S=O vibration peak was appeared. The peak at 990 cm^{-1} was assigned to M-Si-O stretching vibration, which was in accordance with the literature report [8]. Combined with XRD results, it can be concluded that the surface of HT has been covered by KH550. Therefore, the surface of HT sample was effectively modified.

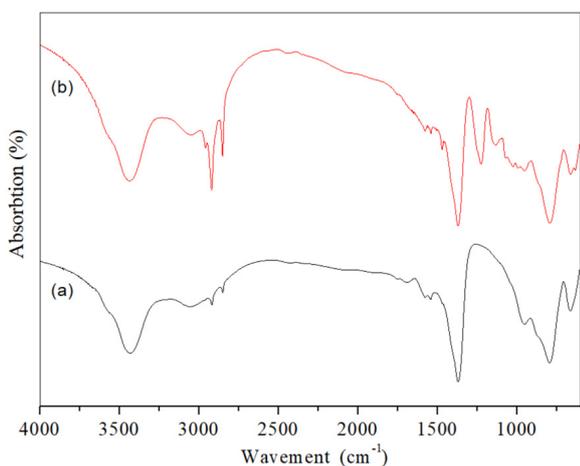


Fig. 3. IR spectra of the HT layered materials prepared before and after modification (a): before modification; (b): after modification

3.3 Thermo stability of HT

Fig.4 shows the TG curve of HT. It can be seen from Fig.4 that the weight loss of HT can be divided into two process. In the first process ($< 250\text{ }^\circ\text{C}$), HT loses the physically adsorbed water on the crystal surface and the interlayer crystal water. The weight loss rate is about 17%. In the second process ($250\text{--}500\text{ }^\circ\text{C}$), HT loses the

hydroxyl group and some interlayer anions on the laminar, and the total weight loss rate is about 54%. When the temperature is higher than $500\text{ }^\circ\text{C}$, the decomposition process of HT is basically completed, which is consistent with the results reported in the literature. The relating TGA data of HT was shown in table 1.

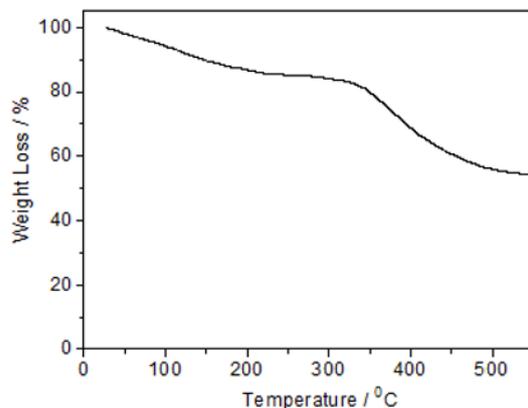


Fig. 4. TG curve of HT

Table 1. TGA data of HT

Sample	Temperature (°C)	Weight Loss (%)
HT	< 250	17
	$250\sim 500$	37
	$25\sim 500$	54

3.4 Effect of HT addition amount

Fig. 5 shows DSC curves of pure PLA and HT/PLA composites prepared by different HT addition. Table 2 shows the glass transition temperature, crystallization peak temperature and melting peak temperature corresponding to each DSC curve. It can be seen from figure 5 and table 2 that the glass transition temperature and crystallization temperature of HT/PLA composite decrease and the melting temperature increases after the HT/PLA composite is prepared compared with pure PLA.

Table 2 Glass transition temperature, crystallization peak temperature and melting peak temperature of HT/PLA

HT additon content	$T_g / ^\circ\text{C}$	$T_c / ^\circ\text{C}$	$T_m / ^\circ\text{C}$
0%	54.23	90.06	164.98
0.5%	51.15	90.04	165.58
1%	52.32	90.02	165.20
2%	51.53	89.76	165.49
4%	51.83	89.84	165.14
10%	51.18	89.28	165.56

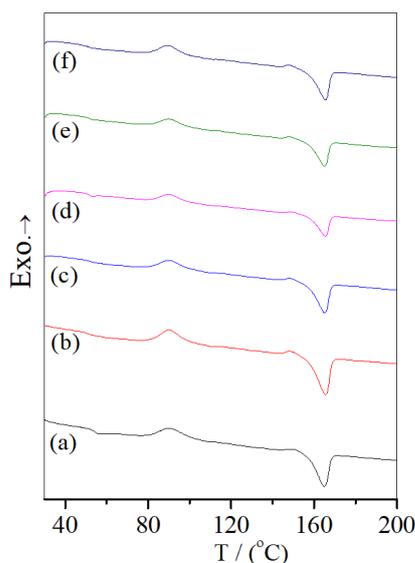


Fig. 5. DSC curves of pure PLA and HT/PLA composites prepared by different HT addition (a): Pure PLA; (b) 0.5%HT/PLA; (c): 1%HT/PLA; (d): 2%HT/PLA; (e): 4%HT/PLA; (f): 10%HT/PLA

Fig. 6 is the curve of the relationship between the addition amount and the change of temperature. It can be seen from Fig. 6 that in the range of 0.5%~10%, the glass transition temperature, crystallization peak temperature and melting peak temperature of HT / PLA composite have no obvious rules with the increase of addition, and the temperature change is higher when the addition is 0.5%, 2% and 10%.

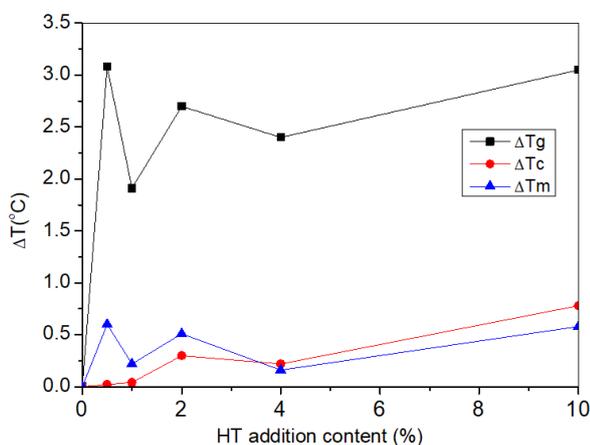


Fig. 6. The curve of the relationship between the addition amount and the change of temperature

3.5 Effect of HT modification

Table 3 shows the data of glass transition temperature, crystallization peak temperature and melting peak temperature of HT/PLA and KH-550-HT/PLA. It can be seen from table 3 that the glass transition temperature and melting temperature of HT / PLA composites before modification decrease, while the crystallization temperature increases. After modification the HT/PLA sample has different situation with the one before modification. The temperature is even lower for glass

transition temperature and melting temperature, while higher temperature for crystallization peak.

Table 3. Data of glass transition temperature, crystallization peak temperature and melting peak temperature of sample

Sample	T _g /°C	T _c /°C	T _m /°C
HT/PLA	52.32	90.02	165.20
KH550-HT/PLA	51.45	92.51	164.86

4 Conclusions

A series of HT layered materials were prepared by coprecipitation. The structure and thermal stability of the layered materials were characterized by XRD, IR and TGA. The following conclusions were obtained.

(1) XRD results show that HT layered materials prepared by coprecipitation have typical HT structure, and have good crystalline.

(2) IR results show that the CO₃²⁻ among the layers of HT samples is arranged in order and symmetrical. After the surface modification of KH550, a large number of -OH and O-Si groups are appeared on the PLA surface.

(3) TG results show that the thermal stability of HT samples is good. The weight loss process can be divided into two processes.

(4) DSC results show that the glass transition temperature and crystallization temperature of HT / PLA composites are lower than those of pure PLA, and the melting temperature increases. After modification, HT/PLA has different effect as one before modification.

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