Preparation and properties of hydrotalcite inorganic filler / polylactic acid composites

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Abstract. Hydrotalcite inorganic fillers with different metal ratios were synthesized by coprecipitation method and hydrothermal method. The hydrotalcite inorganic fillers / polylactic acid composites (HT/PLA) were prepared by melt blending method. The mechanical properties, flame retardancy and thermal properties of the composites were investigated. The results show that HT inorganic filler was successfully prepared by coprecipitation method and it had typical HT structure. Compared with pure PLA, the impact strength and bending strength of HT/PLA composites decreased. The tensile strength, elongation at break, bending strength and tensile modulus of elasticity of the self-made M-Mg/Al-HT/PLA composite were better than those of the purchased C-Mg/Al-HT/PLA composite. The oxygen index of HT/PLA composites increased obviously, and the oxygen index of HT/PLA composites increased with the increase of the amount of HT. Different kinds of HT/PLA composites have different flame retardancy, and the order is Cu/Mg/Al-HT/PLA>Co/Mg/Al-HT/PLA>Ni/Mg/Al-HT/PLA>Mg/Al-HT/PLA>Zn/Mg/Al-HT/PLA. The plasticity of HT/PLA composite is higher than that of pure PLA, and its thermal stability is better.

1. Introduction

Polylactic acid (PLA) is a biodegradable polymer material. Poly (lactic acid) has a wide range of sources. It is usually prepared by the condensation of lactic acid from starch fermentation products. PLA has good biodegradability, compatibility and bioabsorbability. It is harmless to human body and non-toxic to the environment. CO2 is the degradation product of PLA. It can be converted into raw material of PLA through photosynthesis. This meets the requirements of sustainable development of nature and human society [1]. In the field of 3D printing, PLA has attracted more and more attention. PLA is limited in practical application due to its brittleness. PLA was toughened by adding inorganic fillers such as montmorillonite, carbon nanotubes, talc, titanium dioxide, silicon dioxide, calcium carbonate [2]. Wang Ming [3] prepared PLA/CNT composites by different methods. The results showed that the composites had high conductivity, ultra-low permeability threshold and excellent electromagnetic shielding performance. Gao Dasheng [4] prepared Nano montmorillonite modified polyactic acid ultrafiltration membrane by phase inversion method. The results showed that the hydrophilicity of the composite membrane surface was obviously improved, and the porosity and average pore size were obviously increased with the addition of nano montmorillonite. Yin Xing [5] added nano-TiO2 into PLA to prepare new biodegradable antibacterial packaging materials. The results showed that nano-TiO2/PLA antibacterial film had excellent antibacterial effect, and could be used in the packaging of food, medicine and other products.
In view of the disadvantage of PLA and the structure of hydrotalcite (HT) materials, the HT inorganic fillers were dispersed into PLA matrix by melt blending method to obtain HT inorganic fillers/PLA composites, and their thermal properties, mechanical properties and flame retardancy were studied, so as to obtain excellent 3D printing materials and better printing effect of PLA materials in practical application.

2. Experimental

2.1. Preparation and modification of HT inorganic filler

HT inorganic fillers with different metal ratios were synthesized by coprecipitation method: nitrate solution A was prepared according to a certain stoichiometric ratio, and alkali solution B was prepared with a certain amount of NaOH and Na$_2$CO$_3$ ([$\text{OH}^-$] = 1.6 [$\text{[M}^{2+}\text{]}$] + [$\text{[M}^{3+}\text{]}$], $[\text{CO}_3^{2-}]$ = 2.0 [$\text{[M}^{3+}\text{]}$]). The salt solution A was added into the alkali solution B under high speed stirring, and the pH value was controlled to be around 9. The slurry C was transferred into a three-port flask, and was then stirred vigorously. The mixture was crystallized at certain temperature for a certain time. The mixture was filtered and washed to neutral with distilled water. A certain amount of distilled water was added to the filter cake and KH550 was added. The mixture was filtered and dried at 70 ℃ in an oven for 24h. The obtained sample was ground.

2.2. Preparation of HT/PLA composites

A certain amount of HT inorganic filler was added into the dried PLA according to the amount of 0.5%, 1%, 2%, 4% and 10% (by wt.) by melt blending method. The sample was then mixed evenly and added into the twin-screw extruder for blending. The temperature of each section from the barrel to the head of the extruder was 160 ℃, 180 ℃, 185 ℃, 185 ℃, 180 ℃ and 175 ℃ with the screw speed of 20 rad/min. After extrusion and granulation, HT/PLA composites with different contents were prepared.

2.3. Characterization and test of HT/PLA composite

HT/PLA composites prepared by melt blending were molded into standard splines by injection molding machine. The HT/PLA samples were pressed with a plate vulcanizer with a thickness of 1 mm, and then was sliced into standard strips with a slicer. The size of each spline was measured, the specific position was marked before the experiment. X-ray diffraction (XRD) patterns were determined using a Shimadzu 6100X diffractometer equipped with Cu Kα radiation (λ=1.5406 Å) operating with 40 kV and 30 mA. Tensile test was carried out according to GB/T 1040.2-2006, the tensile speed is 10 mm/min. Bending strength was tested according to GB/T 9341-2008, with a speed of 10 mm/min. A side notch with a depth of 1mm for each sample for impact test according to GB/T 1043-1993. The flame retardancy was measured by oxygen index. The sample strips were made into 3 × 13 × 30 mm spline and tested on vertical combustion instrument. Thermal property of the samples was characterized by Shimadzu DSC-60 differential scanning calorimeter. N$_2$ was used as carrier gas. The flow rate was 50 mL/min, the heating rate was 10℃/min, and the temperature range was 30~200 ℃.

3. Results and discussion

3.1. Structure of HT inorganic filler

XRD spectra of HT inorganic fillers prepared by different kinds of metals were shown in Figure 1. It can be seen from figure 1 that all the samples show diffraction peaks at diffraction angle around 11.5 °, 23.3 °, 34.3 °, 38.9 °, 47.0 °, 61.5 ° and 63.6 °. These peaks were typical characteristic diffraction peaks of HT. The sharp peak and stable baseline indicated that the samples were well crystallized. Among the samples, Mg/Al-HT inorganic filler had the sharpest peak type and the highest crystallinity.
Thus, it can be concluded that HT inorganic fillers containing different metal species (Zn, Ni, Cu, Co) could be successfully synthesized under the above conditions.

![XRD spectra of HT inorganic fillers prepared by different kinds of metal.](image)

3.2. Properties of HT/PLA composites

3.2.1 Mechanical properties

Table 1. Mechanical properties of HT/PLA composites prepared with different addition.

| HT addition (wt.%) | Tensile strength (MPa) | Elongation at break (%) | Impact strength (KJ/m²) | Bending strength (MPa) |
|--------------------|------------------------|-------------------------|-------------------------|------------------------|
| 0%                 | 36.89                  | 14.73                   | 65.19                   | 68.65                  |
| 0.5%               | 43.46                  | 43.91                   | 50.64                   | 64.68                  |
| 1%                 | 41.51                  | 14.58                   | 38.74                   | 62.90                  |
| 2%                 | 34.35                  | 7.62                    | 32.78                   | 42.28                  |
| 4%                 | 26.61                  | 6.55                    | 13.32                   | 39.83                  |
| 10%                | 20.28                  | 4.89                    | 7.27                    | 32.41                  |

![Diagram of tensile strength and elongation at break of pure PLA and HT/PLA composites.](image)

Table 1 shows the mechanical properties of HT/PLA composites prepared with different additions. The mechanical properties of pure PLA and HT/PLA composites are also shown in figure 2 and figure 3. It can be seen that the impact strength and bending strength of HT/PLA composites prepared by...
adding HT are decreased compared with pure PLA. The results show that the tensile strength and elongation at break of HT/PLA composites increase obviously when the addition amount is 0.5%, the tensile strength is 43.36 MPa and the elongation at break is 43.91%. With the increase of HT content, the mechanical properties of HT/PLA decrease. It can be concluded that the addition of HT improves the fluidity and plasticity, but does not improve the toughness. When the addition amount is 0.5%, the comprehensive performance of HT/PLA is the best.

![Fig. 3. Tensile strength and elongation at break of pure PLA and HT/PLA composites](image)

Table 2 shows the mechanical properties of HT/PLA composites prepared by different types of HT. It can be seen from table 2 that the tensile strength, elongation at break, bending strength and tensile modulus of elasticity of the self-made M-Mg/Al-HT/PLA composite are better than those of the purchased C-Mg/Al-HT/PLA, while the impact strength is weaker. It is indicated that the plasticity of the sample is enhanced. The tensile strength, bending strength and tensile modulus of elasticity of M/Mg/Al-HT/PLA composites prepared by adding other metals M (M= Cu, Zn, Ni, Co) increase significantly. Cu/Mg/Al-HT/PLA composites have the best comprehensive properties.

| HT type       | Tensile strength (MPa) | Elongation at break (%) | Impact strength (KJ/m²) | Bending strength (MPa) |
|---------------|------------------------|-------------------------|-------------------------|------------------------|
| C-Mg/Al-HT    | 41.51                  | 14.58                   | 38.74                   | 62.90                  |
| M-Mg/Al-HT    | 43.58                  | 16.12                   | 35.32                   | 64.02                  |
| Cu/Mg/Al-HT   | 45.28                  | 20.91                   | 25.70                   | 74.57                  |
| Zn/Mg/Al-HT   | 44.24                  | 12.88                   | 17.65                   | 76.38                  |
| Ni/Mg/Al-HT   | 44.75                  | 17.25                   | 23.30                   | 73.75                  |
| Co/Mg/Al-HT   | 44.38                  | 13.52                   | 21.09                   | 75.26                  |

Table 3 shows the test data of mechanical properties of HT/PLA and modified HT/PLA composites. It can be seen that the tensile strength, bending strength and tensile modulus of elasticity of the modified HT/PLA composite are significantly better than those of the unmodified HT/PLA, while the elongation at break and impact strength decrease slightly. It is indicated that the modified material has better plasticity.

| HT type       | Tensile strength (MPa) | Elongation at break (%) | Impact strength (KJ/m²) | Bending strength (MPa) |
|---------------|------------------------|-------------------------|-------------------------|------------------------|
| Mg/Al-HT      | 41.51                  | 14.58                   | 38.74                   | 62.90                  |
| KH550-Mg/Al-HT| 44.054                 | 13.488                  | 31.396                  | 76.190                 |

Table 2. Mechanical properties of HT/PLA composites prepared by different types of HT.

Table 3. Mechanical properties of HT/PLA and modified HT/PLA composites.
3.2.2 Flame retardancy

Table 4. Oxygen index data of pure PLA and HT/PLA composites with different additions

| HT addition | sample       | oxygen index | Change amount |
|-------------|--------------|--------------|---------------|
| 0%          | Pure PLA     | 16.7%        | 0             |
| 0.5%        | Mg/Al-HT/PLA | 17.9%        | 7.19%         |
| 1%          | Mg/Al-HT/PLA | 18.3%        | 9.58%         |
| 2%          | Mg/Al-HT/PLA | 18.9%        | 13.17%        |
| 4%          | Mg/Al-HT/PLA | 19.2%        | 14.97%        |
| 10%         | Mg/Al-HT/PLA | 19.8%        | 18.56%        |

Table 4 shows the oxygen index data of pure PLA and HT/PLA composites with different additions. It can be seen from table 4 that the oxygen index of pure PLA is 16.7%, and its flame retardancy is poor. With the addition of HT, the oxygen index of HT/PLA composites increases obviously, and the oxygen index of HT/PLA composites increases with the increase of the amount of HT layered materials. When the addition amount was 10%, the oxygen index was 19.8, increased by 18.56%.

Table 5. Oxygen index data of HT/PLA composites with different HT

| HT addition | sample       | oxygen index | Change amount |
|-------------|--------------|--------------|---------------|
| 1%          | Mg/Al-HT/PLA | 18.3%        | 9.58%         |
| 1%          | Zn/Mg/Al-HT/PLA | 18.1%    | 8.38%         |
| 1%          | Ni/Mg/Al-HT/PLA | 18.4%    | 10.18%        |
| 1%          | Co/Mg/Al-HT/PLA | 18.5%    | 10.78%        |
| 1%          | Cu/Mg/Al-HT/PLA | 19.2%    | 14.97%        |

Table 5 shows the oxygen index data of HT/PLA composites prepared by different kinds of HT. It can be seen that the flame retardant properties of HT/PLA composites prepared by different HT are different. Oxygen index of 1% Cu/Mg/Al-HT/PLA composite is 19.2%, which increases by 14.97%. The flame retardant sequence of the flame retardant is as follows: Cu/Mg/Al-HT/PLA>Co/Mg/Al-HT/PLA>Ni/Mg/Al-HT/PLA>Mg/Al-HT/PLA>Zn/Mg/Al-HT/PLA.

Table 6. Oxygen index data of pure PLA and HT/PLA composites

| HT addition | sample       | oxygen index | Change amount |
|-------------|--------------|--------------|---------------|
| 1%          | Mg/Al-HT/PLA | 18.3%        | 9.58%         |
| 1%          | KH550-Mg/Al-HT/PLA | 18.1% | 8.38%         |

Table 6 shows the oxygen index data of HT/PLA composites before and after modification. It can be seen from the table that there is no obvious change in the flame retardancy of HT/PLA composites before and after modification, indicating that the modification of KH550 has no obvious effect on the flame retardancy of the samples.

3.2.3 Thermal property

Figure 4 shows the DSC curves of HT/PLA composites with different HT content. It can be seen from Figure 4 that compared with pure PLA, the glass transition temperature and crystallization temperature of HT/PLA composites decrease, while the melting temperature increases after preparation. It shows that the plasticity of HT/PLA composite is higher than that of pure PLA, and its thermal property is better.
Table 7 shows the data of glass transition temperature, crystallization peak temperature and melting peak temperature corresponding to each DSC curve. It can be seen from table 7 that compared with pure PLA, the glass transition temperature and melting temperature of HT/PLA composites decrease, while the crystallization temperature increases after the preparation of HT/PLA composites. The highest crystallization temperature of Ni/Mg/Al-HT/PLA composite is 94.49 ℃. The results show that the glass transition temperature of HT/PLA composites with transition metal addition is significantly lower than that of pure PLA, indicating that the plasticity of HT/PLA composites is significantly improved. The order of glass transition temperature is PLA>Mg/Al-HT/PLA>Ni/Mg/Al-HT/PLA>Co/Mg/Al-HT/PLA>Zn/Mg/Al-HT/PLA>Cu/Mg/Al-HT/PLA.

4. Conclusions
HT inorganic filler was successfully prepared by coprecipitation method. XRD results show that HT has typical HT structure. Compared with pure PLA, the impact strength and bending strength of HT/PLA composites decrease. The tensile strength, elongation at break, bending strength and tensile modulus of elasticity of the self-made M-Mg/Al-HT/PLA composite are better than those of the purchased C-Mg/Al-HT/PLA composite. The oxygen index of HT/PLA composites increases obviously, and the oxygen index of HT/PLA composites increases with the increase of the amount of HT. Different kinds of HT/PLA composites have different flame retardancy, and the order of their flame retardancy is Cu/Mg/Al-HT/PLA>Co/Mg/Al-HT/PLA> Ni/Mg/Al-HT/PLA>Mg/Al-HT/PLA>Zn/Mg/Al-HT/PLA. The plasticity of HT/PLA composite is higher than that of pure PLA, and its thermal property is better.

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