Fused Deposition Modeling of Montmorillonite Modified Poly (Lactic Acid)/Sunflower Seed Husk Composites

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Abstracts: This work presents the fused deposition modelling of Poly (lactic acid)/sunflower seed husk/montmorillonite (PLA/SSH/MMT) composites filaments. The SSH was treated with NaOH followed by silane. The rheological behavior, thermal stability and the tensile properties were determined. The results showed that the onset temperature at the maximum degradation rate reached to the highest at 5 wt% SSH and 15 wt% MMT. The tensile strength was enhanced to 45.8 MPa by incorporation of 15wt% MMT. The utilization of FDM and SSH reduced the cost of PLA filament by about 35%, and make a good using of the wastes.

1. Introduction

The environmental preservation and energy crisis have created a growing interest in research field to use natural products and biomass surpluses as fillers in polymer matrices [1]. Poly (lactic acid) (PLA) is a biodegradable and recyclable thermoplastic along with a good biocompatibility and processability [2]. It has been used extensively as filaments materials on Fused Deposition Modeling (FDM) technology. However, the slow degradation rate, high cost and hydrophobicity have limited its use in some fields [3].

Sunflowers are cultivated in all regions worldwide to obtain sunflower seed [4], which is extremely popular for its delicious taste. Sunflower seed husks (SSH) are the byproduct produced during sunflower seed production [4]. SSH were often discarded as waste or fuel [5], and a few of them were used as absorbent [6] and used to make particleboard [7]. Recently, SSH was successfully used to fabricate wood-polymer composites with polypropylene (PP) [4], indicating which has a potential to be composed with PLA.

MMT is a type of nanoparticle, which has a high performance in terms of the aspect ratio and specific surface area [8]. A small amount of MMT can improve the physical properties of polymers [8]. Meng et al. [9] found that MMT particles improved the thermal stability of the PLA/clay/wood composites by about 10 °C. Chen et al. [10] found that the incorporation of OMMT resulted a more uniform, more closely and orderly arranged pore inside the plant fiber foam.

The aim of this study was to FDM the relatively cheap PLA/SSH/MMT composite filaments. The main works involved: investigating the melting flow index of the composites; the thermal stability and mechanical properties of composites and characterizing the microstructure of the fractured surface.
2. Experimental and Characterization Methods

2.1. Materials and Preparation

The used Poly (lactic acid) (PLA) powder was supplied by Nature Works LLC (USA) with the trade name 2002D, and had a density of 1.24 g/cm$^3$. The organo-montmorillonite (MMT) was purchased from Haosheng LLC (China), with an average dimension of 25 nm. The Sunflower seed husks (SSH) were collected from the discards of sunflower seed food. Before being further used, the MS were cleaned, ground into powders and sifted using a 300-mesh screen. Then the powders were modified with 5 wt% concentration of NaOH and 2 wt% concentration of a KH550 solution with a pH of 3.5-4.

The SSH and MMT with the PLA powders were mixing together for 24 hours to obtain the composited powder. Then the powders were introduced to a single screw extruder to extrude filaments with a diameter of 1.75±0.3 mm. The formulations of the PLA-SSH-MMT composites filaments are listed in table 1. Finally, the filaments were applied on a commercial fused FDM machine to manufacture four dumbbell shaped tensile samples with a dimension of 63.5 × 9.53 × 3.2 mm based on the ASTM-638 standard.

Table 1. The formulations of the PLA-SSH-MMT composites.

| Samples identification | PLA (wt%) | SSH (wt%) | MMT (wt%) |
|------------------------|-----------|-----------|-----------|
| S1                     | 95        | 5 (untreated) | -         |
| S2                     | 95        | 5         | -         |
| S3                     | 90        | 5         | 5         |
| S4                     | 85        | 5         | 15        |
| S5                     | 95        | 5         | 20        |
| S6                     | 90        | 10        | 5         |
| S7                     | 85        | 15        | 5         |

2.2. Characterization Techniques

Based on the standard ASTM D1238-73, the rheological behaviors of composites were carried out, and the Melt Flow Index (MFI) of composites was recorded with a melt flow tester (Tiansucablication, Shenzhen, China). The thermal stability of the composites was determined using a thermogravimetric (TG) analyzer (Labsys Evolution, Setaram, France). The tensile properties of samples were carried out using a Universal Testing Machine (Germany Zwick Roell, 2KN) with a test rate of 0.5 mm/min and preload of 0.1 N. Morphological studies were characterized using a Scanning Electron Microscopy (SEM, VEGA3 TESCAN). Prior to the scanning, all the fracture surfaces were gold coated.

3. Results and Discussion

3.1. The Thermal Stability of PLA/SSH/MMT Composites

Figure 1 shows the thermal stability of the PLA/SSH/MMT composites. It can be seen that not only the SSH, but also the MMT had a dramatic effect on the thermal stability of their composites. The temperature at maximum degradation rate (Tmax) of S2 (353.3 °C) is much higher than that of S1 (329.5 °C), showing that the interfacial compatibility had been improved through the NaOH/silane treatment. With the increasing of SSH, the Tmax of composites decreases continually from 344.3 °C at 5 wt% SSH (S3) to 326.2 °C at 15 wt% SSH (S7). A suitable amount of SSH acted as nucleating agent of the PLA and prompted the rearrangement and repacking of the PLA molecule chains. However, a redundant SSH particles was easy to aggregate and interfered the continuity of the PLA matrix. The incorporation of the MMT increases the Tmax of composites firstly to 353.9 °C (S4), and then decreases it to 331.4 °C (S5). MMT functioned as nucleating agent which can improve the thermal stability. However, with the increasing of the MMT content, the agglomerated silicate layers showed an advantage over the agent effect.
3.2. Rheological Behavior

Figure 2 shows the rheological behavior of PLA/SSH/MMT composites. It can be observed that all the melt flow index (MFI) of composites with treated SSH increase from 6.15 g/10 min (S1) to 5.83-11.16 g/10 min (S2, S6 and S7) when compared to that of composites with treated SSH. The result showed that the interfacial compatibility between SSH and the PLA matrix was improved due to the removing of impurities and the bridge linking of SSH and PLA. However, the MFI is decreasing with the increase of the SSH content. The adding of the SSH particles might interfere the continuity of the PLA and slow down the heat transfer. More SSH particles had more tendency to aggregate, leading to non-uniform melting and flowing of the polymer. The incorporation of MMT has a strongly fluctuating effect on MFI. The MFI increases from 13.83 g/10 min (S3) to 21.44 g/10 min (S4), following by a drop to 11.16 g/10 min (S5). This result indicated that a suitable amount of MMT was able to improve the MFI by acting as a nucleating agent.

3.3. The Tensile Properties

Table 2 shows the tensile values of the PLA/SSH/MMT composites. The tensile strength of composites with treated SSH increase dramatically from 21.11 MPa (S1) to 40 MPa (S2) when compared to that of composites with treated SSH. The result showed that the interfacial compatibility between treated SSH and the PLA matrix was improved, leading to a well force transfer. With the increasing of the content of SSH, the tensile strength decreases steadily to 19.15 MPa (S7) at 15 wt% SSH. A redundant SSH particles in the PLA matrix would interfere with the continuity of the PLA and affect the force transfer, leading to a drop of the strength. Incorporation of the MMT enhanced the tensile property of the PLA/SSH/MMT composites, which rockets to the peak of 45.8 MPa at 15 wt% MMT (S4), and then gives a small drop to 37.35 MPa at 20 wt% MMT (S5). The material MMT has a high strength and hardness. When MMT was in the PLA matrix, it can absorb some of the energy and stress applied to the PLA [10]. The reduction of the tensile strength can be ascribed to the agglomeration of the MMT. The tensile elongation performs a same tendency with the tensile strength.

4. Conclusions

The present work showed that FDM was successfully used on making a relatively cheap PLA/SSH/MMT composite filament with useful thermal and mechanical properties. The results showed: (1) the increasing of the SSH (5, 10 and 15 wt%) decreased the thermal and tensile properties of the composites; (2) the thermal and tensile properties of the composites increased dramatically when the MMT (5, 15 and 20 wt%) content was of 15 wt%. The utilization of FDM and SSH cut down the cost of PLA filament by about 35%, and make a good using of the wastes.
Figure 2. The melt flow index of the PLA/SSH/MMT composites.

Table 2. The tensile properties of the PLA/SSH/MMT composites.

| Samples | Tensile strength (MPa) | Tensile elongation (%) |
|---------|------------------------|------------------------|
| S1      | 21.1±0.69              | 1.85±0.04              |
| S2      | 40±0.96                | 5.19±0.28              |
| S3      | 17.56±0.4              | 3.04±0.12              |
| S4      | 45.8±1.2               | 4.77±0.08              |
| S5      | 37.35±0.46             | 3.73±0.14              |
| S6      | 33.18±0.9              | 3.05±0.27              |
| S7      | 19.15±0.31             | 4.47±0.16              |

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