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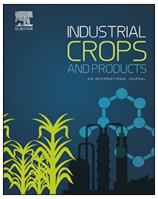

Fabrication of flexible wood flour/thermoplastic polyurethane elastomer composites using fused deposition molding

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ABSTRACT

Using three-dimensional (3D) printing technology, the wood flour (WF)/thermoplastic polyurethane (TPU) composites with different contents of WF and different modifiers were prepared by TPU/WF composite filaments. These filaments were fabricated through the melt-blending and melt-extrusion of TPU and WF. The mechanical properties, microtopography and chemical structures of the 3D printing products were examined by the mechanical testing machine, scanning electron microscopy (SEM), Fourier transformed infrared (FTIR), X-ray photoelectron spectroscopy (XPS), and rheological property tester. The results showed that the tear elongation decreased gradually as the WF content increased, and the tensile strength firstly decreased and then increased. SEM and FTIR results revealed a good compatibility between TPU and WF after the modification with EPDM-g-MAH. The XPS results indicated that the diphenylmethyl propane diisocyanate (MDI) and EPDM-g-MAH modification positively affected the interfacial bonding property between WF and TPU. The examination of rheological properties of the TPU/WF composites indicated that the storage modulus, loss modulus and complex viscosity were significantly increased after the modification with EPDM-g-MAH. The tensile properties of the TPU/WF composites were also greatly increased after the modification with EPDM-g-MAH.

1. Introduction

Three dimensional (3D) printing is to use the principle of “layered manufacturing, and layer by layer” to achieve the additive manufacturing, and the three-dimensional physical model can be accurately built by computer-aided design (Yang et al., 2016; Wang et al., 2017). Fused deposition molding (FDM) is widely used in 3D printing and thermoplastic filaments are usually utilized as printing material to print out products through the method of layer by layer (Wang et al., 2017; Yang et al., 2016a, b). The filaments are melt at a hot nozzle and extruded to build 3D physical models (LuizFerreira et al., 2017; Melnikova et al., 2014). The FDM working schematic is shown in Fig. 1.

Up to date, there are many materials that can be applied to FDM, such as acrylonitrile-butadiene-styrene copolymer (ABS), polylactic acid (PLA), thermoplastic polyurethane (TPU), polycarbonate (PC), nylon, etc. (Chen et al., 2017; Stansbury and Idacavage, 2016; Yu et al., 2017; Kim et al., 2017). However, most of the materials mentioned above, such as PLA and ABS, have poor precision and low toughness, making them difficult to produce soft products with user-defined geometries and sizes. (Chen et al., 2017; Chi et al., 2017; Yang et al., 2016a, b).

Among these materials, TPU is a kind of polyurethane 3D printing elastomer material with good abrasion resistance, excellent mechanical properties and lightweight (Zo et al., 2014; El-Shekeil et al., 2012; Yang et al., 2016a, b; Miller et al., 2017;). TPU’s main components are diisocyanates, polyols and chain extender (Miller et al., 2017; Yao et al., 2014). TPU is a linear block copolymer containing hard and soft segments (Miller et al., 2017; Zhong et al., 2003; Cho et al., 2017), and its chemical reaction equation is shown in Fig. 2. Due to its complexity and flexibility of the TPU, it is possible to be made any complex structure of a soft matter product, which can solve the problems of precision and brittleness of most traditional products (Bates et al., 2016; Shen et al., 2016; Yang et al., 2016a, b; Miller et al., 2017; Chen et al., 2017). In the 3D printing, TPU has various applications, such as such as printing shoes, helmets, textiles, tissue engineering, etc. (Yang et al., 2016a, b; Chen et al., 2017; Lee and Hong, 2016).

However, the cost of TPU's production is high, which limits its application. Therefore, the adding of the low-cost natural fiber is one of the effective ways to make a low cost, biodegradable, and ecofriendly material (Haghighatnia et al., 2017; El-Shekeil et al., 2014a, b). Wood flour (WF) is a kind of biomass material that is environment-friendly, and plenty of sources with low cost, making it a great choice as a filler.

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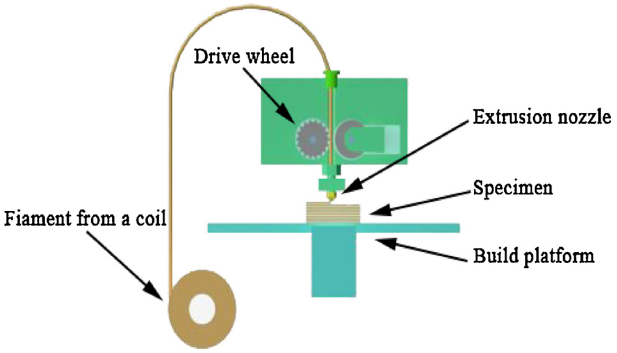

Fig. 1. FDM working schematic.

WF/TPU composite filaments were prepared by the melt-blending and melt-extrusion for 3D printing. The preparation of WF/TPU composite filaments can increase the utilization of waste wood flour, reduce the share of expensive TPU, and make the 3D printing products owning flexibility and natural wood sense. However, with the addition of WF, the interfacial adhesion between WF and TPU could be poor, decreasing the flexibility of composites (Yang et al., 2016a, b). In order to obtain a well-flexible 3D printing TPU/WF composite, it is important to use the appropriate WF content to improve the flexibility of TPU/WF composites. There have been numerous reports about fiber filling TPU, in which, most researchers focused on the investigations of the fiber reinforce TPU materials, and the anti-aging and heat resistance of materials (Akbarian et al., 2008; Zo et al., 2014; El-Shekeil et al., 2012; Vajrasthira et al., 2003; El-Shekeil et al., 2014a, b; Menes et al., 2012; Sánchez-Adsuar et al., 2003). In the literature review, no study has been found to fabricate the 3D printing of flexible TPU/WF composites by adding such a large amount of WF. To compensate the flexibility of TPU/fiber composites, the addition of an effective modifier to improve the interfacial adhesion is one of the practical and easy methods (Alves et al., 2009; Li et al., 2015; Wang et al., 2005; Wang and Luo, 2004; Jaisankar and Radhakrishnan, 2000).

The aim of this work is to prepare 3D printing products and explore the effect of the different WF contents and different modifiers on TPU/WF composite properties. In this study, material properties were examined using the different polymer characterization techniques, namely, the tensile testing, scanning electron microscopy (SEM), Fourier transformed infrared (FTIR) examination, X-ray photoelectron spectroscopy (XPS), and rheological property testing.

2. Materials and methods

2.1. Materials

The Elastollan TPU C95A, EPDM-g-MAH and POE-g-MAH were purchased from Deansheng Plastic Company, Harbin, China. The characteristics of TPU are shown in Table 1. The poplar wood flour, with a size of 150 μm (100 mesh), was purchased from Lingshou County Mineral Processing Plant, Harbin, China. The chemical compositions of WF are shown in Table 2. The Polyethylene glycol 6000 (PEG 6000), chitosan and diphenylmethyl propane diisocyanate (MDI) were purchased from Yongchang Reagent Company, China.

Table 1
Characteristics of TPU.

Density (g/cm^3)	Tensile stress (MPa)	Melting temperature (°C)	Elongation (%)	Hardness(A)
1.24	50	200	550	95

2.2. Composite preparation

TPU and WF were dried in an oven at 103 °C for 12 h; EPDM-g-MAH and POE-g-MAH were dried at 80 °C for 2 h. After that, they were mixed with different TPU/WF weight ratios (Table 3) to explore the effect of different WF contents on mechanical properties of composites. In addition, with a fixed TPU/WF ratio, different modifiers were added to investigate the effect of modifier. Types and contents of different modifiers are shown in Table 4.

The process of mixture was completed using a high-speed mixer for ten minutes, and then the mixture was poured into the twin-screw extruder (JSH30/SJ45) at 190 °C (die temperature) with a screw speed of 20 RPM, followed by natural cooling and granulation. The composite pellets were molded into composite filaments using a high precision 3D printing consumable extrusion. The diameter of the composite filaments was controlled in the range of 1.75 ± 0.1 mm. The composite filaments were then naturally cooled for 24 h, and the FDM 3D printer was used for the specimen printing. The processing parameters for the high precision 3D printing consumable extrusion molding procedure are listed in Table 5.

Using the Pro/Engineer software, the standard specimens were drawn for the material performance tests. The standard specimens were saved as .stl format files and imported into the slicing software of Cura to set the print parameter and saved the file for the .gcode into FDM printer. At the same time, the WF/TPU composite filaments were placed to the FDM printer wire feeding device. After turning the printer on, the specimen was piled up on the worktable following the movement of the hot nozzle. Finally, the standard specimens were fabricated and ready for the property tests.

2.3. Characterization techniques

2.3.1. Machanical properties

Tensile tests were carried out by an electronic universal mechanical testing machine (RGT-20A) according to DIN 53504. The tests were performed at room temperature using a crosshead speed of 500 mm/min.

2.3.2. SEM

The fracture surface of the samples was analyzed with the JSM-7500 scanning electron microscope and operated at 5 kV. The fracture surfaces of the samples were prepared by cryogenic fracturing in liquid nitrogen and coated with gold.

2.3.3. FTIR

The FTIR spectroscopic analysis was performed using a Nicolet 6700

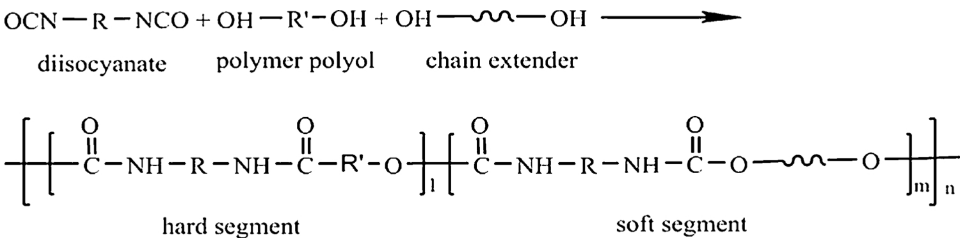

Fig. 2. Thermoplastic polyurethane chemical reaction.