3D-Printed Polymer Composites Based upon Low Melting Point Alloys Filled into Polylactic Acid

Junfeng Liu¹,², Zhen Li²*, Yuan Yu¹*, and Pengfei Wang²*

¹ College of Mechanical and Electrical Engineering, Beijing University of Chemical Technology, Beijing 100029, China
² Qian Xuesen Laboratory of Space Technology, China Academy of Space Technology, Beijing 100094, China
Email: yuyuanjd@263.net (Yuan Yu); lizhen@qxslab.cn (Zhen Li); wangpengfei@qxslab.cn (Pengfei Wang)

Abstract. In this study, advanced low melting point alloys (LMPA)/polymer compositced wires for fused deposition modelling (FDM) processes were developed. The Polylactic Acid (PLA) powder was mixed with LMPA powder and multi walled carbon nanotubes (MWCNTS). The liquid state of LMPA will not hinder the processability of polymer composites when the composites were extruded out as wires. Thus, the compositced wires can be optimally fabricated with high stabilities as well as large quantities. The prepared PLA/LMPA/MWCNTS wires could be further dedicated to print with 3-dimensional (3D) structures. Additionally, the tensile modulus of the printed composites was three times as higher as that of the pure PLA. The tensile modulus of composites is temperature-dependant, specially it would decrease more significantly at the melting point of LMPA. The study on the FDM of the advanced compositced-wires would inspire a new branch in the additive manufacturing. The material could also be potentially applied in variable stiffness components, electromagnetic shielding and other applications.

Keywords: LMPA; 3D printing; PLA; mechanical property

1. Introduction
Additive manufacturing has been at the forefront of manufacturing research for the past couple decades. As a rapidly developed technology, 3D printing technology has a broad application prospect in medical industry, aerospace, electronic circuit devices and so on. There is a wide range of 3D printing technologies and processes such as FDM [1], direct ink writing (DIW) [2], selective laser sintering (SLS) [3], inkjet printing [4], stereolithography (SLA) [5]. Among of them, FDM is widely adopted by printing melting wires of thermoplastic polymers (such as Acrylonitrile Butadiene Styrene (ABS) and PLA) through a hot nozzle followed by natural cooling and solidification to build structures [6].

At present, printing process and materials are the two major factors restricting the development of 3D printing technology. The printing of polymer materials is a current research hotspot, in which the plastics take an advantage of low melting point, good thermoplasticity, excellent fluidity and good forming. In contrast, the printing of metal materials is obstructed by their long-time cost and poor forming quality. Referring to the printing of the mixture of metal materials and non-metal materials, the huge difference in melting point and the poor compatibility between them is the key problem. [7].

LMPA as filler is at liquid state when the temperature is higher than its melting point (not higher
than 300 °C) [8], in which the liquid state of the LMPA will determine the excellent printing of the mixture of PLA/LMPA. In addition, the LMPA as a rigid particle filler can toughen the composites below its melting point.

Herein, the composited wires were extruded with the mixture of PLA/LMPA/MWCNT and were further adopted in the printing process. Tensile modulus of the printed composites was characterized by dynamic thermomechanical analysis (DMA), as well as the heat absorption of the composite was analyzed with the differential scanning calorimetry (DSC). Microscopic appearances of the printed composites and the distribution of LMPA were finally observed by Scanning electron microscope (SEM).

2. Experimental

2.1. Materials
The adopted LMPA was tin-bismuth alloy (Sn42%Bi58%), whose melting point was 138 °C and obtained from Beijing Zhongke yauo New Material Technology Co. Ltd. Beijing, China. The PLA was obtained from Dongguan Huachuang Plastics Co., Ltd. Dongguan, China. The MWCNTS was purchased from Shenzhen Suiheng Technology Co., Ltd. Shenzhen, China. whose nominal diameter was 15 μm and the length was 15 ~ 30 μm.

2.2. Fabrication of the PLA/LMPA/MWCNT Composites Wires
The specific experimental process is depicted in figure 1: (1) PLA powder and MWCNTS powder with the weight ratios of 100:1 was dispersed in dichloromethane by ultra-sonicating for one hour. (2) LMPA powder with a weight ratio of 10% of PLA powder was added into the solvent, then fully stirred to make the LMPA evenly dispersed. (3) The mixed suspension was dried in an oven at 80 ℃ to remove the dichloromethane and to obtained composites sheets. (4) The prepare composite material was added to a desktop single-screw extruder to produce composite feedstock wires with their diameter of 1.75mm. (5) Printing of the wires into the samples for test or utilization.

![Figure 1](image-url)  
Figure 1. Manufacturing process of the PLA/LMPA/MWCNT composites wires.

2.3. Characterization
SEM (S-3400 N) was used to observe the microstructures. Dynamic thermomechanical analyser (TAQ800) was used to measure and record the relationship between the temperature and the tensile modulus of the composites. The relationship between the temperature and heat absorption and release rate of composites was tested by the method of DSC (STA449F3).

3. Result and Discussion
The extruded wires and the corresponding 3D printed products are as shown in figure 2. It can be seen that
the composites and pure PLA wires can be stably produced with large quantities. The samples are printed successfully by adjusting the parameters of printer, and the mechanical properties and microstructure of the samples are further characterized.

![Figure 2. The filament and printed sample of composites (left) and pure PLA (right).](image)

3.1. Mechanical Property

The relationship between the temperature and tensile modulus of the final printed products was measured by DMA. Figure 3 shows the measured temperature-tensile modulus curve. The tensile modulus of the composite is 2 times higher than that of the pure PLA in the temperature of 0 °C ~ 60 °C. The tensile modulus of both materials decreased significantly when the temperature increases to about 60 °C. At 105 °C ~ 120 °C, the tensile modulus of both materials barely increases. Additionally, it can be seen from figure 4(a) that the increase of tensile modulus of the composites is slightly less than that of pure PLA. The curve of this temperature range is enlarged as shown in figure 4. When the temperature continues to rise to 138 °C, the tensile modulus of the composites decreases faster than that of pure PLA. The local enlargement of this temperature range is shown in figure 4(b).

![Figure 3. DMA analysis result of the printed composites and pure PLA.](image)
3.2. **DSC Analysis of the Printed Composites**

Thermal property of the composites was measured by DSC. The DSC curve for the printed composites is shown in figure 5. According to the diagram, the correlation between the tensile modulus of the composites with the loaded temperatures (figure 4) can be therefore analyzed. A phase transition occurred at about 60 °C corresponds to the glass transition process when the polymer transforms to the high elastic state. The molecular segments in the high elastic state are migratable, resulting in a sharp decrease of the tensile modulus of the material. An endothermic transition with a valley at a temperature of 110 °C was also visually observed, which is associated with the cold crystallization of PLA. Comprehensive consideration with the figure 4(a), the addition of LMPA and MWCNTs can inhibit the cold crystallization behavior of PLA. The decrease of the crystallinity further inhibited the increase of tensile modulus. When further approaching to 160 °C, the melting of PLA behaved an endothermic peak.

![Figure 4](image)

(a) 105 °C ~120 °C  
(b) 138 °C ~145 °C

**Figure 4.** Enlarged graphs derived from figure 3.

![Figure 5](image)

**Figure 5.** DSC analysis result of composites and PLA.

3.3. **Microstructures**

Microscopic appearances of the composites are shown in figure 6. The mechanical properties of the composites in 3.1 were interpreted with the micro-appearances. During the cooling process after the wires were extruded, the surface tension of the LMPA would drive the LMPA agglomerate into spherical particles. There are boundaries and even holes around the dispersed particles, which is resulting from to the poor compatibility between metal and nonmetal materials. The particles would thresh from the matrix to form tiny holes when being external loaded, the defects of the holes and boundaries would absorb the
deformation stress referring to the particle reinforcement. The fracture toughness of the composites was improved as well.

![Fractured surface of the printed composites](image)

**Figure 6.** Fractured surface of the printed composites.

4. Conclusion
A 3D printing technology based on LMPA filled PLA was proposed. The liquid state of LMPA will not hinder the processability of polymer composites when the composites were extruded out as wires. The 3D printing process (FDM) of the mixture of metal and non-metal was realized. When the ratio of PLA, LMPA and MWCNTs is 1:0.1:0.01, the tensile modulus of the printed composites is three times as higher as that of the pure PLA in the temperature range of 0°C ~ 50°C. With the increase of temperature, the mechanical properties of printed products will change more sharply than that of the pure PLA around the melting point of LMPA, which provides a new consideration for the realization of variable stiffness based on LMPA composites.

Reference
[1] Long J, Gholizadeh H, Lu J, et al. 2017 *Curr. Pharm. Des.* 23(3): 433–439.
[2] Yuk H, Zhao X 2018 *Adv. Mater.* 30(6): 1704028.
[3] Jasveer S and Xue J 2018 *IJSRP* 8(4): 7602.
[4] Sochol R.D, Sweet E, Glick C, et al. 2016 *Lab Chip.* 16: 668-678.
[5] Park S H, Yang D Y, Lee K S 2010 Laser Photonics Rev. 3(1-2): 1-11.
[6] Parsons P, Mirotznik M, Pa P, et al. 2015 *Smart Mater. Struct.* 1: 1310-1311.
[7] Zhang G, Liu T, Liu X, et al. 2014 *Int Polym Proc* 29(2): 175-183.
[8] Liu Y, Pu L, Yang Y, et al. 2020 *Mater. Today Adv.* 7: 100101.