Performance Characterization of Composite Powders for 3D Printing

Xiangjun Bi 1,*, Hongjie Zhao 1, Yuanxun Gong 1, Xinghong Zhou 2

1 Aerospace Research Institute of Special Material and Processing Technology, Beijing, China
2 Sichuan Mophene3D Technology Co., Ltd., Chengdu, China

*Corresponding author e-mail: xinghong.zhou@mophene3d.com

Abstract. In order to meet the requirements of wave-absorbing and stealthy functions, it is necessary to develop high performance absorbing structures and special materials. This paper introduces the performance characterization of the powder mixed with acetylene black and nylon. It characterizes the mixed state, rheological property and the thermal conductivity of the material using optical microscope and rheometer, and thermal analyzer. The experimental results show that when the content is 5% and 7%, the result is the higher melt index, the significantly reduced specific heat capacity and the small printing process window. And the SEM images of the printed parts also show relatively loose structures. Therefore, it is recommended that the content of acetylene black composite powder should not exceed 5%.

Keywords: Thermal Performance analysis, Nylon, Performance Characterization.

1. Introduction

Due to the requirements of stealth and electromagnetic shielding, the development and application of high-performance absorbing structures have become a development trend. At present, the miniaturization, efficient absorption and light weight of the structure have been added to the research and development objectives of the absorbing structure, then the original materials or structures cannot meet the requirements of absorbing wave. There are two main reasons for this: one is material. Due to the nature of the material itself, it does not have the efficient electromagnetic wave absorbing capacity per unit size, so the original material scheme is not suitable for the new structure. Another is the constraints of manufacturing methods. An effective absorber not only requires the internal unit to have stable size, structure and absorb electromagnetic waves at a fixed frequency environment, but also can transform the internal unit structure to absorb electromagnetic waves at other frequency bands according to the design of electromagnetic impedance. These two aspects restrict the research and process realization of absorbing structure.

With the rise of additive manufacturing technology, layer upon layer and custom designed printing technology gradually become a new fabricating form of absorbing structure. At present, the thermoplastic material is used as the main base material and the absorbent is mixed to make the material, and then the printing technology is used to make various three-dimensional structures according to the impedance design technology. [1,2,3]
Xiong Yi-Jun and et al.[4] printed the three-layer absorbent with SLS process and mixed powders with carbonyl iron particles and nylon. Experiment results showed that the reflection losses of 5.3GHz and 14.1GHz were mainly concentrated in the bottom and surface layers, and the broadband absorption performance could be obtained by the broadband absorption superposition of the three-layer absorption layer, which was close to the proposed model calculation.

Tian Xiaoyong and others [5,6] prepared the silk material using graphene oxide and PLA material, (the mass fraction of 1%, 2%, 3%, 4%, 5%, graphene), and then printed the absorbing plate. The results showed that real dielectric constant and dielectric constant of the imaginary part were increased with the increase of the content of graphene materials.

Ting Liu and others[7] mixed carbonyl iron oxide powder with PLA powder at mass ratio (1:1) and then prepared 1.75mm diameter wire rods. They printed the absorber tower structure with FDM process, then the reflectivity test showed that vertical reflectivity loss is not more than 10 db in 12 to 18 GHz range. The nylon is mixed with hydroxyl iron oxide in the proportion of 100:70 volume to prepare powders, and the SLS process is used to print the microscopic wave-absorbing structure.[8] The addition of high amount graphite can effectively improve the conductivity and absorbing performance of the material, which is convenient to improve the stealth performance, but the printing material is prone to brittle and difficult to be used as a printing part.[9] In this paper, acetylene black and nylon are used as the main materials to prepare composite powders.

2. Experiment

2.1. Materials

Acetylene black: TIANJIN LIHUAJIN CHEMAICAL INDUSTRY CO.,LTD, Compression ratio:75%.
Nylon: Hunan Farsoon High-Technology Co., Ltd, FS 3300PA.

2.2. Mixed process

- Mix nylon with acetylene black;
- Put into twin screw extruder to mix extruder;
- Crush screening in crushing equipment.

2.3. Printing process

1) Warm to 165 ± 5℃, keep warm for 30min.
2) Print the samples using SLS device.
2.4 The test device

1) Laser particle size analyzer, Microtrac S3500SI. Choose the refractive index reference as nylon.
2) Melt Index Meter, Instron MF20. Temperature 230℃, outflow weight/10s, averaged 5 times.
3) SEM, FEI Nova Nano SEM 450.
4) Differential Scanning Calorimeter, NETZSCH DSC 204 F1, Heating rate 10k/min: -30℃~300℃, cooling rate: -10k/min.
5) Flash thermal conductivity instrument, NETZSCH LFA467 HyperFlash. The sample is made into a circle with a diameter of 25.4mm and a thickness of 2mm. A probe with a diameter of 3.189mm is used to test the thermal conductivity in the vertical direction.

3. Discussion

3.1. Powder particle size measurement

Particle size of powder is an important index affecting SLS process. In general, the diameter of particles is required to be 10–100nm. When the diameter is greater than 100nm, the precision of the molded parts is poor. The particle size of the powder was analyzed and tested by particle size analyzer, as shown in Figure 1. The content of pure PA (raw material) meets the material requirements. However, the diameter of the mixed particles increases with the increase of the content. Especially when the content is 5% and
7%, it is mainly concentrated at about 100nm and most of it is less than 200nm, which is enough to meet the use requirements for the sample with low precision.

![Particle size distribution of composite powder](image1)

**Figure.1** Particle size distribution of composite powder

### 3.2. Melt index measurement

As shown in Figure 2, the melting index increases with the increase of material content. This also indicates that the addition of toner improves the high-temperature fluidity, which meets the basic requirements of SLS printing process.

![Viscosity distribution of composite powder](image2)

**Figure.2** Viscosity distribution of composite powder
3.3. SEM Observation

Figure 3 SEM images of composite powders (10μm)

Figure 3, 4 are SEM photographs of various powders: 3a, 3b and 3c are composite powders, and Figure 4 (a,b) are raw materials. As shown in Fig.3a, b and c, the carbon powder (white color) inside the particle gradually increases with the increase of content, and some pores appear with the increase of content, especially in the compound powder with 7% content (Figure. 4c).
Both of the two raw materials (Figure 4a, b) have obvious surface pores, relatively fluffy particles and low apparent density. It can be seen from Fig. 4b and 4c that the surface of pure nylon powder has many pores, compared with that of 7% composite powder. This also proves that there is no small molecule escaping and the pores content can be significantly reduced by freezing crushing process. Through the comparison of the Figures 3 and Figure 4, it is proved that the compactness and density of composite powder are higher than that of raw material (pure nylon powder). So the composite powder is suitable for SLS printing.

3.4. Thermal conductivity analysis

|                  | Conductivity/(W/(m*K)) | Cp-table/(J/(g*K)) |
|------------------|------------------------|--------------------|
| 0%               | 0.537                  | 2.312              |
| 3%               | 0.451                  | 0.589              |
| 5%               | 0.334                  | 0.38               |
| 7%               | 0.304                  | 0.279              |

It can be seen from Table 1 that the thermal conductivity decreases with the increase of the addition amount, but the change is not large. The specific heat capacity was decreased from 2.312J/(g*K)(pure PA) to 0.589J/(g*K)(3%), which indicates that the specific heat capacity of the material is more sensitive to acetylene black. The specific heat capacities of 3%, 5% and 7% were consistent with the change trend of thermal conductivity: decreasing with the increase of content. Through the above comparison, it shows that although the thermal conductivity of the material does not change obviously, dropping rapidly of the specific heat capacity affects the setting of printing parameters.

3.5. DSC analysis

In the SLS process, the sintering temperature window is located between the initial crystallization temperature and the starting melting temperature. Otherwise, it causes the sintered parts to melt and agglomerate or warping deformation [10]. According to DSC curves of each composite powder, the melting peak width in Figure 5a widens with the addition of charcoal powder. In Figure 5b, the crystallization peak of 3% composite powder moved towards low temperature, while 5% and 7% moved...
towards high temperature. This indicates that the powder with 3% additive amount is beneficial to SLS printing process, while the reduction of window with more than 5% is more demanding for printing process.

![DSC curves](image1)

**Figure. 5 DSC curves**

3.6. **SEM measurement of printed section**

![SEM images](image2)

**Figure. 6 SEM images**

According to the electron microscope photos of the printed samples (Figure 6), it shows that there is no obvious particle state powder on the surface of 3% samples, and the surface adhesion performance is relatively good. The 5% sample surface particles can also bond, and the surface uneven; The 7% sample showed obvious unevenness and the whole particle was obviously unbonded, presenting a state of loose stacking of particles.

4. **Conclusion**

Through the comparison of particle sizes, viscosity and SEM images of powders, it was found that the composite particles with uniform dispersion and concentrated particle size could meet the requirements of SLS printing, but the printing accuracy might be low. Through the characterization of the thermal properties, it was found that the specific heat capacity of the material changed greatly due to the addition of acetylene black (the change of more than 10 times with and without addition), so this indicated that the powder increased significantly with the increase of acetylene black content under the same heat condition. The change of crystallization and melting temperature was also shown in the DSC curves. The printing process window of 5% and 7% composite powders was significantly narrowed, but the fluidity at high temperature became very better. This indicates that the dispersion of acetylene black affects the heat conduction of the material and the aggregation structure of nylon. Although parameters are set by DSC results in printing, the section results of members in Figure 6 show that the printing effect or the mechanical bearing of the parts are not ideal. This causes are when the laser heated the
surface of the powder, powder (7% and 5%) temperatures in thermal conductivity and melt fluidity were rapidly increased. So the melt flow rate and heat conduction ability increase in molten pool at the same time, and it easily agglomerate, deformation or get other problems in the printing process. For these reasons, it is recommended that the special power is no more than 5% acetylene black additives. At the same time, the balance between material cost, absorbing property and mechanical bearing should also be considered in the process of material use. [11]

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