SELECTIVE LASER SINTERING OF POLYAMIDE12 COMPOSITES

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ABSTRACT

This work aims to study the reinforcing effect of short carbon fiber (CF)/polyamide12 and halloysite nanotubes (HNTs)/polyamide12 composites. The influences of reinforcing fillings to the processing and character of composite powder are also studied. The experimental results show that the composite powders of HNTs/PA12 exhibited a higher recrystallization temperature and crystallinity than virgin PA12 powder, which revealed a narrower process window and a higher powder bed temperature to avoid warpage; On the contrary, the composite powders of HNTs/PA12 shows a better thermal conductivity and a lower starting melt temperature, which caused a lower powder bed temperature to avoid agglomeration between the powders. As for the reinforcing effect, the tensile strength CF/PA12 composite is higher than HNTs/PA12. That is because the nano- fillers cannot be uniformly dispersed in the PA12 matrix, which instantaneously induced the significant enhancements in tensile strength and tensile modulus.

1 INTRODUCTION

Selective Laser Sintering (SLS), which is one of most widely used techniques in AM, allows complex 3D objects to be built by selectively fusing together successive layers of powdered material [1, 2]. The main advantage of SLS in comparison with other AM technologies is that it can process a wide scope of materials including polymers, metals, ceramics and composites [3-5]. In these materials, polyamide is the most widely used material. Owing to relatively low melt viscosities of during the SLS process, semi-crystalline polymers tend to achieve near fully dense SLS parts with high mechanical properties and can be directly manufactured as functional components. A lot of research has been carried out to study on the influence of process parameters on the mechanical properties, dimensional accuracy, microstructures of the parts prepared by SLS [6-9]. Relevant theoretical research about binding mechanisms and the degree of particle melt in SLS has also been also made [11, 12]. However, SLS parts usually have lower mechanical properties than conventional compression or injecting molded parts due to the existence of small portion of porosity, which cannot fulfil the challenging requirements of industrial applications any more. Many efforts have been made to enhance or tailor the properties of polymer SLS parts by means of preparing composites based on the polymers mentioned above. The reinforcing fillings are usually short fibers (carbon fiber), micro-sized particle (glass bead, metal powder), and nano-sized fillers (carbon nanotube, carbon nanofibers, silica and clay) [13-18]. However, the evaluation of composite powders and its influence on process during SLS are rarely studied.

In the present study, the composites of HNTs/PA12 and CF/PA12 are prepared by SLS. And the influences of reinforcing fillings to the processing and character of composite powder are studied. The reinforcing effects of fillers are evaluated, and the influences of process parameters on the mechanical properties are studied.

2 EXPERIMENT SECTION

2.1 Materials

Polyamide12 used in the experiment was supplied by RAPLAS International Ltd. with an average particle size of 60μm. The HNTs was supplied by Shijiazhuang HuiTeng mineral products trading company Ltd. The PA12 powder and HNTs powder were mixed by V-mixer (V-20L) for 2 hours as the raw materials for SLS process. The volume ratio of HNTs was 1.5%. The composite powder of CF/PA12 was supplied by Hunan Farsoon High-Technology Co.,Ltd with 40% short carbon fibers.

2.2 Fabrication process

The SLS machine used in the fabrication of porous materials was Type SLS 300, developed by Shanxi HengTong Intelligent machines Ltd., China. On the basis of the previous process experiments, different laser energy densities were conducted and the same layer thicknesses of 0.15mm and other processing parameters were set as follows: XY double scan mode, powder bed temperature of 160°C, scanning speed of 3500mm/s, scanning interval of 0.12mm.

2.3 Testing and characterization

Thermal analysis measurements were carried out using a Mettler-Toledo DSC machine under a 60 ml/min nitrogen flow. All samples were heated and cooled between 25 ℃ and 250 ℃ at 10 ℃ /min.

The samples were dumbbell shape tensile testing specimens (90 mm × 5 mm × 4 mm) according to ISO 527 (Plastics -- Determination of tensile properties) standard. Tensile testing was carried out by using an electro-hydraulic servo mechanical testing machine (CMT4304, MTS Corp., USA). Testing speed for all samples was 1 mm/min and the gauge length was 25 mm, five samples were tested for each batch and the testing was performed at ambient temperature (25 ℃). The powders morphology and fracture surfaces of the tested specimens were observed with a Hitachi S-3000N SEM at an acceleration voltage of 15 kV after the surfaces were sputter-coated with conductors.

3. RESULTS AND DISCUSSION

3.1 Evaluation of CF/PA12 and HNTs/PA12 composite powder for SLS compared with PA12

The morphology of the composite powders was investigated (as shown in Figure 1) and it can be found that the HNTs were able to adhere on the surface of the PA powder. The original near-spherical shape of the polymer powders was retained and such shape and morphology of these powders exhibited proper flow ability; while the short carbon fibers and the polymer powders present exclusive and the carbon fibers uniformly dispersed in the PA powder.

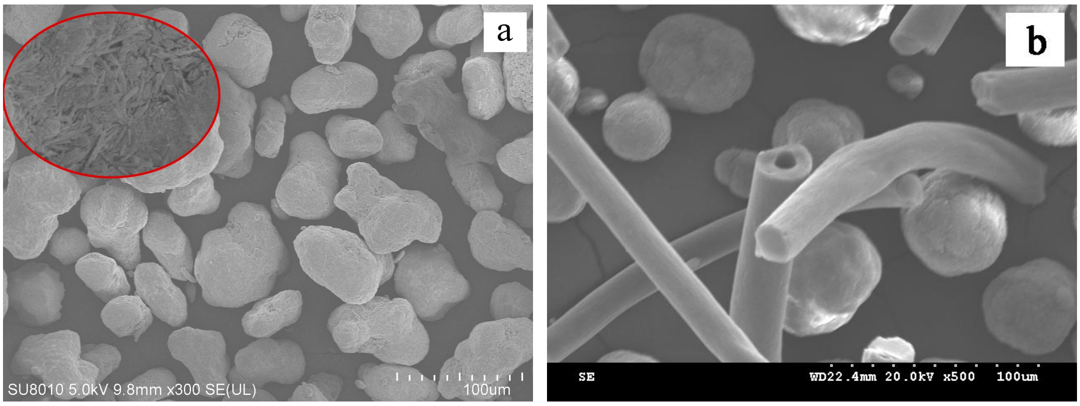

Figure 1: The SEM image of composite powders of HNTs/PA12 (a) and CF/PA12 (b)

The melting and recrystallization of materials were studied using DSC (as shown in Figure 2). The melting peaks provide the important indications on sinter ability of materials. PA12 shows a very sharp melting peak with high enthalpy of fusion because of the high crystal perfection of virgin powders, and CF/PA12 shows a relatively smooth peak and a lower start melting point, that is because the heat conductivity and the efficiency of fusion of composite powder were improved. This observation implies that the powder bed temperature should be reduced to avoid the agglomeration. As for the composite powder of HNTs/PA12, the onset recrystallization point is obviously higher than pure PA12, because the HNTs can act as a nucleating agent and accelerate the crystallization process.

In general, the powder bed temperature (Tb) is set based on the DSC heating-cooling cycle. Usually, the Tb should be set just below the onset melting point to avoid the agglomeration between the powders and higher than the onset recrystallization point to avoid the warpage caused by crystal shrinkage. Material parameters and the powder bed temperature during SLS of PA12 and composite powders are shown in Table 1.

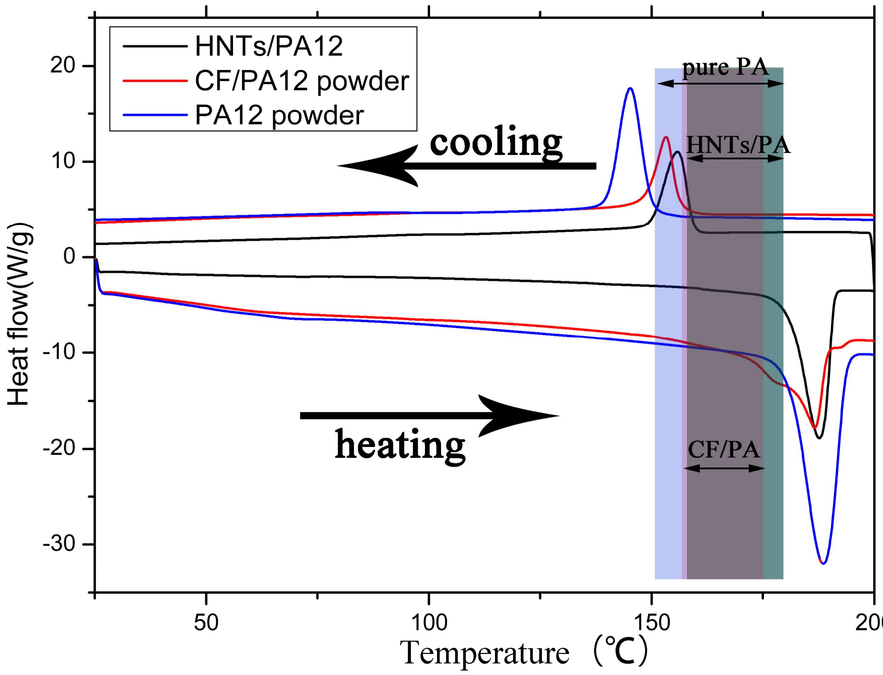

Figure 2: DSC diagrams of PA12, HNTs/PA12 and CF/PA12

Parameters	Pure PA12	HNT/PA12	CF/PA12
Onset melting temperature(℃)	180.67	180.47	176.7
Peak melting temperature(℃)	188.49	186.78	186.66
Onset recrystallization point (℃)	149.94	159.53	156.34
Peak recrystallization point (℃)	145.26	156.32	153.21
Powder bed temperature (℃)	160	167	154

Table 1: Material parameters of PA12 and composite powders

3.2 Mechanical performance of PA12 composites prepared by SLS

The tensile strength and modulus of the PA12 and composites prepared at different laser energy density are shown in Figure 3 and Figure 4. It can be found that the strength and modulus of PA12 composites is obviously higher than pure PA12, which indicates both HNTs and CF can enhance the mechanical properties of sintered PA12. However, the enforcement of HNTs occurred when the energy density is lower than 0.0381J/mm^2, and the enforcement of CF is remarkable when the laser energy density is more than 0.023 J/mm^2, and the optimum laser energy density of these three materials is different. The optimum laser energy density of HNTs/PA12, pure PA12 and CF/PA12 is 0.0286 J/mm^2, 0.0381 J/mm^2 and 0.04286 J/mm^2 respectively when the layer thickness is 0.15mm. This is probably because the reinforcing fillers change the optical characteristics of composite powders for the laser.

Additionally, the elongations at break of composites are all significantly lower than pure PA12. The elongations at break of the pure PA12 part with the best tensile strength is 25%, and this value of HNTs/PA12 and CF/PA12 part is 14% and 5.5% respectively.

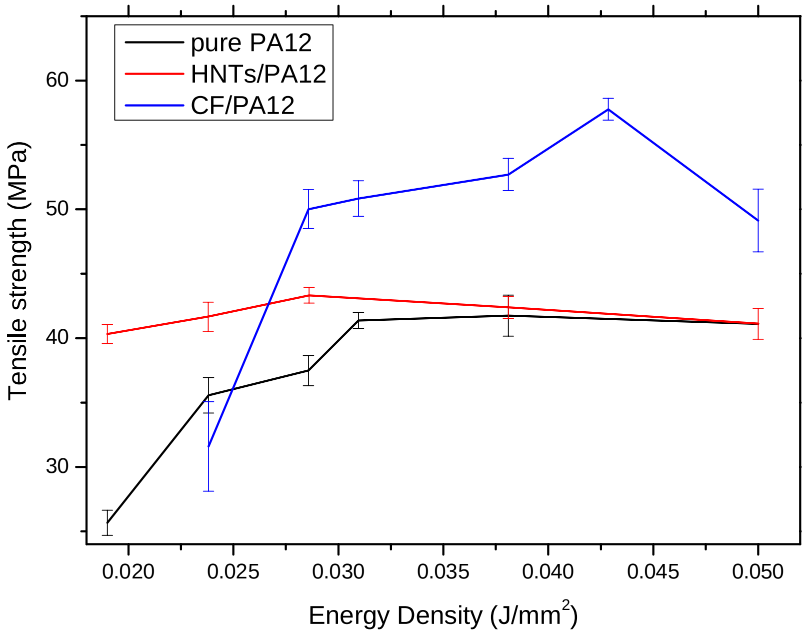

Figure 3: The tensile strength of sintered part at different laser energy densities

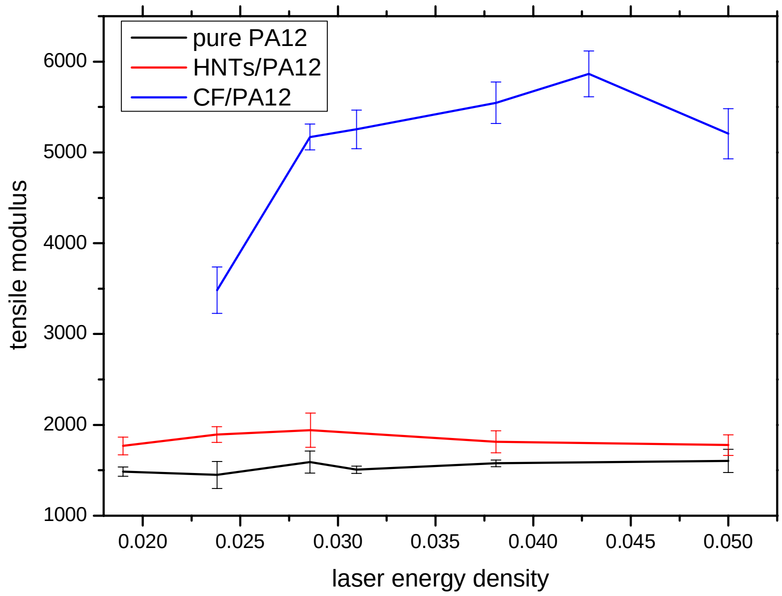

Figure 4: The tensile modulus of sintered part at different laser energy densities

The SEM pictures of fracture surfaces of sintered parts are shown in Figure 6. It can be observed that the plastic deformation is very obvious on the fracture surfaces of pure PA12 part, while this phenomenon cannot be observed for the composites. It also can be found that the HNTs cannot disperse uniformly in the polymer, and the nano fillers tend to be agglomerated during the mix process, which is one of the reasons why the reinforcing effect of HNTs is not significant as short carbon fibers.

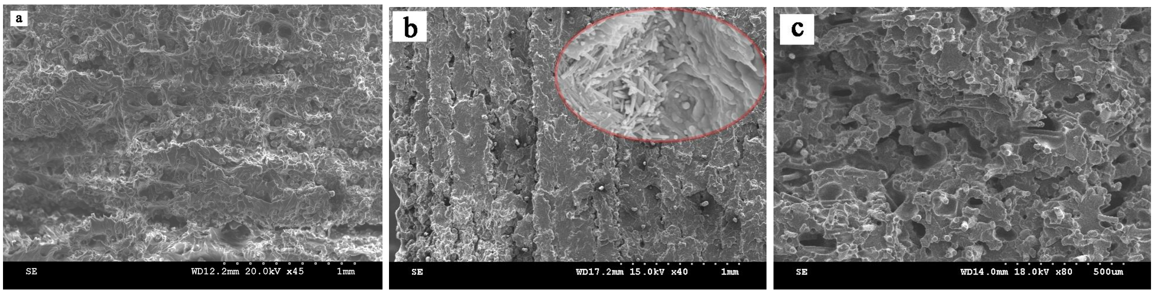

Figure 5: The SEM pictures of fracture surfaces of sintered PA12 (a), HNTs/PA12 (b) and CF/PA12(c)

4. CONCLUSION

In the present work, the reinforcing effects of CF and HNTs to PA12 parts prepared by SLS were studied. The influences of reinforcing fillings to the processing and character of composite powder are also studied. Experimental results show that the composite powders of HNTs/PA12 exhibited a higher recrystallization than virgin PA12 powder, which revealed a narrower process window and a higher powder bed temperature to avoid warpage; On the contrary, the composite powders of CF/PA12 shows a better thermal conductivity and a lower starting melt temperature, which caused a lower powder bed temperature to avoid agglomeration between the powders. As for the reinforcing effect, the tensile strength CF/PA12 composite is higher than HNTs/PA12. That is because the nano fillers cannot be uniformly dispersed in the PA12 matrix and which may instantaneously induced the significant enhancements in tensile strength and tensile modulus.

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