Effect of Carbon Nanotubes on Mechanical Properties of Wood Plastic Composites by Selective Laser Sintering

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Abstract: A new type of low cost, environmentally friendly wood-plastic composites (WPC) containing carbon nanotubes(CNT)of low content 0%, 0.05wt%, 0.1wt% and 0.15wt%, wood fibers of 14wt% and polymer PES of 86wt% was manufactured by the selective laser sintering (SLS) approach of 3D printing. The experimental results showed that the incorporating of CNTs could obviously increase the mechanical properties of the wood/PES composites material. The tensile strength, bending strength and elasticity modulus were 76.3%, 227.9% and 128.7% higher with 0.1wt% CNTs than without CNTs. And the mechanical properties of specimens firstly increased and then decreased with the increasing contents of CNTs. The SEM results of the specimens’ fracture morphology indicated that the preferable bonding interfaces between wood flour grains and PES grains were achieved by adding CNTs to the composites. There are two reasons to explain why the composites possessed the superior mechanical properties: CNTs could facilitate the laser sintering process of wood plastic composites due to their thermal conductivities; also, CNTs could directly reinforce the WPC composites as reinforcement.

Keywords: selective laser sintering (SLS); wood-plastic composites (WPC); carbon nanotube (CNT); mechanical properties; binding mechanism

1. Introduction

Selective laser sintering (SLS) can directly manufacture three dimensional components according to a computer aided design model by selectively sintering layers of powdered materials. SLS offers high-process flexibility with regard to the materials that can be processed[1], such as nylon, elastomer, and metal[2-3]. SLS has been one of the fastest growing additive manufacturing techniques used in different fields[4], because it has great potential to manufacture complex and low volume parts more rapidly[5], also could save time and cost comparing with conventional manufacturing methods.

In recent years, there was a growing need to develop more new materials for 3D printing in order to solve the problem of high cost[6]. Wood plastic composites(WPC), composed of cheap wood flour and waste polymer materials[7-8], is an environmentally friendly material, so it has attracted more attention of the researchers in the area of SLS[9]. The use of WPC in the SLS process offers some advantages over single polymer materials such as better sintering accuracy[10], which are related to the low processing temperatures and different sintering mechanism.

Many efforts have been made to enhance the mechanical properties of SLS parts by means of incorporating some reinforcements into composite materials[11]. Gu et al.[12] found that direct laser-sintered Cu-based alloys can be reinforced by Ni particles and forming CuNi solid solution,
due to a coherent particle/matrix interface after solidification. Hon and Gill\cite{13} prepared SiC/PA composites through SLS and found there was lower tensile strength, but higher stiffness of the composites parts than pure PA parts. Athreya et al.\cite{14} found that the PA-12/carbon black nanocomposites made by SLS showed a higher electrical conductivity but lower flexural modulus than neat PA-12 SLS parts due to the poor dispersion of nanoscale carbon black and a weak polymer-filler interface. Yan et al.\cite{15} found that 3wt% nanosilica could enhance the thermal stability, tensile strength, and tensile modulus of PA-12 SLS parts. Some researchers found that C/C composite complex components with high mechanical performance can be prepared by combining the 3D printing\cite{16}.

Some study showed that CNTs, the reinforcement of rigid PVC/wood-flour composites, is an approach to enhance their mechanical properties by using a melt blending process\cite{17}. An investigation showed that the CNTs/PA12 composites powders exhibited improved heat conduction and heat absorption compared with virgin PA12 powders\cite{18}. CNTs as reinforcement were introduced to facilitate the laser sintering process and enhance the thermal and mechanical properties of polymeric composites. This study investigated the microstructure of wood plastic/CNT composites specimens manufactured by SLS and the influence of the contents of CNT in composites on the mechanical properties and the sintering mechanism of the specimens are discussed. The aim of the present study is therefore to find out the effect of addition of CNTs on the mechanical properties of the WPC fabricated by selective laser sintering.

2. Materials and Methods

2.1 Raw materials characterization and mixing procedure

The wood powder used in the experiment was pine powder (45–90μm) and the polymer powder was polyether sulfone (PES, 60μm). The multi-walled CNTs were purchased from Chengdu Institute of Organic Chemistry and had an average diameter of 50nm and length of 5-10μm, and its purity level was greater than 95%.

The wood powder was over dried at less than 102℃ for 12 hours to remove moisture before processing. The dried wood powder and PES with the mass fraction proportion of 1:6 were blended in a high-intensity mechanical mixer (type SHR-50A) at room temperature for 2min. Then CNTs were mixed with the wood powder/PES composite powder by mechanical mixing. The contents of CNTs were respectively 0%, 0.05%, 0.1% and 0.15% in the composite powder. The optical photograph of the composite powder without CNTs was white, and the composite powder with the increasing of CNTs became grayer, as shown in Fig. 1.

Fig. 2 shows SEM images for the wood flour and the PES mixed at a ratio of 1:6 (by mass fraction) with 0%, 0.05%, 0.1% and 0.15% CNTs. As shown in Fig. 2, the shape of the PES powder is approximately spherical with different sizes. The wood powders present a rough surface with a shape of the fiber with the aspect ratio of 2:1 to 8:1. The CNTs cannot be characterized in the pictures with the low scale, because the size of the CNTs is super tiny and the CNTs, which might cover on the surface of the wood powder and PES particles, can not be found easily.

2.2 Specimen preparation

The test specimens were sintered by selective laser sintering machine (type AFS-360), product of Beijing Longyuan AFS Co., Ltd. Experimental parameters were set as following, preheat temperature: 83℃, internal power: 13kw, external power: 3kw.

Twenty-three specimens for different contents of CNTs in the wood-plastic composites powder were used to test bending strength and elasticity modulus. Strength was appraised on specimens with the three-point bending method. The dimensions of the specimens were approximately 80 mm×13 mm×4 mm with a span length of 60mm. Thirty-six specimens for different contents of CNTs in the wood-plastic composites powder were used to test tensile strength. The dimensions of the specimens were referred to the tensile test standard GB/T 1040-2006.
The mechanical properties were tested by an electron material testing machine (type CMT5504). The dimensions and shapes of the powder grains and the fracture morphology of bending specimens were investigated with SEM (type FEI Quanta 200). Tensile test specimens were built successfully with good definition and uniform color without sintered lumps on the surface of specimens, as shown in Fig. 3a) and b), respectively.

3. Experimental results and discussion

3.1. Effect of CNTs content on the mechanical properties of CNT/WPC specimens by SLS

The mechanical properties of the CNT/WPC composites were investigated through tensile and bending tests. The effect of CNTs content on the tensile properties and flexural properties of the CNT/WPC SLS parts is shown in Fig. 4 and Fig. 5, respectively. The CNTs can greatly enhance the tensile strength, flexural strength and flexural modulus of sintered components. The tensile strengths of 0.05% CNT/WPC, 0.1% CNT/WPC and 0.15% CNT/WPC sintered specimens are increased by 0.8%, 76.4% and 63.4% respectively, and the flexural strengths are enhanced by 91.0%, 227.9% and 80.2%, and flexural modulus are added by 102.7%, 128.4% and 48.0% respectively, when compared with the mechanical properties of the pure WPC SLS specimens. Moreover, all the mechanical properties tend to increase firstly and decrease latterly with the adding of CNT contents. 0.1% CNT/WPC possesses the best mechanical properties, however 0.15% CNT/WPC's properties start to decrease. It is reported that the agglomeration of 4wt% carbon black fillers in the PA composite powders prepare by mechanical mixing method caused much lower flexural modulus (over 20%) to the SLS composites parts, compared to the pure PA-12 [5]. In the present study, only a low mass fraction of CNTs addition of 0.15 wt% causes the decrease of the flexural modulus. This might be because more CNT agglomeration happened to the 0.15% CNT/WPC than 0.1% CNT/WPC, which would be covered by a thinner layer of CNTs with less or no agglomeration.

The significant improvement in mechanical properties might demonstrate that the CNTs could effectively reinforce the WPC matrix due to their homogenous dispersion and strong interfacial bonding. On the basis of the hypothesis, the mechanical properties of the CNT/WPC composites was thought to be attributed to the reinforcement CNT in the matrix WPC, a simple prediction model based on the Rule-of-Mixtures (ROM) has been proposed in the present work to calculate the mechanical properties of the CNT/WPC composites as follows:

\[ \sigma_c = \sigma_{CNT} V_{CNT} + \sigma_{WPC} (1 - V_{CNT}) \]  

where \( \sigma_c \), \( \sigma_{CNT} \) and \( \sigma_{WPC} \) are the tensile strength of the CNT/WPC specimen, the tensile strength of the CNT and the tensile strength of the WPC without CNT, respectively. The tensile strength of CNT is generally thought to be 50Gpa [19] \( \sigma_{WPC} \) is 2.37Mpa as tested and \( V_{CNT} \) (0.05%, 0.1%, 0.15%) are the mass fraction of CNT. The experimental and the corresponding calculated results of composites have been listed in Table 1.

Table 1. Predicted and experimentally tensile strength of wood plastic composites without CNT and with CNT

<table>
<thead>
<tr>
<th></th>
<th>WPC without CNT</th>
<th>CNT/WPC 0.05%</th>
<th>CNT/WPC 0.1%</th>
<th>CNT/WPC 0.15%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental value</td>
<td>2.37</td>
<td>2.39</td>
<td>4.18</td>
<td>3.88</td>
</tr>
<tr>
<td>Predicted value</td>
<td>-</td>
<td>27.37</td>
<td>52.37</td>
<td>77.37</td>
</tr>
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</table>
The calculated results were 11-20 times higher with 0.05-0.15% of CNT content than the experimental values. The large discrepancy between the predicted and the experimental values might be attributed to the higher porosity of the WPC, which have not been taken into consideration in the ROM model, since it is reported that lower strength of the composites of Nylon-12 with 4 wt% carbon black is due to the higher porosity of the composites made by SLS\(^5\), and also because it is not considered in the ROM model that CNTs only stay at the boundaries of sintered powder grains instead of dispersing homogeneously in the whole matrix.

3.2. Analysis of fracture morphology of CNT/WPC composites by SLS

In order to verify the morphological changes in the microstructure of the CNT/WPC composites manufactured with addition of CNTs, SEM images of fractured surface of the pure WPC and CNT/WPC SLS parts were taken in terms of low magnification and high magnification. Fig.6 shows the SEM images of the fracture with low magnification of WPC and CNT/WPC SLS parts. It can be seen that the irregular round PES particles melted partly and bonded part of the wood fibers, which were joined by extensive con-continuous phase formation. And there were also some pores existing in the surface, which were formed under the moderate viscous flow of PES and the block of the wood fiber during sintering. These phenomenon are similar to the previous study\(^9\). A visible difference between WPC and various CNT/WPC composite materials, however, can be observed. The pure WPC sample sintered presented relatively looser or more weakly linked powder particles, showing also more areas where there were bare wood fibers. While CNT/WPC composites obtained showed the reduced number of bare wood fibers and the increasing amount of sintering necks with the adding of CNTs contents. This indicates that low content of CNT can facilitate the laser sintering of WPC.

Furthermore, higher magnification images of the four types of samples’ fractures offered more valuable information (Fig.7). First of all, it can be seen that besides that with the increasing of the CNT content, the amount of bare wood fibers decreased obviously (Fig.7a, c, e, g), some CNTs were located on the fracture surfaces of CNT/WPC sintered parts (Fig.7d, f, h). And also on the fracture surfaces there were broken and unbroken sintering necks, which formed when PES particles close to wood fibers melted and bonded the loose wood particles when obtaining the laser heat\(^{20}\). In Fig.7a and b, there were less number of sintering necks and smaller size of sintering necks compared to Fig.7c-h. This reveals that the CNT/WPC structures become denser due to the more CNTs adding, more PES melting together and a higher degree of melting generates a larger PES continuous phrase wrapping the wood fibers, which increases the amount of bonding area, called sintering necks, of the structure. This can explain well the variation of mechanical properties with the changing of CNT contents (Fig.5 and 6).

Whereas, how CNTs work in the proceeding of sintering should be analyzed more deeply. Jiang et al\(^{21}\) studied mechanical properties and microstructure of SLS limestone/polyamide 12 parts affected by different energy input, including laser power and part bed temperature, it was found that the mechanical properties improve with increasing energy input, but decrease for overly high energy input, and more energy inputs can make denser microstructure due to melt flow rate of the polymer PA12. Moreover, Bai et al\(^{22}\) found that due to the greater thermal conductivity of PA12-CNT, the laser heat was conducted wider and deeper on the 3D temperature distribution in the PA12-CNT compared to PA12. In the present research, CNTs also act as a good thermal conductor between laser beam and polymer powders of low thermal conductivity. The existing of CNT inside polymer powder can effectively add the heat that polymer powders can obtain really in the conditions that energy input such as laser power and part bed temperature must not be increased, which is positive for the sintering of WPC, because overly high energy input could make wood fibers over heated and burned. Therefore, one possible reason why CNTs make the SLS parts of CNT/WPC denser could be CNT’s high thermal conductivity.

SEM images of mechanically fractured sections also provided valuable information for the analysis of fracture mechanism (Fig.7). It is obvious that the main fracture mode of the pure WPC is
interfacial debonding between PES and wood fiber, its secondary one is the fracture of sintering neck, while the CNT/WPC’s dominant fracture mode is the fracture of sintering neck. The former fractures are smooth and flat while the latter ones are rough. And also some CNTs can be found in the fracture surface of the sintering necks (Fig. 7d, f, h). This suggested that CNTs cause stronger interface between PES and wood fiber, and they can enhance the strength of the polymer matrix, i.e. sintering necks because CNT-coated layer, which covered the surface of wood and polymer particles before sintering, had been well embedded within the melted polymer matrix during sintering. Some researchers also got a similar conclusion that CNTs enabled strengthening the polymer matrix and preventing intermolecular movement of polymer chains under loading[18]. However, the mechanical strength showed a decreasing tendency at 0.15% content of CNTs in the WPC, this might be due to the CNT agglomeration caused by too much CNTs, as seen in Fig. 8.

3.3. Schematic of sintering mechanism during laser sintering of CNT/WPC composites

In order to clarify the effects of CNTs on sintering proceeding of CNT/WPC composites, their sintering mechanism were shown in Fig. 9 schematically. The loose composite powder before sintering consisted of PES particles, wood particles and a layer of CNTs, which were on the surface of the PES particles and wood particles, as seen in Fig. 9a. Here the PES can be seen as a binder material being liquefied and the wood can be seen as a structural material remaining solid throughout the process, while CNTs can be seen as a part of the binder PES although they also do not melt as wood particles during sintering, because their sizes are so tiny compared to the wood particles and were embedded into the melting polymer when obtaining the laser heat. Therefore, the CNT/WPC materials’ binding mechanism in selective laser sintering is liquid phase sintering-partial melting[20]. When the heat supplied to a powder particle was insufficient to melt the whole particle, only a shell at the grain border was molten and formed into a sintering neck. Only the rearrangement phase took place, so the sintering process is frozen at this stage resulting in a porous green product, as shown in Fig. 9b. Whereas, CNT/WPC exhibited a strong tendency to form bigger sintering which resulted in better mechanical properties. That is because that CNT with high thermal conductivity can transfer the heat from the laser beam to the PES particles. CNT/PES can obtain more energy in the same time duration to get bigger sintering necks. Meanwhile, PES can be reinforced by the CNT embedded in it, this is verified by the CNTs pulled out in the center of the sintering neck fracture face, as shown in Fig. 7.

3.4. Figures, Tables and Schemes
Figure 1. Optical images of the composite powder of wood flour, PES and various amounts of CNTs, (a) 0% CNT, (b) 0.05% CNT, (c) 0.1% CNT, (d) 0.15% CNT.

Figure 2. SEM images of the composite powder of wood flour, PES and various amounts of CNTs, (a) 0% CNT, (b) 0.05% CNT, (c) 0.1% CNT, (d) 0.15% CNT.
Figure 3. A photograph of the completed CNT/WPC tensile test SLS specimen (a) and flexural test SLS specimen(b).

Figure 4. The effect of CNTs content on the tensile strength of CNT/WPC SLS specimens

Figure 5. The effect of CNTs content on the flexural strength and elasticity modulus of CNT/WPC SLS specimens
Figure 6. Lower magnification SEM images of fracture surface of specimens by SLS with the CNT of (a) 0%, (b) 0.05%, (c) 0.1%, (d) 0.15%.
Figure 7. Higher magnification SEM images of fracture surfaces of specimens by SLS with the CNT of (a)(b) 0%, (c)(d) 0.05%, (e)(f) 0.1%, (g)(h) 0.15%.
Figure 8. The agglomeration of CNTs in the 0.15% CNT/WPC LS part

Figure 9. Sintering mechanism model of the CNT/WPC composites (a) before sintering, (b) after sintering

4. conclusion

A new type of low cost sustainable material, a mixture of low content of CNT (0.05%-0.15 wt %), wood fiber and PES powder, was developed and used in SLS in this research. The effects of CNT on the mechanical properties and microstructure of the CNT/WPC composites materials were investigated. The experimental results indicated that tensile strength, bending strengths and elasticity modulus of 0.10% CNT/WPC composites were about 176%, 328% and 229% higher than without CNT reinforced specimens, and they increased firstly and then decreased with the increasing of CNT content. The microstructure analysis showed that CNTs, as a good thermal conductor between laser beam and polymer powders, can effectively make the wood/polymer powders obtain more heat from the laser beam so that the SLS parts of CNT/WPC were much denser than WPC after laser sintering. Secondly, CNTs on the surface of the composite powder grains were embedded into the polymer when the polymer melted partly during sintering, and they directly reinforced the composites parts as a high strength reinforcement. In addition, CNT agglomeration caused by certain amount of CNTs could lower the mechanical strength at 0.15% content of CNTs in the WPC.

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Authors Contributions: Yunhe Zhang designed all experiments and wrote the paper. Jing Fang carried out all experiments. Jian Li analyzed the data and revised the manuscript. Yanling Guo supervised the projects and revised the manuscript. Qingwen Wang revised the manuscript.
Conflicts of Interest: There are no conflicts to declare.

References


