Carbon nanotube reinforced Polyamide 12 nanocomposites for laser sintering

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Abstract

In this work, Polyamide12 (PA12) and Carbon nanotube (CNT) added PA12-CNT nanocomposites were laser sintered and investigated. The powder morphology and CNT dispersion of the PA12-CNT were examined. Laser sintering process parameters: powder bed temperature and laser power were studied and optimised. The effect of the addition of CNT on the thermal properties of PA12 was identified. Compared to the laser sintered parts produced from commercially available laser sintering PA12 powder, the laser sintered PA12-CNT parts showed increased tensile modulus and tensile strength.

Keywords: Laser sintering; Polymer nanocomposites; Processing parameters; Thermal conductivity

Introduction

One of the most well established additive manufacturing technology, laser sintering (LS), is a powder-based process which uses a laser as a heat source to fuse polymer powders into three dimensions parts[1]. Polyamide 11 and 12 (PA11/PA12) are the most common polymer materials for laser sintering. Other polymers such as polypropylene (PP), polystyrene (PS), polycarbonate (PC), poly(ether-ether-ketone) (PEEK) and couple of thermoplastic elastomers are also available from major materials suppliers[2,3], however these polymers have not been used widely. Compared to traditional polymer manufacturing processes, such as injection moulding or blow moulding, the materials which are available for laser sintering are limited[4]. Furthermore, current laser sintering materials can not completely meet the needs, such as mechanical, thermal or electrical requirements, of all products[5,6]. To further develop laser sintering technology, there is an urgent need on researching and developing materials which can meet the various requirements of different applications (automobile, aircraft, aerospace, sports, medical, etc.)

Nanofiller-reinforced polymers offer the potential to improve the base material's properties while remaining processible by conventional processing techniques, and this potential is also expected for the laser sintering process. Several attempts have been made to improve the mechanical or physical properties of base polymers used for laser sintering by adding a nanofiller[7,8,9,10,11]. A common focal point raised in these studies is how to prepare polymer nanocomposites powders which are suitable for laser sintering[4,11].

In this study, carbon nanotubes (CNT), allotropes of carbon with a cylindrical nanostructure, were used as the nanofiller due to its outstanding mechanical and thermal properties[12]. Well-dispersed, laser sinterable PA12-CNT nanocomposite powders with near-spherical particle morphology were fabricated. The melting, crystallisation, and thermal conduction behaviours of both PA12 and PA12-CNT powders were analysed. The dimensional accuracy and mechanical properties of laser sintered parts were also examined.

Experimental

- **Materials**

PA12 powder (trade name as 'PA2200') was obtained from EOS GmbH, which has an established use in the laser sintering process. Multi-walled carbon nanotubes were supplied by NanoAmor Materials Inc. A novel method developed in the Materials Department at Loughborough University was used to fabricate near-spherical, well dispersed PA12-CNT nanocomposite powders, which had a CNT content of 0.1% by weight.

- **Thermal conductivity measurement**

Laser sintering is a heat transfer process, and the ability of the powder material to transfer heat is an important factor for this process. To identify the influence of the CNT on the thermal conduction of the polymer, thermal conductivity of the PA12 and PA12-CNT powders were measured by a thermal conductivity apparatus P5697 (Cussons Technology Ltd, UK). The apparatus consists of a vertical stack of specimens clamped between an electrically heated source at the top and a water cooled base, all located within a Dewar vessel and furnished with a radiation shield and anti-convection baffle[13], shown in Figure 1.

The sample specimen was designed as a hollow cylinder (height = 38 mm, diameter = 20mm, wall thickness = 0.5 mm) and produced by laser sintering, in which the testing powders were stored. Two small thermocouples were inserted into the specimen cylinder to contact with the testing powders inside. The inlet and outlet water temperatures were recorded. The heating current was supplied from a variable voltage power pack, which was used to vary the testing temperature. In this work, testing temperature was chosen from 100 – 175^{o}C, with an interval of 25^{o}C.

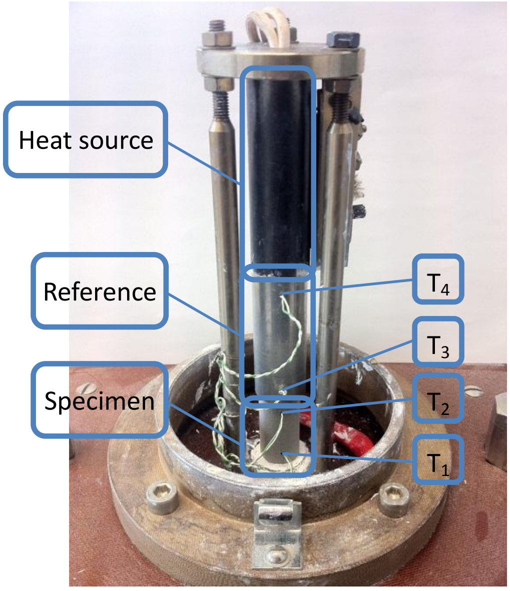

Figure 1: The internal structure of the Dewar vessel. $T_1 - T_4$ are the thermocouples.

The thermal conductivity is calculated as:

$$K = \frac{C_P \times M \times L \times (W_2 - W_1)}{A \times t \times (T_4 - T_3)}$$

where C_P is the specific heat capacity of water (4186 Joules/Kg), M is the mass of water collected in a certain time (t), L is the distance between the two thermocouples (T_1 and T_2), W_1 is the water inlet temperature, W_2 is the water outlet temperature, A is the cross-section area of the specimen, t is the time for collection of M, T_1 to T_4 are the thermocouple temperatures[13].

- **Laser sintering**

Both PA12 and PA12-CNT nanocomposites powders were laser sintered on an EOS P100 Formiga system. In terms of ease of processing, different laser sintering processing parameters, including powder bed temperature and laser power were investigated, which are discussed in details in the Results and Discussion section.

Tensile test specimens for PA12 and PA12-CNT were fabricated to establish the mechanical properties in accordance with ASTM D638-99[14]. All test specimens were oriented with the longest dimension aligned vertically to the direction of the movement of the recoating blade, as shown in Figure 2.

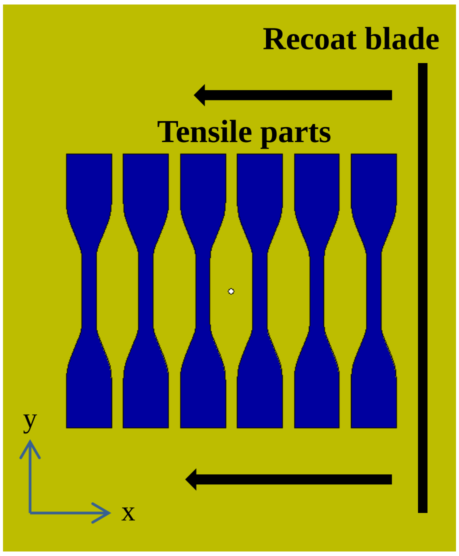

Figure 2: Schematic of the powder spreading direction in relation to the orientation of the parts

- **Other characterisations**

Scanning electron microscopy (LEO440 SEM, Leo Electron Microscopy Ltd) was used to image the morphologies of the PA12 and PA12-CNT powders and the dispersion of the CNT in the polymer matrix. Differential scanning calorimetry (SHIMADZU DSC-60) was used to study the thermal behaviours of these powders. The tensile properties of laser sintered parts were measured on a Zwick 103 testing machine.

Results and Discussion

- **Particle morphology**

Figure 3 shows the SEM micrographs for the PA12 and PA12-CNT nanocomposite powders. It can be seen that the commercial PA12 powder (Figure 3a) had a near-spherical morphology. The PA12-CNT powder (Figure 3b) maintained the same regular, near-spherical morphology as PA12. Powders with near-spherical and regular morphologies tend to arrange themselves more efficiently, which increases the density of parts during laser sintering process[4]. Furthermore, near-spherical powders can flow well and spread uniformly on the powder bed, which is important for the continuous laser sintering process where new powder is deposited each layer.

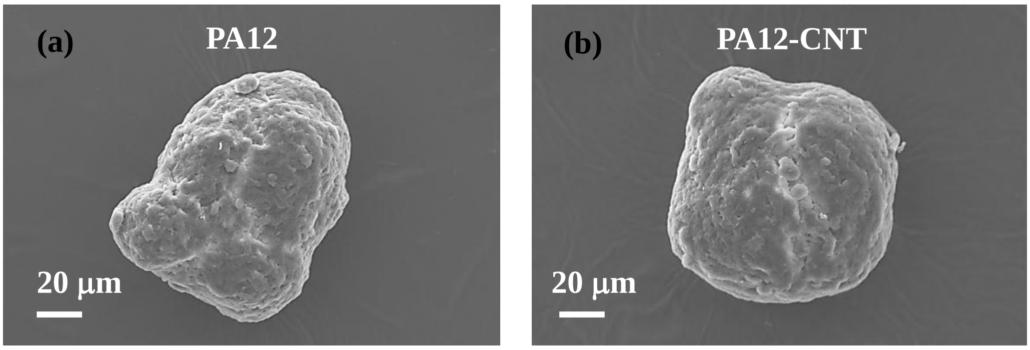

Figure 3: SEM micrographs of PA12 powder (a) and PA12-CNT nanocomposite powder (b)

- **Dispersion of CNT**

Figure 4 shows the FEG-SEM image of the PA12-CNT nanocomposite powders, in which the CNT (white strands) were dispersed uniformly in the PA12 matrix, and no obvious agglomerates were noticed. It is known that nanofiller has a nature to agglomerate together, which could reduce the reinforce effect on the polymer matrix, or even weak the properties of the base polymer[15]. Therefore, when nanofiller is used to reinforce polymer matrix, achieving well dispersed, agglomerates free nanofiller in the polymer matrix is very important[16,17]. Figure 3b and 4 indicated that a near-spherical, well dispersed CNT filled PA12 nanocomposite powders were fabricated successfully.

Figure 4: SEM micrograph of CNT (white strands) dispersion in the PA12 matrix

- **Laser sintering process parameter optimisation**

In the laser sintering process, the powder bed temperature is controlled to prevent ‘curling’ or ‘caking’. Curling occurs when the powder bed temperature is too low, which causes a high thermal gradient between the sintered and un-sintered material. Caking happens when the powder bed temperature is too high, and the powder particle surface starts to melt, which leads to powder agglomeration[18]. When there is no curling and caking, the powder bed temperature should be kept as high as possible to achieve optimum mechanical properties with relatively low laser input. In practice, selecting the precise powder bed temperature for laser sintering is highly dependent on the choice of polymer due to the complex thermal properties of different materials. To determine the optimum powder bed temperature for both PA12 and PA12-CNT, it was initially set to 150^{o}C and increased in 10^{o}C increments until the powder bed became hard or agglomerate lumps formed. When this occurred the temperature was reduced 1^{o}C at a time until free powder flow and a smooth, soft powder bed was obtained again. By this method, the suitable powder bed temperature for PA12 and PA12-CNT were determined as 171^{o}C and 172^{o}C respectively.

In addition to powder bed temperature, laser power is another crucial parameter. Different laser powers were investigated, with the laser scan speed and laser scan spacing being maintained at 2500 mm/s and 0.25 mm respectively. Initial attempts to build parts using relatively low laser powers, 13W and 15W, produced parts whose edges curled up in the initial layers, which lead to failure of the build as the recoater could not pass over the raised section. When the laser power was increased to 17W, there was considerably less curl. When the laser power was increased further to 21W, good definition and no distortion parts were built successfully for both PA12 and PA12-CNT. The summary of the processing parameters used in this study are shown in Table 1.

Laser sintering parameter	PA12	PA12-CNT
Powder bed temperature (^{o}C)	171	172
Layer thickness (mm)	0.1	0.1
Laser power (W)	21	21
Laser scan speed (mm/s)	2500	2500
Laser scan spacing (mm)	0.25	0.25

Table 1: Laser sintering parameters for PA12 and PA12-CNT powders

The laser sintering of tensile specimens is shown in Figure 5. The specimens for both PA12 and PA12-CNT were built successfully with good definition. Apart from the colour difference, there were no obvious differences between the PA12 and PA12-CNT laser sintered parts visible by eyes.

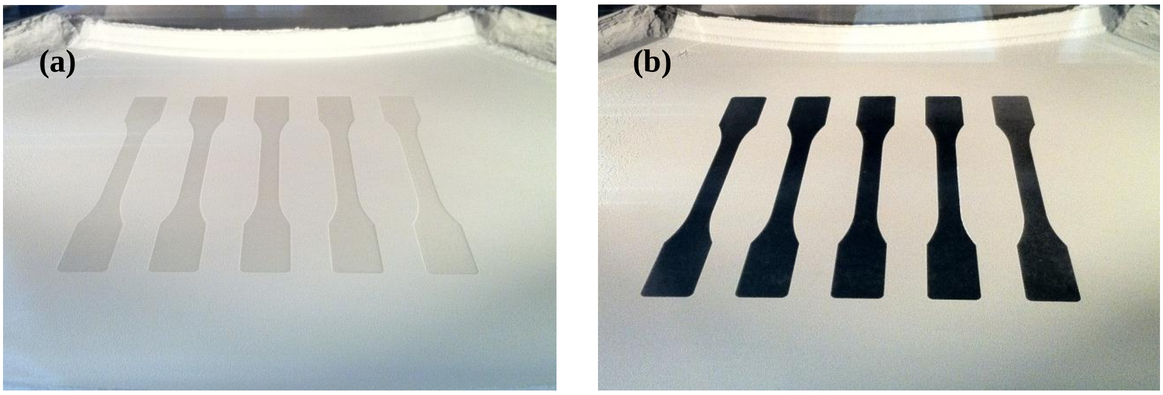

Figure 5: Laser sintering of (a) PA12, and (b) PA12-CNT nanocomposites

- **Thermal analysis of powders**

The melting and cooling characteristics from the DSC curves for the PA12 and PA12-CNT powders are shown in Table 2. There was very small difference (0.6^{o}C) on the melting point between the PA12 and PA12-CNT. The crystallisation temperature of the PA12-CNT nanocomposites powder was 5^{o}C higher than the PA12, which suggested that the CNT had a strong nucleation effect on the PA12. Laser sintering processing window, which is the temperature range between melting and crystallisation temperature, should be wider enough to ensure the feasibility of laser sintering. The processing window for the PA12-CNT was decreased about 5.6^{o}C compared to PA12; however it is still wide enough, which was confirmed during the laser sintering process in the previous section. The crystallinity of both PA12 and PA12-CNT powders were also measured. A theoretical enthalpy of melting for 100% crystalline PA12, $\Delta H_{C100\%}$ = 209.2 J/g was used for calculation[19].

Sample	Melting point (^{o}C)	Crystallisation Temperature (^{o}C)	Crystallinity (%)
PA12	183.4	146.6	27.4
PA12-CNT	184.0	151.6	26.5

Table 2: Melting, crystallization and crystallinity of PA12 and PA12-CNT powders

The results of the thermal conductivity of the PA12 and PA12-CNT powders are shown in Figure 6. It can be seen that as the temperature rise, the thermal conductivity of both PA12 and PA12-CNT increased slightly. PA12-CNT powders appeared average 14.2% greater thermal conductivity than PA12. This might be explained by the remarkable higher thermal conductivity of CNT, which could be over 3000 W/mK[20], compared to PA12. Increased thermal conductivity can improve the laser absorption, which could lead a more efficient powder fusion and melting process.

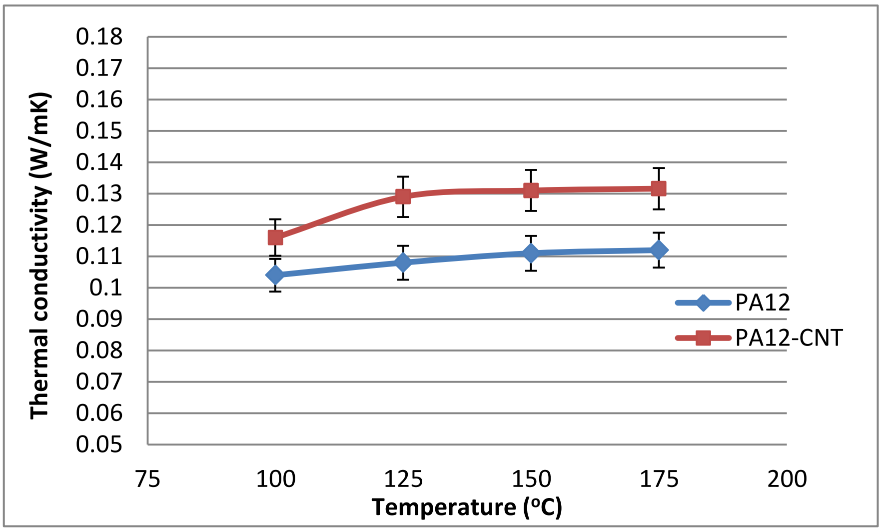

Figure 6: Thermal conductivity of PA12 and PA12-CNT powders

- **Dimensional accuracy of laser sintered parts**

Shrinkage is a common phenomenon for laser sintered parts, which can reduce the dimension accuracy. The dimensional accuracy of PA12 and PA12-CNT laser sintered parts was investigated by comparing predefined part dimensions and laser sintered part dimensions. Both parts showed shrinkage after laser sintering, which caused the dimensional error (Table 3). Compared to PA12, PA12-CNT laser sintered parts showed better dimensional accuracy.

Materials	Dimensional error (%)
PA12	7.9
PA12-CNT	3.7

Table 3: Dimensional error of laser sintered PA12 and PA12-CNT parts

- **Mechanical characterisation of laser sintered parts**

The tensile properties of the PA12 and PA12-CNT laser sintered parts are listed in Table 4. PA12-CNT had 44.5% increased tensile modulus and 7.0% improved tensile strength compared to PA12. This enhancement may come from two aspects: one is the load transfer between PA12 matrix and the CNT, which indicated strong polymer-filler interaction; the other is the enhanced laser absorption of PA12-CNT, which was due to the higher laser absorption coefficient and thermal conductivity of CNT.

Tensile properties	PA12	PA12-CNT
Tensile modulus (MPa)	2554.85 ±78.59	3691.85 ±92.51
Tensile strength (MPa)	49.96 ±1.37	53.45 ±1.25

Table 4: Tensile properties of laser sintered PA12 and PA12-CNT parts

Conclusion

A CNT-filled PA12 nanocomposite was prepared and laser sintered successfully. The PA12-CNT powder had near-spherical morphology with well-dispersed CNT in the polymer matrix. The thermal analysis showed that the thermal conductivity increased slightly with temperature increase for both PA12 and PA12-CNT powders; the PA12-CNT powders had greater thermal conductivity than PA12. Laser sintered PA12-CNT parts showed less dimensional error than PA12 parts. Tensile results showed 44.5% greater tensile modulus and 7.0% higher tensile strength for PA12-CNT, which might be explained by the load transfer between the polymer and nanofillers, and the enhanced laser absorption.

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