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Graded Composites of Polyamide/Carbon Nanotubes Prepared by Laser Sintering

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Abstract In this study, the mechanical and electrical properties of graded composition material (GM) were investigated in order to evaluate the effects of the addition of multi-walled carbon nanotubes (MWCNTs) to a polyamide 12 (PA12) matrix in different proportions. A graded component of PA12/MWCNTs was designed and manufactured by selective laser sintering (SLS) and variations in the morphology as well as in the mechanical and electrical properties were observed. The effect of different proportions of MWCNTs in the PA12 was investigated by microscopy, flexural test and resistivity measurements. The addition of 0.5 and 1.0 wt% of MWCNTs promoted an increase in the composite strength and flexural modulus. A significant reduction in the resistivity was verified with the addition of 3.0% of MWCNTs in the polyamide matrix. The mechanical and electrical behavior presented by the PA12/MWCNT composites suggests that the percolation concentration is around 3 wt%, when an effective inter-nanotube contact seems to be reached, improving the electrical conductivity but reducing the mechanical strength. A GM component with an MWCNT concentration gradient along the vertical axis was designed and manufactured by SLS. A gradual controlled variation in the composition of GM component leads to variations in the microstructure as well as in the mechanical and electrical properties.

Keywords Graded Composites · Polyamide/carbon nanotubes · Laser sintering

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Introduction

Multi-walled carbon nanotubes (MWCNTs) have emerged as promising materials for a great range of applications. The main contributions consist of improving the mechanical and electrical properties of insulated materials, particularly thermoplastics [1]. Parts and system components based on carbon nanotube composites can improve the mechanical and electrical properties, such as wear tribology, strength, conductivity and permissivity to specific applications in satellites (support bearings, axles and other components).

Yu et al. and Haggenmueller et al. developed composites by in-situ polymerization using single-walled carbon nanotubes (SWCNTs), treated chemically with the aim of adding surface carboxylic groups, and obtained a threshold of percolation with the addition of around 1.0 wt% of nanotubes [2, 3]. The results showed an improvement in the electrical resistivity (10^7 Ωcm) compared with the pure material (10^{16} Ωcm). Kim et al. performed the in-situ polymerization of polyamide 6.10 and MWCNTs and obtained a decrease in the electrical resistivity from 10^{17} to 10^{12} Ωcm with the addition of only 0.1 wt% [4].

Studies using different grades of polyamide have been carried out aiming to improve the mechanical properties of the material. The technique used to obtain the composite is an important factor with regard to the performance of the final component. Authors such as Zheng et al., Kim et al. and Kang et al. prepared composites using MWCNTs and polyamides, including PA6.6, PA6.10 and PA10.10 [4–6]. They observed increases of up to 170% in the values for the elastic modulus with the addition of 1.5 wt%. Chen et al. performed the blending of molten polyamide 6 and MWCNTs treated by oxidation [7]. They reported lesser effects, with around a 40% increase in the mechanical strength and elastic modulus with 0.5 wt% of MWCNTs, while the addition of 2 wt% resulted in a 50% increase in these parameters [7].

The additive manufacturing technologies, also known as rapid prototyping, are emerging as fabrication processes for composites and graded materials (GM). The major advantages over other processing methods is the discretization of the composition/properties along the part, due to the versatility in the production of free and complex forms from layering manufacturing aided by the computer programs CAD and CAM [8]. The selective laser sintering (SLS) technique has advantages over the other additive manufacturing techniques since fabrication with particulate material enables the incorporation of many kinds of fillers or blends. In previous work, Salmoria et al. studied the microstructure and mechanical properties of thermoplastic blends and controlled composites manufactured by SLS and demonstrated that this technique can be used to obtain parts with structural specificity in defined component areas, allowing the fabrication of graded components [9–14].

The incorporation of CNTs provides a considerable improvement in the elastic modulus of laser sintered polyamide parts. Dynamic mechanical analysis shows that the higher loss modulus for PA12-CNT nanocomposites is due to the interaction between the CNTs and the polymer matrix, which causes restricted segmental motions and this, in turn, leads to a decrease in the thermal expansion coefficient [15, 16]. These studies revealed that the CNTs were agglomerate-free in the PA12-CNT parts obtained by laser sintering, which helps to explain the previously reported improvement in the mechanical properties of laser-sintered PA12-CNT parts [17].

In this study, mechanical and electrical properties were analyzed in order to evaluate the effects of the addition of MWCNTs to the PA12 matrix in different proportions. The different MWCNTs content were investigated by microscopy, flexural tests and resistivity measurements. A graded PA12/MWCNT composite was used to manufacture a part component by SLS and demonstrate the potential application of this material and the technique.

Materials and Methods

Materials

The powder material used in this study was Polyamide 12 DuraformTm (3D systems), supplied by the Multibras SA company. The material has an average particle size of 58 μm and melting temperature of 184 °C (3D system, 2008). The multi-walled carbon nanotubes were purchased from MER Corp. The nanotubes were obtained by chemical vapor deposition (CVD) and had an average diameter of 140 +/− 30 nm and length of 7 +/− 2 μm, with purity greater than 90%.

Specimen Fabrication

Multi-walled carbon nanotubes were dispersed in polyamide powder by mechanical mixing using a cylindrical blender for 70 min at 90 rpm. The specimens used to investigate the mechanical and electrical properties were fabricated according to pre-determined parameters identified in an optimization procedure. The specimens were manufactured in atmospheric air using a CO_2 laser (wavelength of 10.2 μm) with a power of 3.1 W, a 250 μm focused beam diameter and scan speed of 56 mm/s. The building layer thickness used was 200 μm, the spacing between the laser scans was 125 μm and the temperature chamber was set at 145 °C. Figure 1 shows an image of the composite specimens after SLS fabrication.

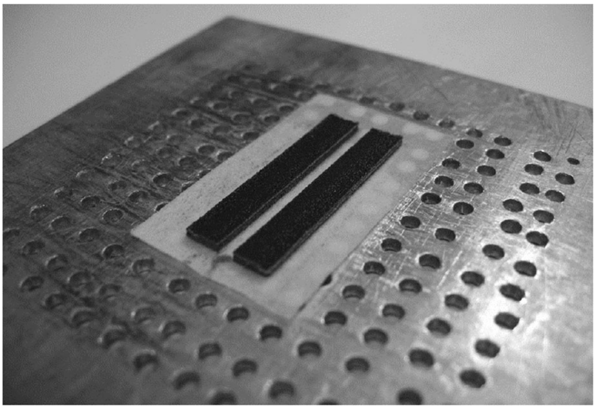

Fig. 1 Composite specimens manufactured by SLS

Manufacturing of GM Component

A graded PA12/MWCNT component was designed for fabrication by SLS with MWCNT contents of 0.5, 1.0 and 3.0 wt% and dimensions of 15.80 mm outer circle diameter, 12.30 mm inner circle diameter, 22.10 mm base length and 15.80 mm mean height (Fig. 2). The GM was manufactured using a single group of processing parameters, since the equipment and software permit only single values for the laser power and scan speed during the layer fabrication. The composition gradient was obtained in the powder deposition direction, namely the Y direction. The laser power applied was 3.1 W and laser scan speed was 56 mm/s. The powder layer was spread with a thickness of 200 μm, the spacing between the laser scans was 125 μm and the temperature chamber was set at 145 °C.

Morphology and Mechanical Tests

The morphological analysis was performed on a Philips scanning electron microscope (XL 30). All samples were covered with gold in a Bal-Tec sputter coater (SCD005). The mechanical properties were obtained in a DMA TA Q800 analyzer, using a single cantilever clamp with a ramp force of 2 N/min. Flexural tests were performed to obtain the stress value at 10% of elongation and the flexural modulus.

Electrical Measurements

Resistivity measurements were performed using a Megabras Megohmmeter (ME2550). The samples, with 8 mm length, 5 mm width and 1.4 mm thickness, were fixed in a

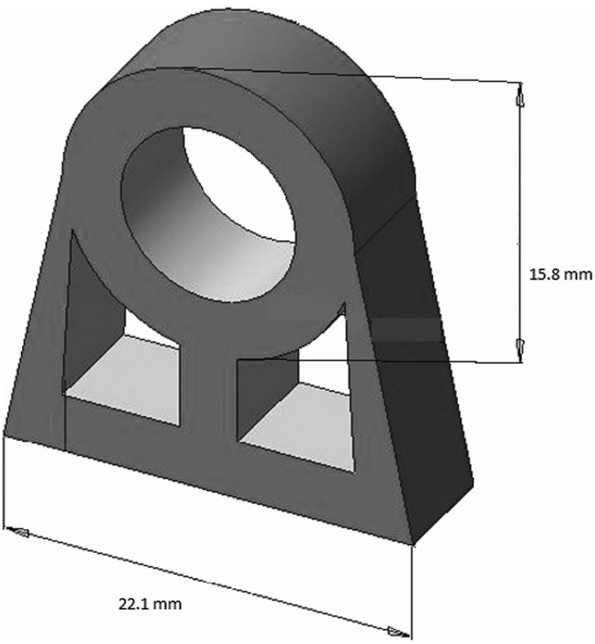

Fig. 2 3D model of the designed graded PA12/MWCNTs component

clamp with copper ends in order to ensure the electrical contact. The resistivity value for each sample was obtained using a single voltage (500 V). Each sample was fixed and measured five times, allowing the mean and standard deviation values to be calculated.

Results and Discussion

Table 1 provides a summary of the mechanical and electrical properties of the specimens manufactured with different MWCNT contents. On analyzing the mechanical properties (stress at 10% and flexural modulus), it is possible to verify that the addition of 0.5 and 1.0 wt% of MWCNTs caused increases of 17.7 and 25.8%, respectively, in the strength of the composites at 10% of elongation. The flexural modulus increased by 4.1 and 10.4% with the addition of 0.5 and 1.0 wt% of MWCNTs, respectively. A reduction in the values for the mechanical properties with the addition of 3% w of MWCNTs was observed.

The resistivity values obtained for the pure PA12 and composites with 0.5 and 1.0 wt% of MWCNTs had similar orders of magnitude (10^{12} to 10^{11} Ω.cm) indicating that MWCNT contents of < 1.0 wt% are below the percolation concentration, when conduction pathways are formed in the polymer matrix. On the other hand, a significant reduction in the resistivity was verified with the addition of 3.0% of MWCNTs in the polyamide matrix. The mechanical and electrical behavior of the PA12/MWCNTs suggests that the percolation concentration is between 1 and 3 wt%, when an effective inter-nanotube contact is reached, improving the electrical conduction and reducing the mechanical strength due to shear mechanisms.

Manufacturing of GM Component

The manufacturing of component with controlled gradients requires variations in the composition, structure and properties, in order to obtain optimal functionalization. The combination of this concept with the possibility of layer manufacturing permits the design of complex geometries. A GM component with moderate complexity and compositional change over its vertical axis was designed. The SLS fabrication of the component was carried out in the horizontal position and the composition gradients were built in the Y direction, as described in the experimental section. Figure 2 shows the 3D model of the design for the component built by SLS.

Table 1 Mechanical and electrical properties of composites as function of MWCNTs content in PA12 matrix

MWCNTs (%)	Stress at 10% (MPa)	Flexural Modulus (MPa)	Electrical Resistivity at 500 V (Ω.cm)
0	62.0 +/− 8.8	480 +/− 86.6	1.0 E + 12
0.5	73.0 +/− 12.1	500 +/− 73.8	9.0 E + 11
1.0	78.0 +/− 8.3	530 +/− 63.9	7.2 E + 11
3.0	50.0 +/− 10.4	410 +/− 79.2	5.4 E + 6

Table 2 Dimensional values for manufactured GM component

	Designed value (mm)	Obtained value (mm)	Deviation (%)
Outer diameter	15.80	(18.40 ± 0.16)	14
Inner diameter	12.60	(10.39 ± 0.11)	21
Base length	22.10	(25.72 ± 0.01)	14
Mean height	15.80	(16.29 ± 0.02)	3

The dimensions of the fabricated component were analyzed in order to evaluate the possible variation caused by failures at the software interface and/or sinter shrinkage. Table 2 shows the dimensional values and the fabricated component values of the design. The dimensional variations ranged from 3 to 21%. These variations seem to be caused by software interface failures. The highest deviation from the designed dimensions was observed for the inner circle diameter, due probably to radial shrinkage during sintering.

Figure 3 shows an image of the GM component built by SLS and its microstructure in regions with 0.5 and 1.0% of MWCNTs. The areas with different MWCNT contents did not presented an abrupt interface between layers with different compositions, as shown in Fig. 3. The gradual variation in the composition of the GM component lead to variations in the microstructure as well as the mechanical and electrical properties. This results in a component with maximum mechanical strength in areas with 1.0% of MWCNTs, i.e. the circle base area, and lower resistivity in areas with a 3.0% MWCNTs content, i.e. the fixation base area.

Micrographs of the GM component with 0.5, 1.0 and 3.0 wt% of MWCNT contents are shown in Fig. 4. The morphologies of the GM component regions show some similar aspects concerning the sintering degree and densification. The microstructure of

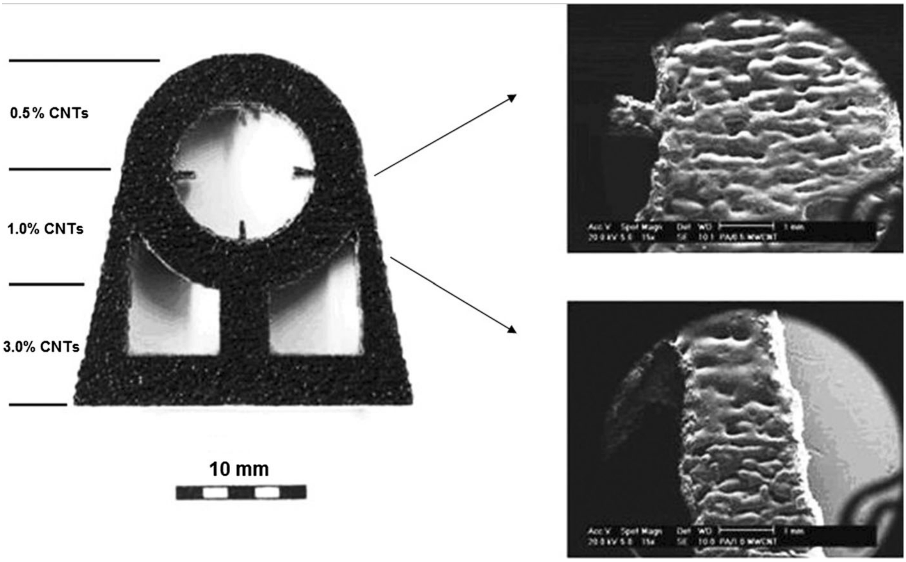

Fig. 3 The image of the graded component built by SLS and its microstructure at regions with 0.5 and 1.0% MWCNTs content

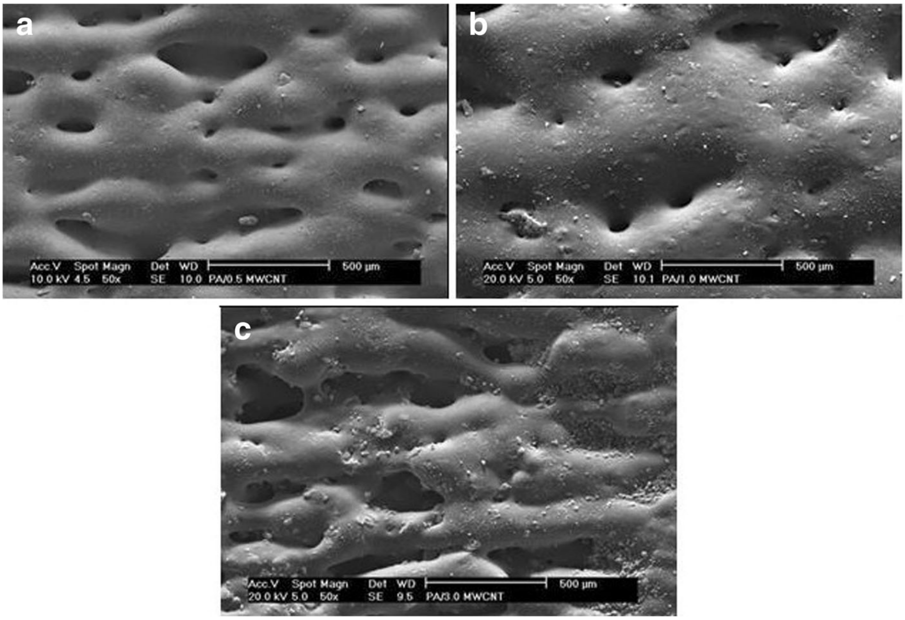

Fig. 4 Micrographs of the graded component regions with 0.5 (a), 1.0 (b) and 3.0 wt% (c) of MWCNTs content

areas with 0.5% of MWCNTs shows the formation of a co-continuous matrix with extensive particle coalescence and phase densification during the sintering process.

The component region within 1.0% of MWCNTs shows similar morphological features, matrix densification and particle coalescence, resulting in an SLS component with intermediate roughness in these regions. The microstructure presented in areas with 3.0% of MWCNTs shows the formation of a less co-continuous matrix (which explains the reduction in the resistivity values) and some particles show neck formation, indicating less extensive particle coalescence during the sintering process. This explain the lower values obtained for the mechanical properties, probably due to the higher MWCNT content.

Conclusions

The addition of 0.5 and 1.0 wt% of MWCNTs promotes increases of 17.7 and 25.8%, respectively, in the strength of composites at 10% of elongation. The flexural modulus increased by 4.1 and 10.4% with the addition of 0.5 and 1.0 wt% of MWCNTs, respectively. The resistivity values observed for pure PA12 and composites with 0.5 and 1.0 wt% of MWCNTs had similar orders of magnitude (10^{12} to 10^{11} Ω.cm). On the other hand, a significant reduction in the resistivity was verified with the presence of 3.0% of MWCNTs in the polyamide matrix. The mechanical and electrical behaviors presented by the PA12/MWCNTs suggest that the percolation concentration is between 1 and 3 wt%, when an effective inter-nanotube contact is reached, improving the electrical conductivity and reducing the mechanical strength.

A GM component with an MWCNT concentration gradient along the vertical axis was designed and manufactured by SLS. Dimensional variations ranged from 3 to 21%. The inner circle diameter showed the greatest deviation from the design value, probably due to radial shrinkage during sintering. The microstructure observed for MWCNTs contents of 0.5 and 1.0% shows the formation of a co-continuous matrix with extensive particle coalescence and phase densification during the sintering process. This results in an SLS component with intermediate roughness. The microstructure observed for a MWCNT content of 3.0% shows a co-continuous matrix and some particles with neck formation, indicating less extensive particle coalescence during the sintering process.

A gradual variation in the composition of GM component leads to variations in the microstructure as well as in the mechanical and electrical properties. As a result, the part obtained in this study showed maximum mechanical strength in regions with 1.0% MWCNT content and lower resistivity in regions with 3.0% MWCNT content.

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