PROCESSING AND PROPERTIES OF CARBON BLACK-FILLED ELECTRICALLY CONDUCTIVE NYLON-12 NANOCOMPOSITES PRODUCED BY SELECTIVE LASER SINTERING

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Abstract

Electrically conductive polymer composites are suitable for use in the manufacture of antistatic products and components for electronic interconnects fuel cells and electromagnetic shielding. Selective laser sintering (SLS) was used to investigate the fabrication of electrically conductive nanocomposites of Nylon-12 filled with 4% by weight of carbon black. The effect of laser power and the scan speed on the flexural modulus and part density of the nanocomposite were studied. The set of parameters that yielded the maximum flexural modulus and part density was used to fabricate specimens to study the tensile, impact, rheological and viscoelastic properties. The electrical conductivity of the nanocomposite was investigated. The densities and the microstructures of the nanocomposites were studied using optical microscopy and scanning electron microscopy (SEM). The morphology of the nanocomposites was investigated using X-Ray diffraction (XRD) and differential scanning calorimetry.

Introduction

Polymer nanocomposites are a radical alternative to conventional filled polymers and polymer blends, showing enhanced overall performance even at low reinforcement loadings [1]. The main and most practical fabrication method for nanocomposites is melt-mixing followed by injection molding. However, many applications require a complicated part shape which causes difficulties during mold design and/or filling. Selective laser sintering (SLS) can lead to functionally graded materials that incorporate deliberately designed transitions in materials composition and properties within a component in a preferred direction and optimize the functional value of that component [2] with no limitations in the shape and features resolution of the part. The benefits of selective laser sintering for glass filled nylon-11 composite are demonstrated in Figure 1 [3].

The fabrication method and processing conditions of the composites affect strongly the properties and overall performance of the composites. In case of electrically conductive reinforcements the manufacturing method can plays an important role in the percolation threshold and conductivity of the composites since it can alter the orientation, dispersion and interparticle spacing within the polymer matrix and the filler's aspect ratio or enhance the interactions between filler and matrix.

The present study is a comparison between selective laser sintering and melt-mixing/injection molding of carbon black reinforced polyamide 12 nanocomposites in terms of mechanical properties such as flexural strength and modulus, tensile strength and modulus and impact strength. Melt-mixing is chosen as the "baseline" fabrication method due to its simplicity and compatibility with existing polymer processing techniques such as extrusion and injection molding.

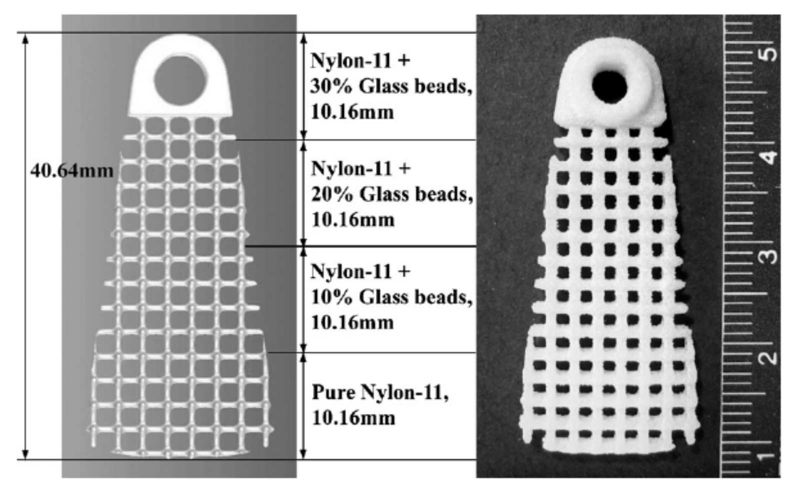

Figure 1 Schematic description of a rotator cuff scaffold and the corresponding functional graded material (FGM) component fabricated by SLS [3].

Materials and Methods

Materials

Nylon 12 powder with the trade name VESTOSINT® X 1553 white (Evonik Industries, Essen, Germany) was used in this study. VESTOSINT® X 1553 is a white, odorless thermoplastic polymer belonging to the aliphatic polyamide family. It is a semicrystalline polymer having a melting temperature in the range of 176-184^{o}C [4].

The reinforcement employed in the study is nanosize carbon black (KETJENBLACK EC-600 JD, Akzo Novel Polymer Chemicals LLC) with high electrical conductivity. This highly agglomerated structured carbon black has a high degree of porosity and a surface area of 1400 m^2/g, that allows for polymer penetration. It can create a conductive network by occupying a large occluded volume at low concentrations and by eliminating many of the particle-polymer interfaces through its aggregated structure.

Compounding

High wear resistant zirconia grinding media (Glenmills Inc., Clifton, New Jersey, USA) having a diameter of 5 mm was used to ball-mill the carbon black pellets in a rotary tumbler (784 AVM, U.S. Stoneware, Ohio, USA) for 24 hours. The ball-milled carbon black was sieved using a US standard 140 mesh sieve with 106 µm opening. The sieved carbon black was blended with the pure Nylon 12 powder (4% by weight of carbon black) in a rotary tumbler for 24 hours. Scanning electron microscopy (SEM) was used to image the Nylon 12 powder and the composite powder (Figure 2). The Nylon 12-carbon black composite powder as well as the pure Nylon 12 powder was processed in a Sinterstation® 2000 (3D Systems Inc., Rock Hill, South Carolina, USA).

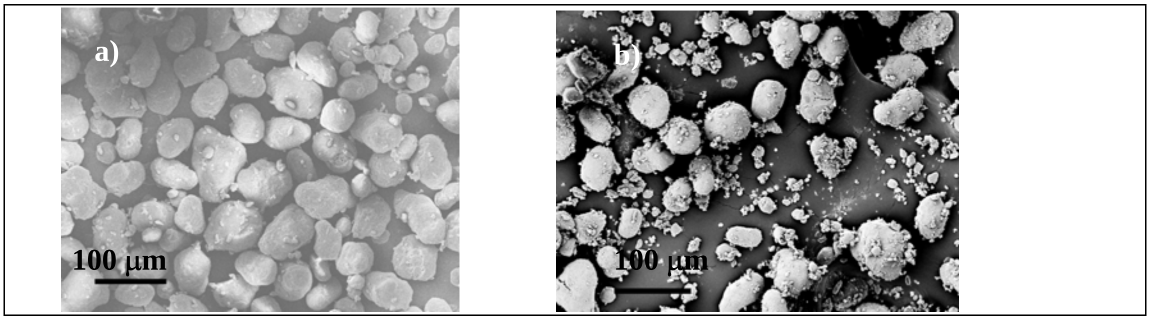

Figure 2 a) SEM image of Nylon 12 powder, b) SEM image of Nylon 12 – carbon black composite powder

In case of the nanocomposites made by extrusion and injection molding two other compounding methods were also used, in addition to the compounding method described above, in order to verify that the results truly reflect the differences between SLS and extrusion and are not masked by possible compounding effects. So the three versions of compounding investigated are i) composite powder was of ball milled CB and nylon 12 mixed using the tumbler was fed in the extruder, ii) ball milled CB pellets were melt mixed with the nylon 12 powder in the extruder and iii) ball milled CB was exposed to laser for the same duration and at the same conditions used in the SLS process and then it was melt mixed with nylon into the extruder. The sample notation used in the study and a brief description of the basic difference among them is provided in Table 1.

Sample ID	Description
1. PA Ex-IM	Pure nylon 12 (PA) sample made by extrusion and injection molding
2. PA-4CB Ex-IM	4wt% CB in PA, made by extrusion/injection molding
3. PA-4CB Ex-IM (melt mixing)	As #2 but the mixing was done in the extruder
4. PA-4CB Ex-IM (LE)	As #3 but CB was first exposed to laser
5. PA SLS	Pure nylon 12 (PA) sample made SLS
6. PA-4CB SLS	4wt% CB in PA, made by SLS

Table 1 Notation and description of the samples used in the study

Extrusion Injection Molding

A DSM Micro 15cc Compounder, (vertical, co-rotating twin-screw microextruder) was employed for melt-mixing. The conditions used are $T_{feed}=T_{barrel}= 190\ ^{o}C$, mixing time of 3 minutes and 200rpm screw speed. A Daca Micro Injector with a cylinder temperature at 190 ^{0}C and the $T_{mold}= 90\ ^{0}C$. An injection pressure of 110 psi was used. It is noted that the

DSM equipment used is sufficient for screening experiments but has limitations when trying to relate this to a larger scale extruder-injection molder system. For instance, the maximum allowable packing pressure during injection molding is 80psi, which is much lower than the pressure used normally with large size injection molding systems. This means that the degree of orientation and alignment of the reinforcements in the DSM composites is smaller indicating that the performance of nanocomposites made using DSM may be limited by this processing system.

Selective Laser Sintering

Selective laser sintering (SLS) is a type of solid freeform fabrication (SFF) or layered manufacturing (LM) technique in which a part is built layer-by-layer using powdered materials, radiant heaters and a computer controlled laser [5, 6]. The SLS process like other SFF processes starts with a CAD model of the part to be built. The CAD file is subsequently sliced at discrete intervals (approximately 100 – 200 μm) and the resulting cross-sections are stored sequentially in a "build file". Scanning algorithms are used to plan the path of the laser for each cross-section which is scanned onto a preheated bed of powder. Exposure to the scanning laser elevates the temperature of the powder to the point of melting, resulting in the sintering of the particles. After scanning an entire cross-section onto the powder surface, the power bed is lowered by a distance equal to the slice layer thickness used in the build process and a fresh layer of powder is deposited by a roller mechanism. The next cross-section is then laser-sintered deep enough to fuse it to the underlying layer and in this way, by sintering layer upon layer, the entire part is fabricated. A schematic diagram of the SLS process is shown in Figure 3.

The most important parameters in the SLS process, that affect the quality and microstructure of the resulting part are laser power, laser scan speed, laser scan spacing, part-side temperature set-point, powder feed temperature set-point, powder layer thickness and roller speed. In this study, only the laser power and laser scan speed were varied at discrete intervals. All the other parameters were set at a fixed value. The part-side temperature set-point was maintained as close as possible to the melting temperature of the polymer. This minimized the thermal gradients around the sintered region thereby reducing the out-of-plane curling and distortion. However, if the set-point was too high the powder in the build area caked severely. Similarly, if the powder feed temperature set-point was too high, the roller was not able to deliver the powder across the entire build area. Lowering the temperature set-points below a critical value resulted in curling of the sintered region. Powder layer thickness was chosen to be 4 mils (101.6 μm) since the average size of the polymer particles is less than 100 μm. The roller speed was set at the lowest allowable value on the Sinterstation® 2000 to ensure that the powder was uniformly spread across the entire build area. The laser scan spacing was set at 6 mils (152.4 μm) since this value corresponds to a beam overlap factor (beam diameter divided by the scan spacing) of around 3 and has been used in previous studies [3, 7]. The laser power was varied from 3W to 7W (in intervals of 1W) and the laser scan speed was varied between 30 in/s to 60 in/s (in intervals of 10 in/s).

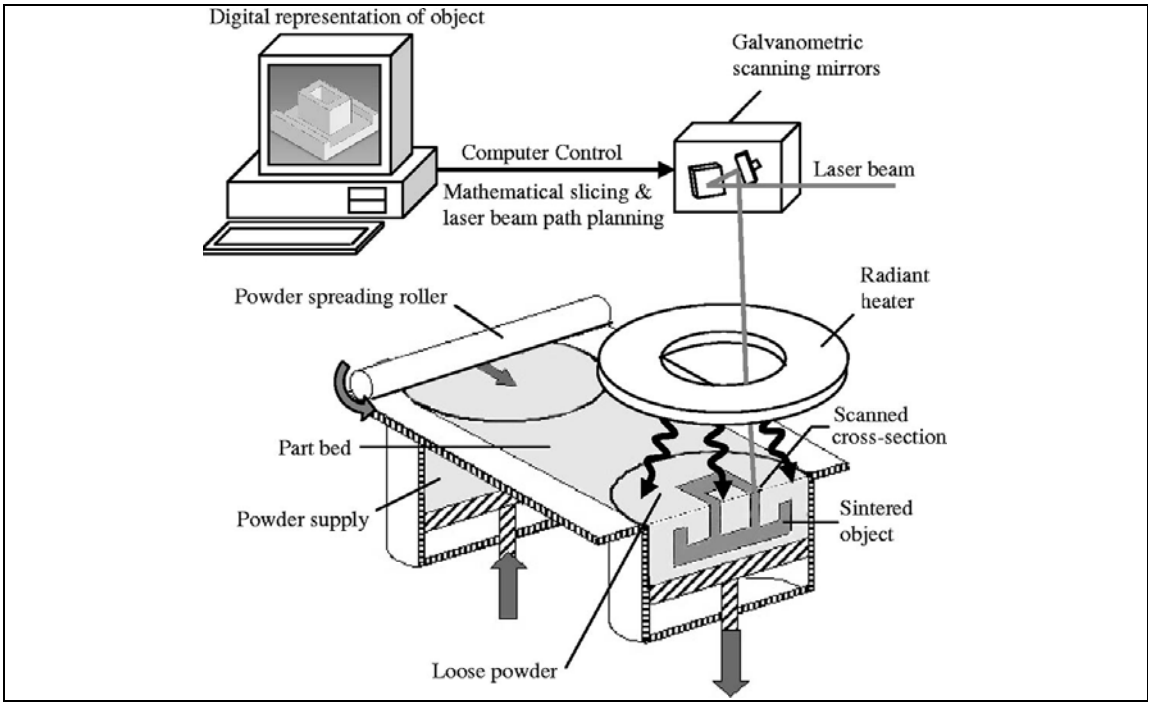

Figure 3 Schematic diagram of the SLS Process [7]

The aim of undergoing this exercise was to explore a wide range of laser powers and scan speeds and to identify the combination that yielded the highest flexural modulus and flexural strength. Specimens made with combinations of laser powers and scan speeds as mentioned above were fabricated and subjected to flexural testing. The combination that yielded specimens with the highest flexural modulus and flexural strength were used as a starting point for subsequent "refining" of the parameters. The range of parameters investigated for the polymer powder and the composite powder are summarized in Table 2.

Process parameter	Nylon 12	Nylon 12-carbon black
Laser power	3W-7W (intervals of 1W)	3W-7W (intervals of 1W)
Laser scan speed	30 in/s – 60 in/s (intervals of 10 in/s)	30 in/s – 60 in/s (intervals of 10 in/s)
Laser scan spacing	152.4 μm	152.4 μm
Part-side temperature set-point	172 ^{o}C	174 ^{o}C
Powder feed temperature set-point	80 ^{o}C	80 ^{o}C
Roller speed	3 in/s	3 in/s
Powder layer thickness	101.6 μm	101.6μm

Table 2 Summary of process parameters investigated for processing Nylon 12 and Nylon 12 – carbon black composite powders

Characterization of Nanocomposite Properties

The tensile and flexural properties of the composites were characterized using an UTS testing machine at a test speed of 2.54mm/min and1.27mm/min respectively. The impact strength was determined using a pendulum impact tester. All the tests were performed according to ASTM. The electrical conductivity was measured using the four probe technique. In addition to the above properties the porosity of the composites made by SLS was also determined because obtaining dense and high quality parts by SLS is the most common challenge. Each of the flexure test specimens were cleaved parallel to the build direction using a single-edged razor blade. A black colored wax was applied on the surface of the cleaved Nylon 12 parts. The wax remained in the void spaces when the excess was wiped off and this increased the contrast when viewed under an optical microscope. In the case of the cleaved Nylon 12/carbon black parts, the pores were clearly distinguishable under an optical microscope and hence there was no need to treat the cleaved surface. Fifty photomicrographs were taken from each test specimen and analyzed using ImageJ [8] image analysis software.

Results and Discussion

Porosity of SLS Made Nanocomposites

Parts made of Nylon 12 and Nylon 12 – carbon black were fabricated using the process parameters mentioned in Table 1 and subjected to flexure testing and porosity measurements using optical microscopy. A combination of 3W and 30 in/s yielded the highest flexural modulus (1750 MPa) for the Nylon 12 specimens whereas a combination of 4W and 30 in/s yielded the highest flexural modulus (1448 MPa) for the Nylon 12 – carbon black parts. These parts had a density ranging between 94% - 98%. Optical micrographs of the cleaved surfaces of the Nylon 12 parts and the Nylon 12 – carbon black parts are shown in Figure 4. During the processing of the Nylon 12 – carbon black composite powder by SLS, a glow was observed from regions of the powder bed that were being scanned. This can probably be attributed to the laser induced light emission of carbon black [9, 10]. Woicke et al [9] also observed that the polymer in the immediate vicinity of the carbon black was getting locally heated. In order to reduce or possibly avoid the local heating and accompanying degradation of the polymer we decided to investigate the flexural properties and porosity of parts made at 2W and 15 in/s (by reducing both the laser power and scan speed by half we have maintained the power/scan speed ratio thereby maintaining the same level of energy density). The flexural modulus of the parts made at 2W and 15 in/s was 1454 MPa. A significant improvement in part density was not observed. However, the thickness of the part (dimension parallel to the build direction) was closest to the design dimension. This observation can be explained by the fact that a lower laser power results in fewer particles from getting fused to the bottom of the first layer of the part. Hence, a combination of 2W and 15 in/s was chosen for processing Nylon 12 – carbon black using SLS.

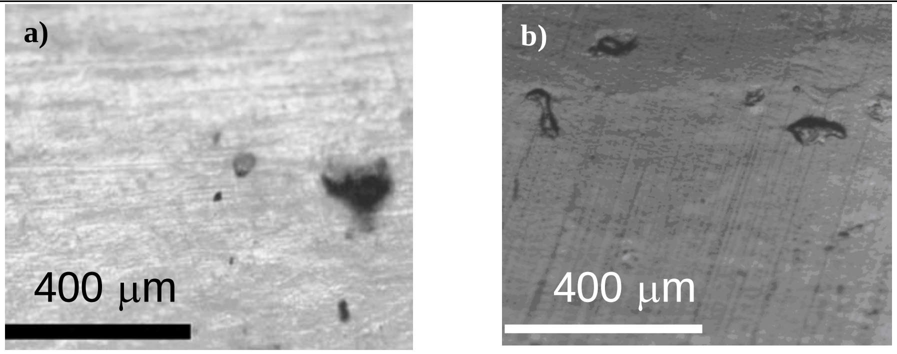

Figure 4 Optical micrograph of cleaved surfaces of a) Nylon 12 b) Nylon 12 – carbon black (scale bar corresponds to 200μm)

Mechanical properties and electrical conductivity

The flexural modulus, tensile modulus, impact strength and the electrical conductivity of the six systems is summarized below in Table 3. As indicated in Table 3, the tensile modulus and flexural modulus of the Nylon 12 parts made by SLS is greater than the modulus of parts made by injection molding. This can be due to a couple of reasons. The parts made by SLS remained at an elevated temperature (approximately 173^{o}C) during the build stage (approximately one hour) for a significantly greater time than the parts made by injection molding where the temperature drops off from the melt state to room temperature in a matter of minutes. This could result in larger spherulites in the case of PA SLS since the radius of the spherulite is strongly dependent on the thermal history of the part [11]. A larger spherulite size has been shown to result in a higher modulus and lower strength in the case of neat polymers [12]. This observation seems to be applicable to the results from this study. As seen in Table 3, the impact strength of the PA Ex-IM system is greater than the PA SLS system. However, the error bar is significantly higher in the case of the PA Ex-IM system. This could possibly be due to differences in the size and spatial distribution of the spherulitic regions in the amorphous regions. Preliminary DSC and XRD results indicate very small differences in the degree of crystallinity and the thickness of crystalline lamellae in the PA Ex-IM and PA SLS systems. The other possible reason for the significant difference in the flexural and tensile moduli of the PA SLS and PA Ex-IM systems is sub-optimal injection molding process parameters (such as barrel temperature, mold temperature, injection pressure and packing pressure). SEM imaging of the fracture surfaces of the PA Ex-IM system confirms the presence of long cracks that possibly correspond to the cooling isotherms of the molten material as it cools down inside the mold during the packing stage.. This might be a result of the low packing pressures available in the micro-injection molding machine used in this study and a possible reason for the low tensile and flexural moduli.

	PA Ex-Im	PA-4CB Ex-Im	PA-4CB Ex-Im (melt mixing)	PA-4CB Ex-Im (LE)	PA-SLS	PA-4CB SLS
Flexural modulus (MPa)	1352±35	1472±40	1491±31	1606±88	1750±10	1454±75
Tensile modulus (MPa)	1273±61	1364±87	1392±39	1382±40	1728±44	1042±84
Impact strength (J/m)	31±9	28±4	12±2	20±3	22±3	23±1
Electrical conductivity (S/cm)	3.58E-10 ±1.73E-10	3.09E-10 ±5.66E-11	6.13E-10 ±3.75E-10	2.70E-10 ± 1.09E-10	3.7E-10 ±1.4E-10	3.17E-3 ± 1.52E-4

Table 3 Summary of flexural moduli, tensile moduli, impact strength and electrical conductivity of the six systems

The flexural properties of the four PA–4CB composite systems are shown in Table 3. The tensile and flexural moduli of the three PA-4CB systems prepared by the melt mixing method are greater than the PA Ex-IM system. However, the flexural and tensile moduli of the PA-4CB SLS system is less than that of the PA SLS system. Similar results have been obtained for low loading of nanosilica powder in Nylon11/nanosilica nanocomposites prepared by SLS [13] but the reasons for these observations are still not clear. Unlike in the case of neat polymers, the modulus of nanocomposites is not a simple function of spherulite size and degree of crystallinity but also involves other factors such as lamella thickness, crystalline long order, properties of the filler and state of dispersion and distribution of the filler in the composite [12]. Another observation from Table 3 is that the flexural properties of the PA-4CB Ex-IM (LE) system are not significantly different from the PA-4CB Ex-IM system. This implies that the differences in properties of the composites prepared by SLS and melt mixing are due to the manufacturing process itself and not due to possible changes in reinforcing properties of the carbon black due to interaction with the CO_2 laser in the SLS process.

The electrical conductivity of the six systems is shown in Table 3. The electrical conductivity of the PA-4CB SLS system is seven orders of magnitude higher than the electrical conductivities of the five other systems. SEM imaging of the fracture surfaces of the PA-4CB SLS system show the presence of a segregated structure with regions rich in carbon black. These carbon black rich regions might be forming conductive networks that result in a higher conductivity. In contrast, the PA-4CB Ex-Im system does not have any such region that is rich in carbon black. The high shear forces in the extruder result in the break-up of the carbon black agglomerates and cause the particles to be more uniformly dispersed. The breakdown of the agglomerates and more uniform dispersion prevents thecarbon black particles from forming a conductive network thus resulting in a conductivity comparable to the neat polymer. Further SEM and TEM imaging is underway to further develop this theory.

Conclusions

A Nylon 12 – (4 wt. %) carbon black composite was successfully processed using selective laser sintering. The SLS process parameters were optimized in order to maximize the flexural modulus and flexural strength. The tensile and impact properties of the composites were evaluated. The optimized parameters yielded parts that were nearly fully dense. The mechanical properties of parts made by SLS were compared to those made by melt mixing/injection molding. The tensile and flexural moduli of the Nylon 12 parts made by SLS were higher than those made by injection molding. Preliminary XRD and DSC results indicate that the degree of crystallinity and the width of the crystalline lamellae are comparable in the PA SLS and PA Ex-IM systems. An estimation of size of the spherulitic regions in various systems through polarized optical microscopy is necessary in order to completely understand the variation in mechanical properties. The Nylon 12 –carbon black composites made by SLS and injection molding had comparable mechanical properties. The addition of carbon black particles that were exposed to the laser prior to melt mixing did not have a significant effect on the mechanical properties. This implies that the carbon black was not degraded during the SLS process. The electrical conductivity of the six systems was investigated. The electrical conductivity of the PA-4CB SLS system was 7 orders of magnitude higher than the electrical conductivity of the five other systems. Preliminary SEM images of the fracture surfaces of the various systems indicate the presence of carbon black rich regions in the PA-4CB SLS system. This highly segregates structure is believed to be responsible for the enhanced electrical conductivity.

Acknowledgements

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