Composites Science and Technology 71 (2011) 506–510

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Mechanical and microstructural properties of Nylon-12/carbon black composites: Selective laser sintering versus melt compounding and injection molding

Siddharth Ram Athreya [1], Kyriaki Kalaitzidou, Suman Das *

Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0405, USA

ARTICLE INFO

Article history:
Received 23 July 2010
Received in revised form 8 December 2010
Accepted 22 December 2010
Available online 25 December 2010

Keywords:
A. Nano composites
B. Mechanical properties
E. Extrusion
E. Injection molding
E. Sintering

ABSTRACT

Composites of Nylon-12 reinforced with 4 wt.% carbon black (CB) manufactured by selective laser sintering (SLS) are compared in terms of flexural strength and flexural modulus, tensile strength and tensile modulus, and impact strength to composites made by extrusion and injection molding (Ex-IM). The Nylon-12 system made by SLS had 25% and 35% higher flexural and tensile modulus, respectively, compared to the Nylon-12 system made by Ex-IM and ~10% higher strength. However, upon addition of CB both the modulus and the strength of the composites made by SLS were significantly lower compared to composites made by Ex-IM. This is due to the poor dispersion of nanoscale CB and due to the higher porosity of the composites made by SLS, which also explains the relatively low impact strength observed. Based on XRD and DSC studies, it is concluded that the composites made by the two processing methods did not differ significantly in their crystallization characteristics such as the degree of crystallinity, crystal type, and lamellar thickness. However, it was found that CB acted as a nucleating agent for Nylon-12 when Ex-IM was used, leading thus to smaller but more numerous polymer crystals.

1. Introduction

Composites of polymers filled with nanoparticles are a radical alternative to conventional micro-composites showing enhanced overall performance at low reinforcement loadings. The most widely used processing methods for such composites have been melt-mixing and injection molding [1–4]. However, many applications require complicated part geometries which cause difficulties during mold design and filling. An alternative approach to manufacturing nanoparticle-filled polymer composites is the selective laser sintering (SLS) process, a type of solid freeform fabrication (SFF) or layered manufacturing (LM) technique in which a part is built layer-by-layer using powdered materials, a radiant heater and a computer controlled laser [5,6].

Recent research in SLS processing of polymers has mainly focused on optimizing the process parameters and their effects on the mechanical properties of components made from polyamide based material systems [7–10]. SLS has also been used to process nano-Al_2O_3 polystyrene composites [11] and nylon 6-clay reinforced composites [12]. The layer-by-layer manufacturing approach of SLS was exploited to fabricate one-dimensional functionally graded components made from blends of Nylon-11 and glass beads [13], as well as blends of Nylon-11 and nanosilica powder [14]. However, only one previous study reported by the authors [15] has focused on thermally and electrically conductive fillers with an aim of enhancing the thermal and/or electrical conductivity of the resulting composite.

The manufacturing technique and the processing conditions have a significant effect on the mechanical properties of polymer composites because they dictate the degree of dispersion and distribution of the filler in the polymer matrix. In the case of electrically conductive fillers, the manufacturing process has a significant effect on the percolation threshold and electrical conductivity of the composites; properties that depend on the orientation, dispersion, inter-particle spacing [16–18], and the filler's aspect ratio [19,20] within the polymer matrix. In our earlier study, the SLS process parameters were optimized in order to maximize the flexural modulus of a Nylon-12/CB (4 wt.%) composite [15]. The present study represents the second stage of the investigation and provides a comparison between SLS and melt-mixing/injection molding in terms of the flexural strength and the flexural modulus, the tensile strength and the tensile modulus, and the impact strength of the composites. The state of dispersion of carbon black, the crystallization behavior of the polymer, and the porosity of the composites are investigated in order to understand the observed

* Corresponding author.
E-mail address: sumandas@gatech.edu (S. Das).
[1] Present address: Dow Chemical Company, 1616 Building, Midland, MI 48667, USA.

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doi:10.1016/j.compscitech.2010.12.028

differences in the mechanical properties. Melt-mixing and injection molding is chosen as the "baseline" fabrication method due to its simplicity and widespread use in the polymer processing industry.

2. Material and methods

2.1. Materials

Nylon-12 powder with the trade name VESTOSINT® X 1553 (Evonik Industries, Essen, Germany) and with melting temperature in the range of 176–184 °C was used in this study. Nanosized carbon black with the trade name KETJENBLACK EC-600 JD (Akzo-Novel Polymer Chemicals LLC) with a highly agglomerated structure, high degree of porosity and a surface area of 1400 m^2/g, as reported by the manufacturer was also used.

2.2. Processing

2.2.1. Compounding

High wear-resistant zirconia grinding media (Glenmills Inc., Clifton, New Jersey, USA) having a diameter of 5 mm were used to ball-mill the CB pellets in a 784 AVM rotary tumbler (US Stoneware, Ohio, USA) for 24 h. The ball-milled CB was sieved using a US standard 140 mesh sieve with 106 μm opening and then was blended with the pure Nylon-12 powder (4% by weight of CB) in a rotary tumbler for 24 h. The Nylon-12/CB composite powder as well as the pure Nylon-12 powder were processed in a Sinterstation® 2000 (DTM Corporation, Austin, Texas, now 3D Systems Inc., Rock Hill, South Carolina, USA) selective laser sintering machine.

2.2.2. Selective laser sintering

The SLS process starts with a CAD model of the part to be built that is subsequently sliced at discrete intervals (100–200 μm). The resulting cross-sections are scanned onto a preheated bed of powder using scanning algorithms that plan the path of the laser. 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. The most important parameters in the SLS process, that affect the quality and microstructure of the resulting part along with the set values used in this study, which were optimized in a prior study [15] are shown in Table 1.

2.2.3. Extrusion–injection molding

A DSM Micro 15 cc Compounder (Xplore, Barrington, Illinois, USA), comprising a vertical, co-rotating twin-screw micro-extruder was employed for melt-mixing. A mixing time of 3 min, a screw speed of 200 rpm and a barrel temperature and feed temperature setpoint of 190 °C were employed. A Daca micro-injector (DACA Instruments, Santa Barbara, California, USA) with a cylinder temperature of 190 °C, mold temperature of 90 °C and injection pressure of 110 psi was used for molding. It is important to note that the DSM equipment used is sufficient for screening experiments but has limitations due to the low pressure used when attempting to relate this to a large-scale extrusion-injection molding system.

Three compounding methods were investigated in case of injection molded composites to verify that the results truly reflect the differences between SLS and extrusion–injection molding. The composites made by the three compounding methods are: (i) PA-4CB Ex-IM, composite powder prepared by rotary tumbling was fed into the extruder; (ii) PA-4CB Ex-IM (melt mixing), CB pellets melt-mixed directly with the Nylon-12 powder in the extruder, and (iii) PA-4CB Ex-IM (LE), ball-milled CB was irradiated with the CO_2 laser (3.8 W, 0.762 m/s) and subsequently melt mixed with Nylon into the extruder.

Table 1
Summary of process parameters investigated for processing Nylon-12 and Nylon-12/carbon black composite powders.

Process parameter	PA SLS	PA-4CB SLS
Laser power	3.08 W	3.80 W
Laser scan speed	0.762 m/s (30 in./s)	0.762 m/s (30 in./s)
Laser scan spacing	152.4 μm	152.4 μm
Part-side temperature setpoint	172 °C	174 °C
Powder feed temperature setpoint	80°C	80 °C
Roller speed	0.0762 m/s (3 in./s)	0.0762 m/s (3 in./s)
Powder layer thickness	101.6 μm	101.6 μm

2.3. Characterization

The tensile (ASTM D638) and flexural (ASTM D790) properties of the composites were characterized using an UTS testing machine at a test speed of 2.54 mm/min and 1.27 mm/min, respectively. The impact strength (ASTM D256) was determined using an Izod pendulum test. Fracture surfaces of composites obtained by Izod impact testing were used to study the morphology and the CB dispersion using a Zeiss Ultra 60 (Carl Zeiss, Oberkochen, Germany) scanning electron microscope (SEM) at 5 kV–20 kV.

The crystallinity characteristics of the neat polymer and composites were assessed through the X-ray diffraction (XRD) patterns obtained using a X'Pert Pro Alpha 1 (PANalytical, Almelo, Netherlands) diffractometer in the Bragg–Brentano geometry using a monochromatic, filtered Cu Kα1 radiation. A Seiko 220 (Seiko Instruments, Chiba, Japan) differential scanning calorimeter (DSC) was used to determine the melting and crystallization behavior.

The true density and envelope density of the polymer and composites were determined using a Geopyc 1360 and a Accupyc II 1340 (Micromeritics, Norcross, Georgia, USA) pycnometer, respectively. The envelope density was calculated by a displacement technique using a quasi-fluid comprised of small, rigid spheres approximately 25 μm in diameter. The true density was calculated using a nitrogen gas displacement technique. Finally, the porosity of the samples was calculated as function of the true and envelope densities. The samples were created by cutting flexure test specimens along the width with a razor blade and polishing the obtained surfaces using P1200 and P2400 grade sandpaper for 15 min.

3. Results and discussion

3.1. Flexural and tensile properties

The flexural and tensile properties of the six different systems are shown in Fig. 1a and b, respectively. Both the flexural and tensile moduli follow similar trends except for the PA-4CB SLS system, which shows a very low tensile modulus and strength indicating insufficient load transfer. Both moduli are greater in case of the PA SLS system compared to the PA Ex-IM system due to the low pressure used in injection molding. However, the flexural and tensile moduli of the PA-4CB SLS composite are less than those of the composites made by injection molding. Moreover, the comparable values of flexural strength for all the four systems manufactured by extrusion-injection molding indicate weak polymer-filler interactions.