

Full Length Research

Graded PA6/PA12 blends prepared by selective laser sintering

Gean Vitor Salmoria*, Janaina Lise Leite and Rodrigo Acacio Paggi

CIMJECT Laboratory, Department of Mechanical Engineering, Federal University of Santa Catarina, 88040-900, Florianópolis, Santa Catarina, Brazil.

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In this study, the manufacturing of graded PA6/PA12 blends by selective laser sintering (SLS) was investigated. Sintered blend specimens were analyzed by scanning electronic microscopy and flexural tests. The PA6/PA12 parts with functionally-graded composition in the Y and Z directions were built by SLS. Information on the pure component properties and the microstructure and mechanical properties of the sintered blend specimens was used for the design and fabrication of the PA6/PA12 parts with functionally-graded compositions. These parts showed different microstructures depending on the process parameters and blend compositions, which demonstrates the potential of the SLS process for manufacturing parts with property gradients.

Key words: Graded blends, PA6/PA12, laser sintering.

INTRODUCTION

Graded material (GM) is a concept in material design characterized by variations in the composition and morphology of a material, leading to variations in its chemical, thermal, electrical, optical and/or mechanical properties (Kieback et al., 2003; Jiang et al., 2004). The gradient can be formed to satisfy specific necessities or functions according to the use of a component. Graded materials have applications in different fields, such as electrical and mechanical engineering and the aerospace, automobile and medical areas (Shishkovsky, 2001; Calder, 2001).

Additive manufacturing (AM) technology is an advanced manufacturing process that offers many advantages and possibilities for the fabrication of complex three-

dimensional products through material addition. Selective laser sintering (SLS) is a AM process that have the capability of fabricating complex parts that are made with the functionally graded material (FGM) in a single manufacturing process. (Shishkovsky, 2001; Calder, 2001; Joshi et al., 2012). In this process a solid object is created layer-by-layer by sintering powder materials using infrared laser beams. One of the advantages of the SLS process is the ability to sinter a great variety of metals, ceramics and polymers (Joshi et al., 2012; Mahamood and Akinlabi, 2017). Polymeric blends and composites offer an alternative way to obtain SLS parts with specific structures and properties, permitting the development of new applications in the graded materials

*Corresponding author. E-mail: gean.salmoria@ufsc.br.

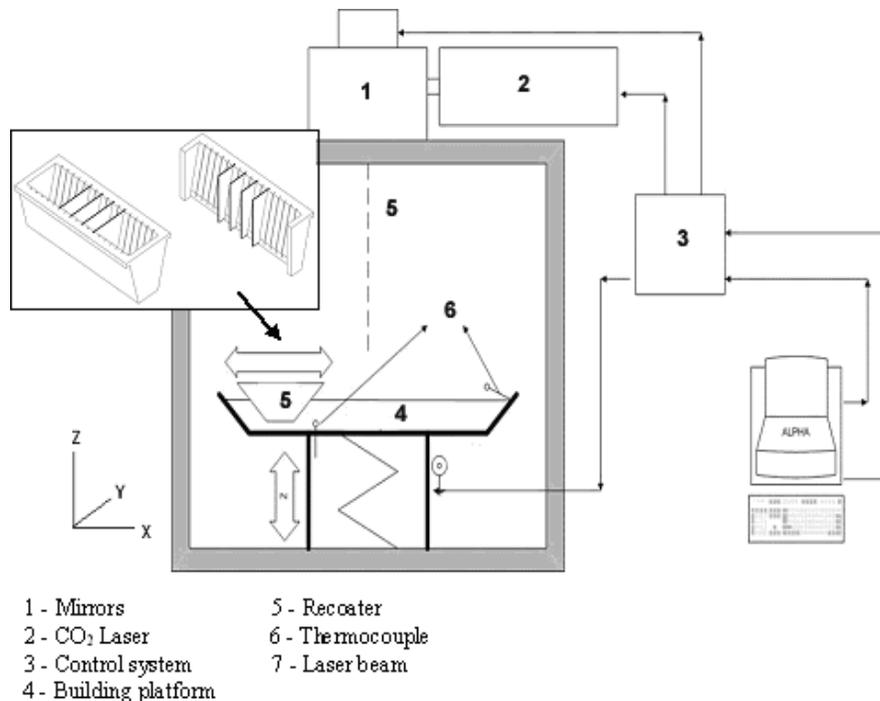


Figure 1. Diagram of SLS equipment, showing in detail the recoating device used for the deposition of different blend compositions.

fields (Haseung and Suman, 2006, 2008; Leite et al., 2010, 2012; Yusufu et al., 2014;). Polyamides are polymers commonly used in antifriction components due to their mechanical and tribological properties. Polyamide 6 (PA6) and polyamide 12 (PA12) present different chemical structures, mechanical and tribological properties (Palabiyik and Bahadur, 2000; Kim et al., 2012), and their mixtures can produce blends for special tribological applications. In this study the processing of a binary polar system containing PA6 and PA12 by SLS was investigated. The microstructural and mechanical characterization of different blend compositions and that manufacture by SLS of graded PA6/PA12 blend components with potential application in antifriction materials are described herein.

MATERIALS AND METHODS

Materials and manufacturing procedure

The polymers used were polyamide 6 MAZMID B260 (Mazzafero Tecnopolímeros; PA6) and polyamide 12 (PA2200, EOSINT; PA12) and the average particle sizes were 150 and 60 μm , respectively. The blend compositions were prepared through the physical mixing of PA6 and PA12 in PA6/PA12 proportions of 20/80, 50/50 and 80/20 (w/w). The sintered specimens (dimensions 35 \times 5 \times 1.4 mm) of PA6, PA12 and PA6/PA12 blends were prepared on the building platform of a prototype SLS machine (Figure 1) using 10 W RF-excited CO₂ (wavelength 10.6 μm ; laser beam diameter 250 μm). The processing parameters are listed in Table 1.

In order to build parts with a graded composition in the Y and Z directions (coordinates showed in Figure 1), the pure material and the physical mixtures were placed into the recoating device (part number 5 in Figure 1) for powder deposition of the materials with different compositions.

The PA6/PA12 part with functionally-graded composition in the Y direction (dimensions 45 \times 35 \times 3 mm) was manufactured using a medium energy density (0.242 J/mm²). A circular part with functionally-graded composition in the Z direction (dimensions: inner radius 10 mm, outer radius 25 mm, thickness 5 mm) was manufactured using energy densities which varied as a function of the layer compositions. This part is a model of an antifriction component. The dimensions of the built parts were determined in order to define the manufacturing process accuracy. The graded directions Y and Z (Figure 1) were chosen due to the facility of control over the composition by deposition system (Y direction) and by the layer deposition (Z direction).

Microstructural and mechanical analyses

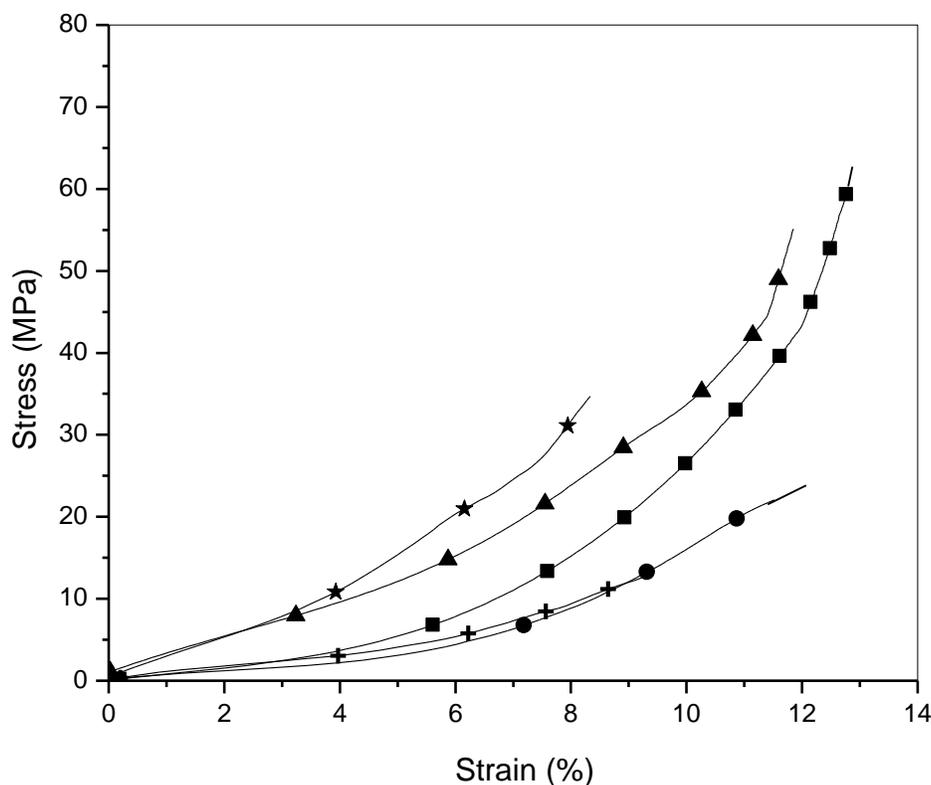
The specimen microstructures were investigated using a Philips XL30 scanning electron microscope. The specimens were coated with gold in a Bal-Tec Sputter Coater SCD005. The mechanical analysis was carried out in a TA Instruments DMA Q800 dynamic-mechanical analyzer. A single cantilever clamp was used in the flexural test. The stress versus strain test was performed at 30°C with a force rate of 2 N/min up to 18 N (maximum force).

Dimensional and melt flow measurements

The dimensional measurement were conducted in triplicate with an high-accuracy Mitutoyo micrometer based on the DIN 16 901

Table 1. Processing parameters for the preparation of PA6/PA12 blends by SLS.

PA6/PA12 blend	Laser power (W)	Energy density (J/mm ²)	Powder bed temperature (°C)
100/0	2.34	0.210	120
80/20	2.52	0.226	120
50/50	2.70	0.242	120
20/80	2.97	0.266	120
0/100	3.33	0.299	140

**Figure 2.** Stress versus strain curves for the sintered PA6/PA12 blend specimens: (■) 100/0, (●) 80/20, (+) 50/50, (★) 20/80, (▲) 0/100.

standard for plastic part measurements. The determining of the melt flow index of polyamides were conducted in a Zwick extrusion plastometer based on the ASTM D1238 standard.

RESULTS AND DISCUSSION

Figure 2 shows the stress versus strain curves for the pure components and the PA6/PA12 blends (80/20, 50/50 and 20/80) obtained by flexural mechanical analysis. Table 2 shows the average values for the flexural modulus, flexural strength and elongation at break for PA6, PA12 and the PA6/PA12 blends. The average values for the flexural modulus obtained for PA6 and PA12 were 166.6 and 205.0 MPa, respectively, and the average values for the ultimate strength were 62.4

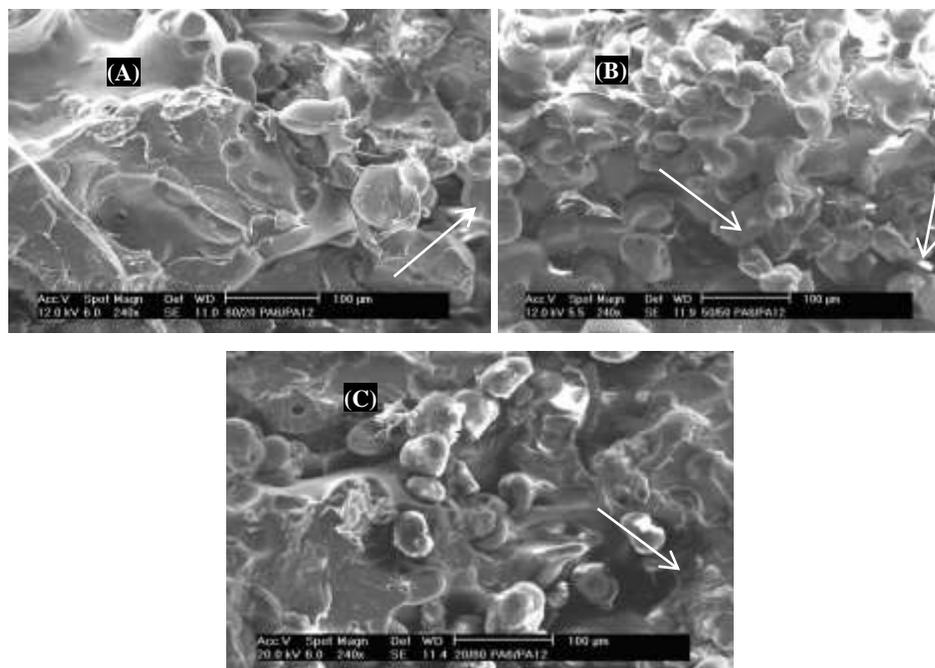
and 57.74 MPa, respectively. The sintered PA6 specimen had a lower value for the flexural modulus than the sintered PA12 specimen in the mechanical tests.

The PA6/PA12 80/20 blend specimen showed average values for the flexural modulus and flexural strength of 110.0 and 24.4 MPa, respectively, these being lower than the respective values for PA6. This behavior is probably due to the low chemical affinity between the two polar polymers, that is, the PA6 and PA12 particles. The PA6/PA12 50/50 blend specimen showed average values for the flexural modulus and flexural strength of 126.0 and 12.9 MPa, respectively. The low value for the flexural strength provides evidence of the low affinity between the PA6 and PA12 phases.

The average values for the flexural modulus and flexural strength for the PA6/PA12 20/80 blend specimen

Table 2. Mechanical properties of PA6/PA12 blends.

PA6/PA12 blend	Flexural modulus(MPa)	Flexural strength(MPa)	Elongation at break(%)
100/0	166.6 ± 77.8	62.4 ± 16.0	10.9 ± 3.7
80/20	110.0 ± 60.0	24.4 ± 11.2	10.6 ± 1.3
50/50	126.0 ± 52.5	12.9 ± 4.3	8.6 ± 0.8
20/80	225.7 ± 23.3	30.4 ± 3.2	9.8 ± 1.2
0/100	205.0 ± 29.3	57.7 ± 10.3	11.5 ± 1.3

**Figure 3.** Micrographs of the surface fracture for PA6/PA12 specimens: (A) 80/20, (B) 50/50 and (C) 20/80 w/w composition, at a magnification of 240X.

were 225.7 and 30.4 MPa, respectively. The higher flexural modulus and flexural strength are due to the greater PA12 content in the blend in comparison to the other blends. The values calculated for the standard deviation of the flexural modulus and flexural strength results for PA6 and the PA6/PA12 20/80 and 50/50 blend specimens indicated the presence of defects (pores) due to the particle packing process, which influences the mechanical behavior of the material.

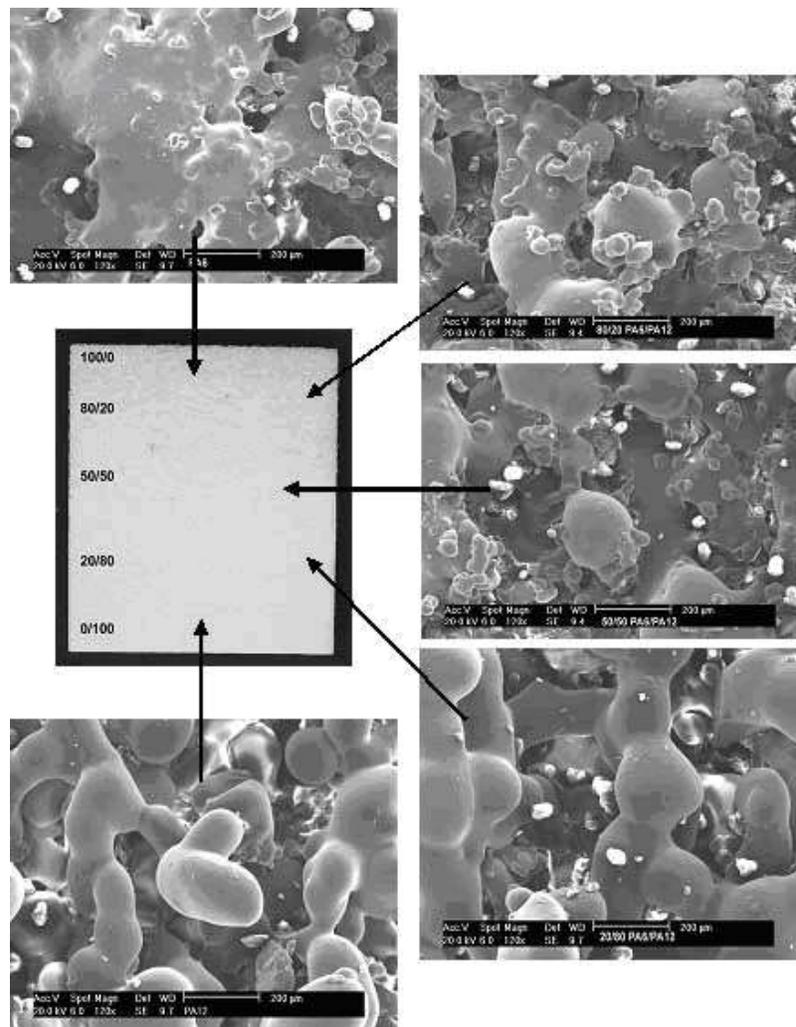
The fractured surfaces of the PA6/PA12 specimens with compositions of 80/20, 50/50 and 20/80 (w/w) at a magnification of 240X are shown in Figure 3. The PA6/PA12 80/20 specimen showed microstructural features indicating PA6 coalescence, large interconnected pores and PA12 particles dispersed in coalescent regions. The presence of PA12 domains encapsulated in regions of PA6 coalescence demonstrated the low interaction between the PA6 and PA12 phases. The polyamides present the same chemical

function, but a different extension of methylene groups (CH₂) in each chain, resulting in a low attraction force and immiscibility in the blend structures. The PA6/PA12 50/50 specimen showed low coalescence of the PA6 phase, as observed in the surface analysis. The PA6/PA12 20/80 specimen showed the joining of the PA12 particles through the formation of necks and coalescence, resulting in a porous sintered PA12 matrix. This porous microstructure is formed under the moderate viscous flow of PA12. The melt flow index (MFI) for PA6 is higher than that for PA12 at 230°C (Table 3), which influenced the blend microstructure formed.

Based on the information obtained regarding the microstructure and mechanical properties, the PA6/PA12 parts were designed with functionally-graded compositions in the Y and Z directions (Figures 4 and 5). In Figure 4, it can be observed that the microstructure of the part is gradually modified as a function of the composition, which generates a gradient in the

Table 3. Melt flow index values for PA6 and PA12 at different temperatures.

PA6/PA12 blend	Temperature (°C)	MFI (g/10 min)
PA6	230	23.2
PA6	260	38.3
PA6	278	45.8
PA12	200	2.38
PA12	230	17.9
PA12	260	41.8

**Figure 4.** The PA6/PA12 part with a functionally-graded composition in the Y direction and surface micrographs of regions with different compositions: PA6/PA12 100/0, 80/20, 50/50, 20/80 and 0/100.

mechanical properties along the part. The PA6/PA12 blends in compositions of 100/0 and 80/20 showed regions with the formation of a co-continuous phase of PA6. The PA6/PA12 blends in compositions of 50/50, 20/80 and 0/100 had regions with the partial coalescence

of the PA12 particles. A circular part, as a model of an antifriction component, was designed and built in order to investigate the manufacture of gradients in the Z direction by SLS (Figure 5).

The laser power used in the circular component

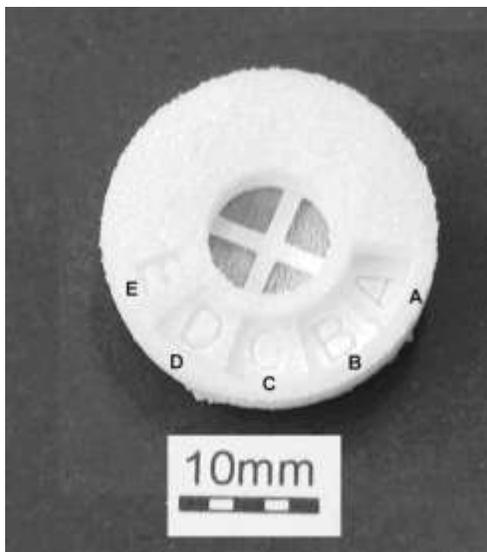


Figure 5. PA6/PA12 part with graded composition in the Z direction: (A) 0/100, (B) 20/80, (C) 50/50, (D) 80/20 and (E) 100/0.

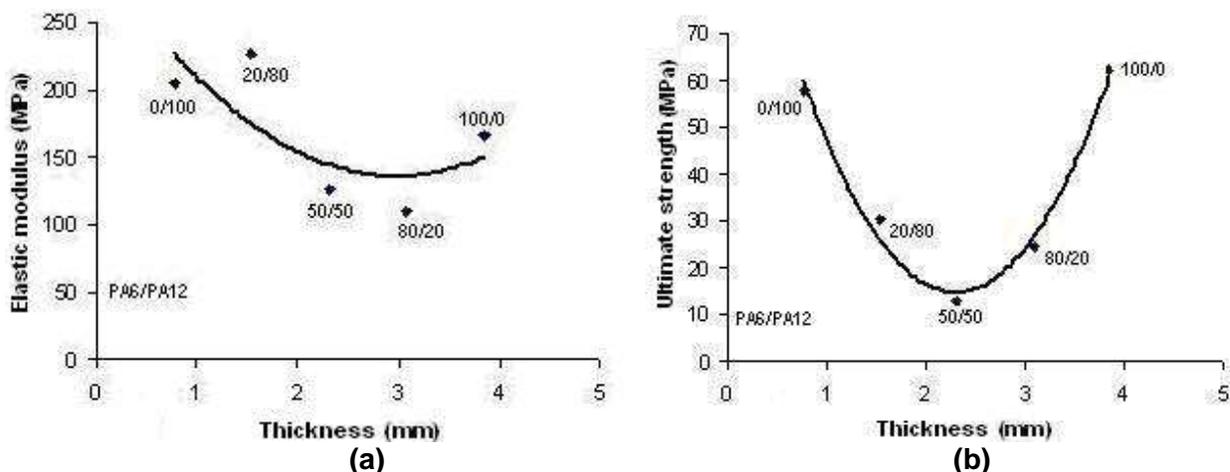


Figure 6. The mechanical properties profile of the PA6/PA12 parts with Z-graded composition: (A) flexural modulus versus thickness and (B) flexural strength versus thickness.

manufacturing was dependent on the composition of each layer, according to the parameters used for the PA6/PA12 blend specimens (Table 1). The fabrication accuracy was determined by comparing the computational model and final part dimensions. Deviations of 6.0, 1.08 and 23.0% were observed for the inner radius, outer radius and thickness of the part in relation to the computational model.

The mechanical properties profile of the PA6/PA12 part with a Z-graded composition (Figure 6) was estimated from the mechanical properties of the PA6/PA12 blends (Table 2). The flexural modulus (Figure 6A) showed a decrease with an increase in the PA6 content in the

composition, as expected. Figure 6B shows the flexural strength as a function of the thickness. The curve trend shows a lower flexural strength for PA6/PA12 blends with compositions of 80/20, 50/50 and 20/80 in relation to the pure polymers (PA6/PA12 100/0 and 0/100), due to the low toughness and phase separation observed for these blends.

Conclusion

Information on the microstructural and mechanical properties of pure polymers and blend specimens was

used for the design and fabrication of PA6/PA12 parts with graded composition. The melt flow and the particle size and shape had a strong influence on the formation of the microstructure of sintered polymers and blends produced by the selective laser sintering. The microstructure of the blend specimens showed the characteristics of the pure polymers proportionally to their content. The blend immiscibility was evidenced in the fracture analysis, where regions with PA12 particles weakly adhered to the PA6 phase were observed. The mechanical tests for the PA6/PA12 blends showed that the flexural strength values were lower than those for the pure polymers, due to the low affinity between the PA6 and PA12, particularly in the case of the PA6 matrix originated from larger particles. The graded PA6/PA12 parts showed a variation in their microstructures as a function of the process parameters and the blend composition, allowing control of the part properties. The results obtained demonstrated the potential of the SLS process to control the manufacturing of blend parts with graded structures and mechanical properties.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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