THE MANUFACTURING AND MECHANICAL PROPERTIES OF PA6/PA12 BLENDS BY SELECTIVE LASER SINTERING

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Abstract: This study evaluates the preparation of a polyamide 6 (PA6) and polyamide 12 (PA12) blends using the selective laser sintering process (SLS) with pulsed CO₂ laser (10W). The blends were prepared by the physical mixing of PA6/PA12 20/80, 50/50 and 80/20 (w/w) and specimen sintering. The blends were characterized by scanning electronic microscopy (SEM) and dynamical mechanical analyses (DMA). The PA6/PA12 immiscibility was evidenced by cryogenic fracture analysis and it resulted in lower ultimate strength of the blends compared to the pure polymers. The blends specimen showed different microstructures and mechanical properties according the proportions of the components and the process parameters permitting the development of new area applications using rapid manufacture technologies.

Introduction

Selective laser sintering (SLS) is a commonly used process in rapid prototyping (RP) field and has proved to be suitable for various applications including electronic, mechanic and biomedical areas. SLS is an additive process that produces parts using an infrared laser to selectively sinter (or melts) individual layers of a material in a powder form (polymers, ceramics, metals, composites, etc.) [1,2]. This process is an advanced rapid prototyping technology for the manufacture products in high or medium volumes reducing the production cost and offering advantages such as high geometrical freedom and dimensional precision allowing the manufacturing of parts with well defined details [3-5].

In the SLS process the level of control over the microstructure and mechanical properties of the SLS parts depends on the process parameters (laser power, scan speed, etc.) and the powder properties (particle shape, size distribution, melting flow and laser energy laser absorption)[6, 7]. For metallic, polymer and glass material, sintering has produced many materials/components with unusual microstructure and properties, which can not be obtained using other manufacturing technologies [8]. Polymeric materials in the SLS process offers some advantages over metallic and ceramic materials, which are related to the low processing temperatures, melting flow control and high corrosion resistance. However, the variety of commercial polymeric materials available for the SLS process is restricted, which reduces the options available during the material selection for the manufacturing of parts. Polymeric blends offer an alternative means to obtain SLS parts with
specific structures and properties, permitting the development of new applications [7]. This study investigated the microstructure and mechanical properties of PA6/PA12 blend specimens manufactured by Selective Laser Sintering.

**Experimental**

The polymers used were polyamide 6 MAZMID B260 (Mazzafaro Tecnopolímeros) and polyamide 12 (PA2200 - EOSINT P). The average particle size was 150 µm and 60 µm for the PA6 and PA12, respectively, used in this study.

The blend compositions were prepared through physical mixing in the proportions of 20/80, 50/50 and 80/20 (w/w) of each component. The sintered specimens (dimension: 35 x 5 x 1.4 mm) of PA6, PA12 and PA6/PA12 blends were prepared using a 10W RF-excited CO₂ (wavelength; 10.6 µm; laser beam diameter: 250 µm). The processing parameters are listed in Table 1.

The mechanical analysis, stress versus strain, storage modulus (E’), loss tangent (Tan δ), creep and fatigue test, was carried out using a dynamical-mechanical analyzer - DMA Q800 TA Instruments. The clamp used for the mechanical analysis was single cantilever (flexural test). The stress versus strain test was carried out at 30 °C with a force rate of 2 N/min up to 18N (maximum force). The test to obtain the loss tangent (Tan δ) and storage modulus (E’) curves were performed from -50 °C up to close melting temperature according to the blend compositions. The heating rate was 3 °C/min, frequency: 1Hz and maximum strain: 0,5%. In the creep test a stress was applied so as to generate approximately 50% of the maximum deformation in the rupture, during 10 min and then maintained constant for a time of 20 min in isothermal conditions (30 °C). The fatigue test was carried out using a strain amplitude of approximately 50% of the rupture strain (according the stress x strain curves), frequency 1Hz in isothermal conditions (30 °C). The specimens microstructure fractured during the flexural test (stress versus strain) were investigated using a Phillips XL30 scanning electron microscope (SEM) in order to investigate their fractured surface. The specimens were coated with gold in a Bal-Tec Sputter Coater SCD005.

<table>
<thead>
<tr>
<th>PA6/PA12 (%)</th>
<th>Laser Power (W)</th>
<th>Energy Density (J/mm²)</th>
<th>Scan Speed (mm/s)</th>
<th>Powder bed temperature (°C)</th>
<th>Chamber temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>2.34</td>
<td>0.210</td>
<td>44.5</td>
<td>120</td>
<td>115</td>
</tr>
<tr>
<td>80/20</td>
<td>2.52</td>
<td>0.226</td>
<td>44.5</td>
<td>120</td>
<td>115</td>
</tr>
<tr>
<td>50/50</td>
<td>2.70</td>
<td>0.242</td>
<td>44.5</td>
<td>120</td>
<td>115</td>
</tr>
<tr>
<td>20/80</td>
<td>2.97</td>
<td>0.266</td>
<td>44.5</td>
<td>120</td>
<td>115</td>
</tr>
<tr>
<td>0/100</td>
<td>3.33</td>
<td>0.299</td>
<td>44.5</td>
<td>140</td>
<td>115</td>
</tr>
</tbody>
</table>
Results and Discussion

Figure 1 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. In Table 2 are presented the average values for the elastic modulus, ultimate strength and elongation at break for PA6, PA12 and PA6/PA12 blends. The average values for the elastic modulus presented to PA6 and PA12 were 166.6 MPa and 205.0 MPa and the average values for the ultimate strength were 62.4 MPa and 57.74 MPa, respectively. The sintered PA6 specimens had a lower value for the elastic modulus than sintered PA12 specimen in the flexural tests.

The PA6/PA12 80/20 blend specimens showed average values for the elastic modulus and ultimate strength of 110.0 MPa 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 PA6 and PA12.

The PA6/PA12 50/50 blend specimens showed average values for the elastic modulus and ultimate strength of 126.0 MPa and 12.9 MPa, respectively. The low value for the ultimate strength provides evidence of the low affinity between the PA6 and the PA12 phases.

The average values for the elastic modulus and ultimate strength for the PA6/PA12 20/80 blend specimen were 225.7 MPa and 30.44 MPa, respectively. The higher elastic modulus and ultimate strength is due to the greater PA12 content in the blend in comparison to the other blends.

![Figure 1](image)

*Figure 1 – Stress versus strain curves to the PA6/PA12 blends specimens sintered: (■) 100/0, (●) 80/20, (+) 50/50, (▲) 20/80, (▲) 0/100.*

The results presented by PA6/PA12 blends showed a significant decrease in the ultimate strength in relation to the pure components. This is due to the low chemical affinity (miscibility)
between the polyamides and the existence of pores formed during the compaction and the blend sinterization. The values calculated for the standard deviation for the elastic modulus and ultimate strength results for PA6 and PA6/PA12 20/80 and 50/50 blend specimens indicated the existence of defects (large pores) influencing their mechanical behaviors.

Table 2 – Mechanical properties of PA6/PA12 blends

<table>
<thead>
<tr>
<th>PA6/PA12 Blends</th>
<th>Elastic modulus (MPa)</th>
<th>Ultimate strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>166.6 ± 77.8</td>
<td>62.4 ± 36.0</td>
<td>10.9 ± 3.7</td>
</tr>
<tr>
<td>80/20</td>
<td>110.0 ± 60.0</td>
<td>24.4 ± 11.2</td>
<td>10.6 ± 1.3</td>
</tr>
<tr>
<td>50/50</td>
<td>126.0 ± 52.6</td>
<td>12.90 ± 4.3</td>
<td>8.63 ± 0.8</td>
</tr>
<tr>
<td>20/80</td>
<td>225.7 ± 23.3</td>
<td>30.44 ± 3.2</td>
<td>9.84 ± 1.2</td>
</tr>
<tr>
<td>0/100</td>
<td>205.0 ± 29.3</td>
<td>57.74 ± 10.3</td>
<td>11.56 ± 1.3</td>
</tr>
</tbody>
</table>

The micrographs of the fractured surfaces of the PA6/PA12 blend specimens with compositions of 80/20, 50/50 and 20/80 (w/w) are shown in Figure 3. The PA6/PA12 blend specimen with 80/20 composition had a PA6 co-continuous phase, with PA12 particles adhered to it.

The PA6/PA12 blend specimen with 20/80 composition showed more dense regions due to PA6 and PA12 coalescence. Other regions showed partial coalescence of PA12 particles due to the high viscosity of this polymer under the process conditions. The MFI of PA6 is higher than that of PA12 at 230 ºC (Table 3), which influenced the blend microstructure formation.

The micrographs showed that failures occurred during the flexural test since blend specimens had few regions with plastic deformation. This is due to the low deformation capacity of sintered polyamides under the test condition. The blend immiscibility was confirmed by the fracture analysis in Figures 3d and 3f, where there are regions with more than one phase and the pullout of PA12 particles.
Figure 2 – Micrographs of the surface fracture for PA6/PA12 specimens: (a) and (b) 80/20, (c) and (d) 50/50 and (e) and (f) 20/80 w/w composition at 120x and 240x magnification, respectively.

Table 3 – Melt Flow Index to PA6 and PA12 at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>MFI (g/10 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PA6</strong></td>
<td></td>
</tr>
<tr>
<td>230</td>
<td>23.2</td>
</tr>
<tr>
<td>260</td>
<td>38.3</td>
</tr>
<tr>
<td>278</td>
<td>45.8</td>
</tr>
<tr>
<td><strong>PA12</strong></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>2.38</td>
</tr>
<tr>
<td>230</td>
<td>17.9</td>
</tr>
<tr>
<td>260</td>
<td>41.8</td>
</tr>
</tbody>
</table>
Figure 3 shows the behavior of the storage modulus, $E'$, as a function of temperature for PA6, PA12 and PA6/PA12 blend specimens. PA6 showed a slight decrease in $E'$ up to 50°C, followed by a sharper decrease in the $E'$ value up to 50°C. After 50°C, $E'$ presented a small decrease with the temperature increase. The $E'$ value for PA6 (660 MPa) was lower than that for PA12 (1060 MPa) at -50°C. The $E'$ behavior for PA12 was similar to the PA6 behavior, which presented a decrease in $E'$ up to 20°C, followed by a sharper decrease up to 80°C and after that a less sharp decrease until the PA12 melting point (178°C).

The PA6/PA12 blend specimens had an initial $E'$ values lower than that for pure components. The PA6/PA12 80/20 blend specimen showed $E'$ value lower than that the others blends (470 MPa at -50°C). The $E'$ value for PA6/PA12 80/20 blend specimen presented a small decrease with the temperature increase up to 20°C. From 20°C, $E'$ value decreases rapidly with temperature up to 75°C. In higher temperatures the $E'$ value remain constant until the PA12 melting temperature (178°C).

The PA6/PA12 50/50 blend specimen showed intermediary $E'$ value related to the others blends (770 MPa at -50°C). In this blend was evidence the behavior of pure components, which can be notice that the $E'$ modulus decrease with the temperature increase up to 100°C, as in the case of PA12, and after 100°C the $E'$ value remain the same until PA12 melting temperature, as in the case of PA6. The PA6/PA12 20/80 blend specimen had an initial $E'$ value around 900 MPa, this value is the higher than that the others blends. The $E'$ modulus showed a decrease up to 20°C, followed a great decrease up to 80°C. After 80°C a less sharp decrease up to PA12 melting temperature (178°C) was observed. This blend showed a similar behavior to that of PA12 behavior, due to the PA12 content (80%).

![Figure 3 – $E'$ modulus of pure components (a) and blends PA6/PA12 (b) as a function of temperature.](image-url)
Figure 4 shows the loss tangent $\tan \delta$ for pure components and PA6/PA12 blend specimen, as a function of temperature. PA6 had a glass transition when $\tan \delta$ reached the maximum point in the curve at around 25 °C, relating the $\alpha$ relaxation. This relaxation is caused by segmental motion of the chains, referent to amorphous phase [9, 10]. The $T_g$ value is bellow the usually reported $T_g$ value for PA6 (~ 45 - 60 °C) This fact is probably due the moisture degree that PA6 can absorb. Polyamides can absorb up to 10% of water from the ambient atmosphere and this effectively decreases the glass transition temperature [11,12,13]. Other relaxation to PA6 can be observed at 170 °C, it can be attributed to the crystalline regions, before the melting point ($\alpha_c$’ relaxation) [12]. PA12 had a glass transition around 48,8 °C, correspondent the $\alpha$ relaxation, relating the amorphous phase (molecular motion that involve the mainly polymeric chain segmental). Other relaxation to PA12 can be observed at 145 °C, it can be related to the crystalline regions before the melting point ($\alpha_c$’ relaxation) as showed to PA6 [14].

![Figure 4](image)

*Figure 4 - Loss Tangent (Tan $\delta$) for pure components (a) and blends PA6/PA12 (b) as a function of temperature.*

The maximum values of $\tan \delta$ to PA6 and PA12 were approximately 0,14 and 0,12, respectively. These values show that PA6 and PA12 have close visco-dissipative behavior. The $\tan \delta$ behaviors to blends PA6/PA12 were according to the relaxation shown by the pure components proportionally to the blend composition. Figure 4 (b) shows the similar $\tan \delta$ behaviors between PA6/PA12 80/20 and PA6, and PA6/PA12 20/80 and PA12. The PA6/PA12 50/50 blend showed $\tan \delta$ behavior of both pure components (PA6 and PA12).

Figure 5 shows the strain (%) caused by a stress applied for 10 minutes, and the elastic recovery and plastic deformation after the stress is removed for 20 minutes (recovery time) for PA6, PA12 and PA6/PA12 blends in the creep test.
The PA6 had 3.8% of elastic recovery and 4.2% of plastic deformation when it was deformed up to 8.0%. PA12 had 4.2% of elastic recovery and 1.8% of plastic deformation when it was deformed up to 6.0%. This results shows that PA6 has low elastic recovery and high plastic deformation by creep than PA12, under the test conditions.

The PA6/PA12 80/20 blend specimen had 3.4% of elastic recovery and 5.1% of plastic deformation when it was deformed up to 8.5%. PA6/PA12 50/50 blend specimen had 2.3% of elastic recovery and 4.0% of plastic deformation when it was deformed up to 6.3%. This blend showed similar behavior as in the case of PA6, lower propensity for elastic recovery. The PA6/PA12 20/80 blend specimen had 4.0% of elastic recovery and 2.0% of plastic deformation when it was deformed up to 6.0%. The behavior presented for this blend is similar as in the case of PA12, i.e., elastic recovery with moderated capacity of plastic deformation by creep, under the test conditions.

![Figure 5](image_url)

**Figure 5** – (a) Creep test curves showing values for strain (%) versus time for the PA6/PA12 blend specimens: ■ 100/0, ● 80/20, + 50/50, * 20/80, ▲ 0/100.

Figure 6 shows the fatigue curves (stress versus cycles number) for pure components and PA6/PA12 blends. The PA6 specimen in the fatigue test with 3.3% of deformation amplitude, showed a small increase in the stress applied as function of cycle number. PA12 showed a small variation in the stress applied as a function of cycles number with 3.0% of deformation amplitude. These results indicate that PA6 shows higher fatigue strength than that the PA12, according the test conditions.

The PA6/PA12 80/20 blend specimen showed a slight reduction in the stress applied as a function of cycles number in the fatigue test with 3.4% deformation amplitude. The PA6/PA12
50/50 blend specimen showed initially a decrease in the stress up to 800 cycles. After 800 cycles this blend had a constant value in the stress up to the end of test, with 2.7% of deformation amplitude. Both blends presented good fatigue strength under the test conditions.

The PA6/PA12 blend 20/80 specimen in the fatigue test with 3.0% of deformation amplitude had initially a great decrease in the stress applied up to 1000 cycles, followed by a slight reduction in the stress applied up to 4400 cycles. After 4400 cycles the stress value remains constant up to the end of test. The behavior of this blend is due probably to the efforts happened in the plastic deformation region (irreversible deformation) leading a fatigue by creep of material.

![Fatigue curves showing the values of stress versus cycles number for the PA6/PA12 blend specimen: (■)100/0, (●) 80/20, (+) 50/50, (★) 20/80, (▲) 0/100.](image)

**CONCLUSION**

The mechanical tests for the PA6/PA12 blends showed that tensile strength was significantly lower compared to the pure components, due to the large average particle size of PA6 (200 µm) and the low affinity between the PA6 and PA12.

The melt flow index, along with the particle size and shape, had a great influence on the microstructure of the sintered specimens of pure PA6 and PA12 under the process conditions. The blend immiscibility was confirmed by the fracture analysis, and in some regions PA12 particles were weakly adhered to the PA6 matrix.

The DMA analyses, E’ modulus and Tan δ, for PA6/PA12 showed behavior according the pure components considering the proportion defined by blend composition. The creep test (% stra) showed that blends with greater PA6 amount had presented great plastic deformation and less elastic recovery. The fatigue test to blends presented good fatigue strength in the test conditions to 20/80 and 50/50 blends.
The manufacturing of blends using a selective laser sintering process demonstrated that it is possible to prepare PA6/PA12 blends with controlled structures and properties by selecting the polymer powder characteristics, such as particle size, melting flow behavior and adjusting the process parameters according to the blend composition. The selective laser sintering of polymer blends permits the preparation of functional components and the development of new applications for rapid manufacturing by SLS technology.

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REFERENCES