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PROCESS OPTIMIZATION OF LASER SINTERED PA12/MWCNT NANOCOMPOSITES

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Abstract: *Rapid prototyping technologies are able to build parts in different materials and it is possible to obtain very unique composites with distinctive properties. Among rapid prototyping technologies, Selective Laser Sintering (SLS) is an interesting technology because it uses materials like metals, ceramics and polymers and obtained parts have good mechanical properties. Despite the properties that are possible to obtain with standard SLS materials it is possible to explore new composites to generate unusual properties. In this work it was investigated the mixture of carbon nanotubes to standard polyamide powder used in the SLS process. The aim of this work was to improve mechanical properties of the generated composite. Nevertheless, SLS process has many variables that need to be set and optimized to achieve the desired material processability and properties. The studied influence factors were the laser average power, the laser scanning speed and the carbon nanotubes content in the polyamide matrix. The study was developed using statistical methods to achieve optimal combination of the factors. In order to obtain optimal experimental factors, it was performed a factorial design evaluating laser power of 1.35, 2.70 and 4.05W, laser scan speed of 36.3, 39.9 and 44.5mm/s and multi-walled carbon nanotubes (MWCNT) weight of 0, 0.5, 1.0 and 3.0%. Results showed strong correlation between the factors that affected the obtained mechanical properties.*
Keywords: *Carbon nanotubes, selective laser sintering, process optimization, mechanical properties*

1. INTRODUCTION

Rapid prototyping is a versatile group of technologies that can produce rapidly complex parts. Among other kinds of technologies, Selective laser sintering has becoming an important technology because it is possible to use metals, ceramics and a variety of thermoplastic materials with good mechanical properties. In this process a thin layer of powder is spread over a platform and a laser beam scans the surface of the power. Layer after layer, a part can be built in hours with high accuracy and virtually freeform (Zheng, 2006). Polyamide (PA) is a thermoplastic material widely used on engineering applications, like aerospace and engine parts. On the other hand, multi-walled carbon nanotubes (MWCNT) had appeared as alternative filler to improve polymer matrix properties to achieve higher mechanical. By using a relative small quantity of MWCNT dispersed in the polymer matrix is possible to improve mechanical properties significantly. Nowadays, MWNT can be obtained for prices that make them reasonable for applications as fillers for thermoplastic materials in commercial products. Especially for electrically dissipative or conductive composite materials there is great potential for a high market share (Pegel, 2008). Many efforts have been released by many authors in order to obtain nanocomposites using different kinds of polyamide and MWCNTs, but none using a rapid prototyping method. The increment registered by authors reached 200% on elastic modulus (Wang, 2008), but in the most of time the improvements were in the range of 40% for tensile strength and elastic modulus, using up to 9%wt of carbon nanotubes (Zhu, 2006), (Zhao, 2005), (Chen, 2006).

Although SLS is a versatile process, it has many parameters that have be adjusted for each processed material. Two very important parameters are the laser average power and the scanning speed. These parameters combined with the laser diameter spot determine the amount of laser energy delivered to the material. As MWCNTs have high absorption of the CO_2 laser wave length (10.2µm) compared to normal PA used in the SLS process, it was expected very different conditions to process mixed powder of PA and MWCNT. In this work the optimization of the parameters and their influence over different amounts of MWCNT dispersed in PA matrix was studied in order to process and obtain parts with desired properties.

2. MATERIALS AND METHODS

2.1. Materials

The particulate material used in this work was Polyamide Duraform^{Tm} of 3D systems. The material shows the average particle size of 58µm and melting temperature of 184 ^{0}C (3D System, 2006). The MWCNTs were purchased from MER Corp.. These MWCNTs were obtained from the chemical vapour deposition and have an average diameter of (140 + / - 30) nm and length of (7 + / - 2) µm, with level of purity greater than 90%.

2.2. Methodology applied to process parameters determination

In order to achieve results statistically reliable was develop a design of experiment involving the main processing parameters. The range of each parameter was selected by identification of equipment limits, since that the machine consists on a prototype built by researcher of own laboratory. A summary of statistical design used in this work is presented on Tab. 1.

Table 1. Summary of statistical design.

Class of Project				*Factorial multi-level*
Experimental Factors				3
Responses				4
Number of runs				72
Degrees of freedom				61
Randomized				yes
Confidence interval				95%
Input factors	**Laser power**	Low	1.35	**W**
		Mid	2.70	
		High	4.05	
	Scan speed	Low	36.3	**mm/s**
		Mid	39.9	
		High	44.5	
	MWCNTs	Pure	0	**%wt**
		Low	0.5	
		Mid	1.0	
		High	3.0	
Output factors	**Bulk and Apparent density**			g/cm³
	Flexural Modulus			MPa
	Stress at 10%			MPa

2.3. Mechanical tests and densities

Mechanical properties are obtained with DMA equipment, using a single cantilever clamp and ramp force of 2N/min. Density values were obtained with physical dimensions of samples and by picnometry method. The samples were manufactured with 35x5x1.4 mm of physical dimensions.

3. RESULTS AND DISCUSSION

Table 2 presents a summary of significant and predominant factors for each analyzed property. Since that A means MWCNTs content, B is the Laser power and C is the Scan speed. It can be seen that MWCNTs content is the predominant factor for most of the responses analyzed. This result revealed a great influence of MWCNTs on microstructure and mechanical consistency of parts.

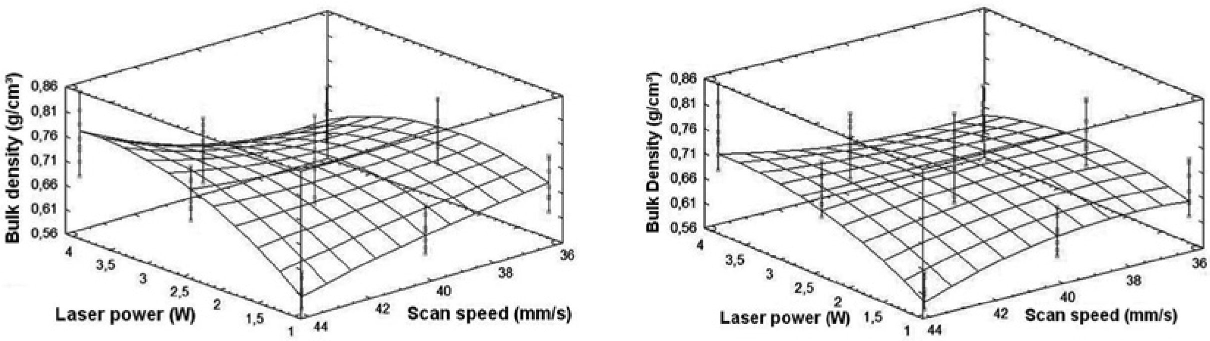
Table 2. Significant and predominant factors for each property.

Property	*Significant Factors*	*Predominant Factor*
Apparent Density	A	A
	AA	
Bulk Density	AA	AA
	BB	
	BC	
	AAA	
Stress 10%	AA	AA
Flexural Modulus	B	B
	AA	
	BB	
	BC	

3.1. Bulk density

The variance analyzes for bulk density was proceeding with cubic factor adjust intending the best correlation with the experimental points. The interaction scan speed/laser power presented more significant effect (P-value of 0.0057). The others significant factors were double interaction of laser power (0.0003), laser power and beam scan speed interactions (0.0000) and triple interaction of MWCNTs content (0.0427).

The Fig. 1 shows the response surface for bulk density and different values of MWCNTs content. The laser power and scan speed were selected as visible axes in the graphics because they present a greater significance in accordance with the analysis of variance (ANOVA). They are presented the graphics obtained with pure polyamide and composite containing 3%wt of MWCNTs, that is, only the extremes of composition. Graphs with intermediate responses were removed because the similar profiles presented by exposed curves.



(a) (b)

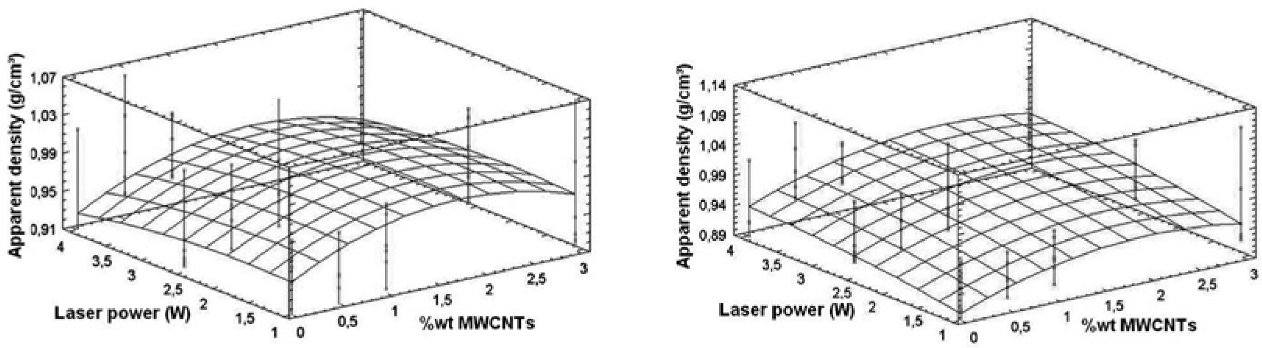
Figure 1. Responses surfaces analyzing bulk density for different MWCNTs contents, PA pure (a) and 3%wt (b).

According to graphic of pure material (PA 12), the property analyzed was more significantly changed with laser power and scan speed variation. The inclination of lines parallel with the coordinates can express these variations. Lower modification on these coordinates are visible when are manufacture the composite material with 3%wt of MWCNTs, which indicates that the presence of filler modify the mechanism of sintering and transfers heat of the process.

3.2. Apparent density

Analysis of variance obtained for the apparent density was performed using a second order analysis. Certain parameters like a MWCNTs content was identified as the most significant factor (P-value equal to 0.0107), as well as its quadratic factor (0.0234), showing great influence of this parameter on the property studied.

Response surfaces were obtained by analyzes of laser power and MWCNTs content (Fig. 2). Different behaviours of the curves were recorded for the different speeds used in the experiment. The graph obtained with the intermediate range of speed (39.9 mm/s) was excluded due to the very similar profile of the response surface obtained with 36.3 mm/s.



(a) (b)

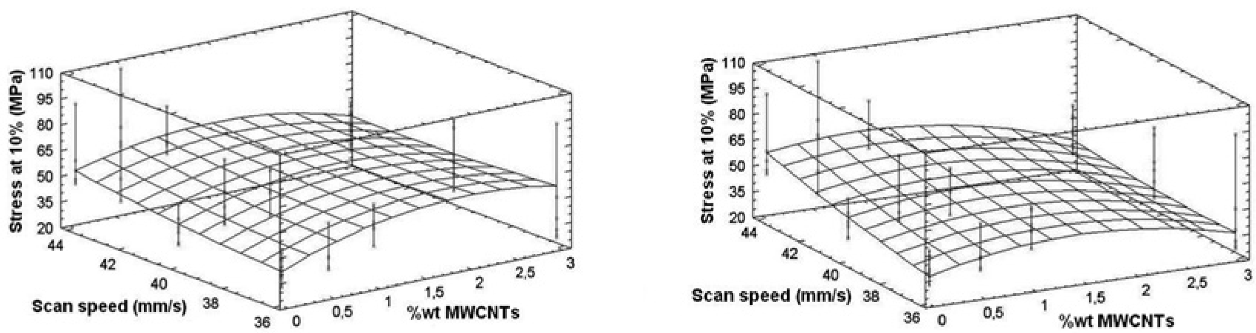
Figure 2. Responses surfaces for apparent density obtained with scan speeds of 36.3 (a) and 44.5mm/s (b).

It was verified that increasing the laser power during manufacture, only the degree of sintering was improve. The curve obtained with 44.5mm/s of scan speed do not present a significant drop of analyzed property. For the joint graphical analysis, can be deduced that the addiction of MWCNTs affects more pronounced the behaviour of property for lower scan beam speeds.

3.3. Stress at 10%

With the ANOVA results for the stress at 10% of deformation become possible to verify that only the quadratic factor of MWCNTs content made relevant influence on the result (P-value equal 0.0127). Again, an analysis of second order was the most appropriate for the adjustment of the data to the model.

Figure 3 (a and b) show the response surfaces to stress 10% of deformation according to the scan speed and MWCNTs content. They presented the extremes of laser power because of greater relevance of these results.



(a) (b)

Figure 3. Response surfaces for stress at 10% obtained with 1.35W (a) and 4.05W (b).

The comparative analysis between the curves showed opposite behaviours for the property with the increase in the MWCNTs content. For lower laser powers the curve was growing almost everywhere extension. On the other hands for higher laser power was verified a peak of maximum on the curve followed by a decline. This implies that the material does not support an overload of energy supplied. Higher levels of MWCNTs improves the thermal transfer due to greater energy absorption. Regarding speed, faster displacements of the beam produced samples with greater strength in both analyses. The dispersion on results recorded in both cases was similar.

3.4. Flexural modulus

The significant factors obtained from ANOVA for flexural modulus were the quadratic factors of three main responses (0.0002, 0.0007, 0.0001 of P-values respectively to %wt MWCNTs, laser power and scan speed), and laser power individually (0.0149). Again, was performed an analysis of the second order, which generate a set of results more adjusted the model proposed by the software.

Responses surfaces to flexural modulus are shown in Fig. 4 (a and b). Following the same methodology previously practiced, the selected axes exposed were laser power and MWCNTs content. Were submitted only the extremes of scan speed because of the similarity profile in the intermediate curve.

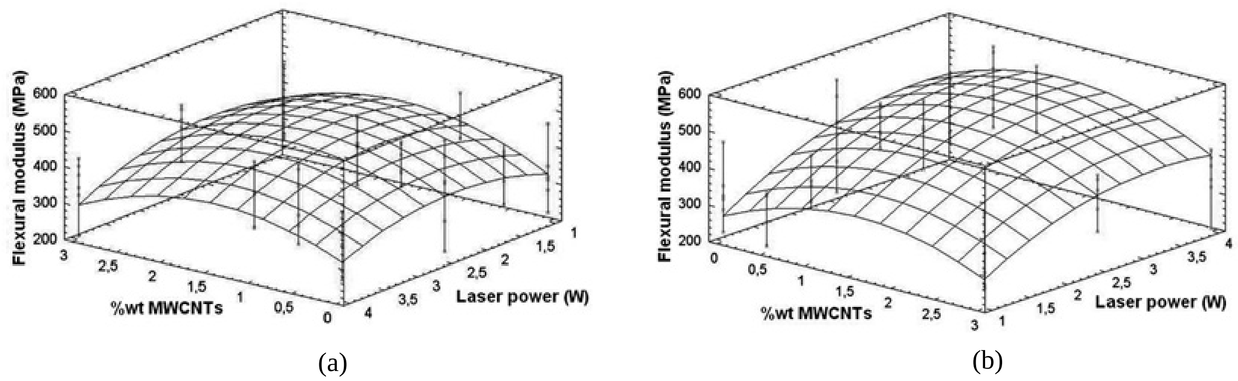


Figure 4. Response surfaces for flexural modulus with 36.3mm/s (a) and 44.5mm/s (b).

Both curves presented parabolic profiles, however the behaviour of property modification was different since that laser can modify more significantly the analyzed property for higher scan speeds. Higher speeds demonstrated ability to raise bigger values of modulus. Then, higher energy densities are responsible for greater densification of the material and consequently increase its rigidity. Regarding spread of values was not recorded very significant differences.

3.5. Multiple optimization

The comparison analysis of data from each individual analysis described so far could bring a combination of parameters which include the best features selected for each case. According final intention, determined property can be maximized, minimized or constant. Then, an intersection of these curves is made and the meeting point is awarded as the optimum condition of the experiment. Depending on the percentage of approximation can be obtained have a good indication for subsequent processing.

Figure 5 show the response surface of optimization trough the modification of the laser power values and MWCNTs content in two speeds (44.5 and 39.9mm/s). These were selected because the relevance of the curves. The Y-axis, in these cases presents an amount of optimization obtained. The proximity of one reveals the greater optimization adjust obtained by the intersection of the curves.

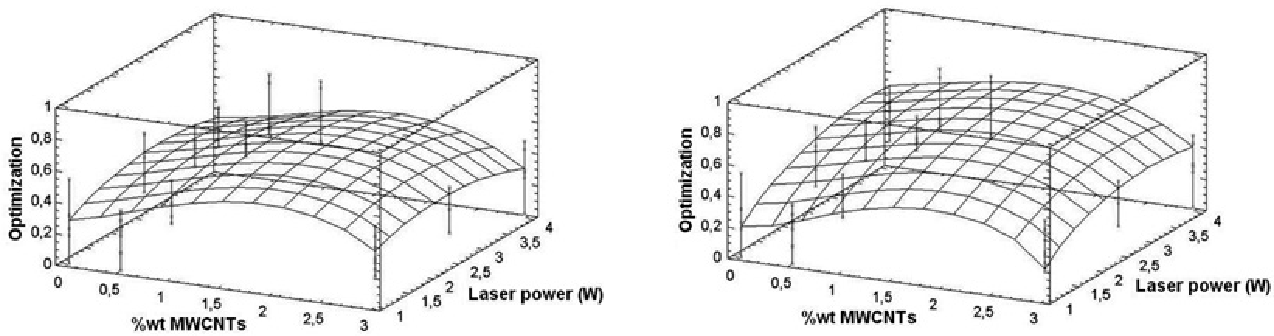


Figure 5. Multiple responses optimization

Although the profiles have recorded a difference, the values of optimization to stay near from 0.70. This shows a good fit the curves and obtaining satisfactory parameters in accordance with the goals. Table 3 shows this combination of certain parameters set as "excellent". The values indicates an intermediate amount of MWCNTs, relatively high power and high beam speed as the best combination for this event. It was pretended maximize properties.

Table 3. Parameters obtained by multiple optimization.

Optimization value = 0.70			
Factors	***Lower***	***Higher***	***Optimized***
%wt MWCNT	**0,0**	**3.0**	**1.69**
Laser Power (W)	**1.35**	**4.05**	**3.36**
Scan speed (mm/s)	**36.3**	**44.5**	**44.5**

4. CONCLUSIONS

Generally, analyzing the most factors significant in the modification of each investigated property, it was determined that the MWCNT content have a more global significance over analyzed responses. This shows that the MWCNTs even added in small proportions in the polymer matrix, causes pronounced effects on mechanical properties and densification of the sample. A problem found in the results was the dispersion of values that were high and provided a setting unsatisfactory in some cases. The variations observed are inherent in the process of sintering used to obtain the samples. Since the process has no prior compaction of the deposited powder material, there are existence of pores in all parts on greater or lesser amount. Thus, places of possible failures in loading become extremely variable in terms of location and degree of severity of each one.

The results obtained with multiple optimization verified that the values of MWCNTs content is not directly proportional to improve the mechanical properties. The fraction of 1.70%wt of MWCNTs was more appropriate for this kind of case, where the mixture of direct materials can cause difficulties in dispersion depending on the amount added. Among the parameters for higher speeds (44.5mm/s) were more favourable to obtain more dense and strength parts. The laser power optimized was located closest to high values (3.36W), but not maximum, reflecting also nonlinear behaviour of this parameter. The fact that moderate laser powers and faster beam speeds have been found as more favourable to the processing can be related to issues of thermal transfer of material and the possible occurrence of deteriorating even when the energy density provided to the material becomes excessive.

5. ACKNOWLEGDEMENTS

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6. REFERENCES

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7. RESPONSIBILITY NOTICE