

# Evaluation of Surface Modification of PA 2200 Parts Made by Selective Laser Sintering Process

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*Cellular adhesion on surface structures from PA 2200 made through Selective Laser Sintering (SLS) process can be improved by modifying the parts surface. In this paper, different methods for surface modification are presented. The PA 2200 samples were immersed in six different solvents. SEM images and surface roughness tests were performed in order to evaluate the surface modification both for the control group and for the tested groups. The obtained results clearly show that there is a significant difference between the roughness of the control (untreated) surface and each of the treated surfaces. Modifying by immersion, of the PA 2200 structures produced by Selective Laser Sintering process, brings original approaches concerning the use of those procedures in the increase of the surfaces quality.*

*Key words: PA 2200, Selective Laser Sintering, surface analysis, surface roughness*

Polyamides have a common, structural chemical nucleus, - amide (- CONH -) a group that is found repeatedly in the polymer. Polyamides, such as nylon 6, nylon 66, nylon 610, nylon 11, nylon 12, have properties that are different because of their order in the molecule, and because of their high degree of intercatenary attraction, that is a result of their ability to undergo a hydrogen chemical bond, [1]. Polyamide, symbolized in literature with the acronym PA, has characteristics that are favourable for tribological applications, such as mechanical strength, stiffness and hardness, good fatigue resistance and good mechanical damping properties, good sliding properties and excellent wear resistance, making it useful in some industrial fields and applications, [2]. Typical applications of the material are plastic parts fully functioning at highest quality. Due to its excellent mechanical properties, the material is often used to replace the typical plastic parts obtained by injection moulding. Biocompatibility allows its use for prostheses and medical devices. High abrasion resistance also allows the achievement of the mobile connections, [3].

In the literature there are a number of references about the use of PA 2200 in the medical field [4-7]. The use of polyamides in medicine needs coating procedures requiring or the change of the electrical charge surface through various technologies, [8]. Some researchers, [9], consider that *Scaffold* polyamide structure is necessary for the perfect adaptation of the implant geometry to bone structure; the pore sizes should be adapted to the size of bone cells to allow osteoblast development. Another researchers tried to coat the surface of an implant made of polyamide with calcium phosphate (CaP). After coating the permeability water degree was 0, and the cell adhesion was much tempered, according to the results of in vitro testing [5].

One study [10] is focused on polyamide samples (DuraForm 12) manufactured by SLS method, with different laser powers (2.5W and 6W), where the functionality of the surfaces parts is tested for using them as substrates for SERS technique. A roughness between 50 and 150 nm at 2.5 W laser power was obtained. This is a wide range of sizes that can generate SERS effect. Bacchewar P. B. [11] studied the effect of working

parameters, on the EOS 380P Sinterstation Machine (the scanning speed, thickness of the powder, laser power, piece orientation in workspace), on the surface roughness obtained in SLS process of the PA 2200 powder. The experimental results led to determining the optimum values for these parameters in order to obtain good quality parts of the surfaces.

A comparison between the characteristics of the Rapid Prototyping processes on various materials, made by [12] emphasizes that the SLS process is profitable when rough surfaces need to be obtained with high precision and good values of roughness. Schmid M. [13] investigated the roughness values obtained after applying various types of coatings of the formed parts by selective laser sintering of PA12 powder. Another researchers [14] conducted a comparative study on the changes of surface properties of polymers Nylon-6 (PA6) and Nylon-12 (PA12) using dielectric barrier discharges. Modified polymers were characterized by various methods: contact angle, ATR-FTIR spectroscopy and SIMS technique.

Taking into consideration the previous researches in the field, the purpose of this study was to evaluate the surface modification of polyamide PA 2200 parts, achieved through SLS technique, on DTM Sinterstation 2000 Machine, by treating them with a series of solvents.

There were followed the manufacture conditions, the surface modification of the obtained product and the evaluation of the surface roughness before and after the treatment with substances: resorcin and ethyl alcohol, formic acid, phosphoric acid, ortho-meta-para-xylene, glacial acetic acid, dimethylformamide.

## Experimental part

The material used in this research was the PA 2200 polyamide powder, produced by the Electro Optical Systems - EOS GmbH, Munich, Germany. The PA 2200 parts (with melting point between 172-180° C) were produced by Selective Laser Sintering Technology (SLS) on DTM Sinterstation 2000 Machine. Thus based on the virtual model designed in SolidWorks software, there were obtained three-dimensional parts, by heating and sticking powder at a temperature under the melting point. The

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samples were obtained at 170° C temperature, 7.5 W laser power, 0.1 mm thickness of the deposited layer, for 12 hours at room temperature.

For the surface modification there have been used each 5 samples (10x4mm) in 6 solutions: resorcin and ethyl alcohol in a ratio of 1:1, formic acid (concentration 80%), phosphoric acid (concentration 85%), ortho-meta-para-xylene, glacial acetic acid, dimethylformamide and the control samples for 12 h at room temperature. Table 1 shows the encoding based on the surface area of samples studied.

**Table 1**  
SAMPLES ENCODING

Sample No.	Surface 1	Surface 2
1	1A	1B
2	2A	2B
3	3A	3B
4	4A	4B
5	5A	5B

It must be noted that surface 2 represented the upper surface of the sample (the last sintered layer of the part). Surface 1 was considered as surface area in direct contact with the powder bed on the working cylinder of the machine.

The use of metallographic techniques is suitable for studying metal and plastics surfaces [15]. The identification of the surfaces changes was made both by scanning electron microscopy (SEM - 3D Quanta FEG) before and after the surface treatment and surface roughness measurement (Mitutoyo SJ 210) in each 5 points on the two surfaces of each sample. The samples subjected

to scanning electron microscopy, has been previously coated with a thin layer of gold to allow for better interaction between electrons and material. The voltage used to obtain surface topography analyzed by SEM was 30 kV, and magnification power was 3000 x.

The results were statistically analysed by comparing the obtained averages between the control group and each test group, using Microsoft Excel, IBM SPSS and other online tools.

## Results and discussions

The proposed null hypothesis (H0) for the statistical analysis was that *There is no significant difference in roughness between the control group and the treated surface. The alternative hypothesis (H1) was that There is a significant difference in roughness between the control group and the treated surface.* To test these hypotheses, a two-tailed independent sample t-test was conducted with a significance level of  $\alpha=0.05$ .

The sample data and descriptive statistics (average and standard deviation) for each sample group taken into consideration are shown in table 2 (for surface 1) and table 3 (for surface 2).

The average roughness was different in the control group for the first surface (M = 12.009  $\mu\text{m}$ , SD=0.178) and the second one (M = 10.461 $\mu\text{m}$ , SD=0.354).

An independent-samples t-test was conducted to compare surface roughness in untreated and treated surfaces for both surface 1 and surface 2.

In the case of surface 1, there was a significant difference in the values for roughness of the control group (M=12.009, SD=0.178) and the roughness of the surface

**Table 2**

COMPARISON OF THE CONTROL GROUP AVERAGE WITH THE TEST GROUPS AVERAGES FOR SURFACE 1 OF THE SAMPLES

Sample No.	Surface 1 of the samples						
	Roughness, average of the values determined in 5 points, [ $\mu\text{m}$ ]						
	Control group	Group test					
Resorcin		Formic acid	Phosphoric acid	Ortho-meta-para-xylene	Glacial acetic acid	Dimethylformamide	
1A	11.787	11.220	11.090	11.791	9.817	8.915	10.845
2A	12.282	10.818	10.754	11.221	9.945	10.650	11.757
3A	11.960	11.228	11.283	10.992	8.933	9.179	11.674
4A	12.007	11.093	11.039	11.121	9.868	9.579	11.414
5A	12.008	11.083	11.046	11.547	9.264	9.583	11.436
<b>Average</b>	<b>12.009</b>	<b>11.088</b>	<b>11.042</b>	<b>11.334</b>	<b>9.565</b>	<b>9.581</b>	<b>11.425</b>
<b>Std. Dev.</b>	<b>0.178</b>	<b>0.166</b>	<b>0.189</b>	<b>0.328</b>	<b>0.444</b>	<b>0.661</b>	<b>0.357</b>

**Table 3**

COMPARISON OF THE CONTROL GROUP AVERAGE WITH THE TEST GROUPS AVERAGES FOR SURFACE 2 OF THE SAMPLES

Sample No.	Surface 2 of the samples						
	Roughness, average of the values determined in 5 points, [ $\mu\text{m}$ ]						
	Control group	Tested Group					
Resorcin		Formic acid	Phosphoric acid	Ortho-meta-para-xylene	Glacial acetic acid	Dimethylformamide	
1B	10.588	10.521	10.829	8.723	9.628	10.300	9.754
2B	9.911	10.298	13.084	10.834	10.217	10.075	9.994
3B	10.886	10.845	10.652	9.669	11.772	10.750	10.328
4B	10.429	10.561	11.522	9.682	10.684	10.367	10.063
5B	10.492	10.547	11.519	9.804	10.394	10.383	9.986
<b>Average</b>	<b>10.461</b>	<b>10.554</b>	<b>11.521</b>	<b>9.742</b>	<b>10.539</b>	<b>10.375</b>	<b>10.025</b>
<b>Std. Dev.</b>	<b>0.354</b>	<b>0.195</b>	<b>0.959</b>	<b>0.749</b>	<b>0.790</b>	<b>0.243</b>	<b>0.206</b>

Control group vs.	t-value	p-value	Cohen's d	Effect size
Resorcin	8.47	0.001	5.361	Large
Formic acid	8.324	0.001	5.269	Large
Phosphoric acid	4.046	0.004	2.562	Large
Ortho-meta-para-xylene	11.418	0.001	7.224	Large
Glacial acetic acid	7.93	0.001	5.017	Large
Dimethylformamide	3.275	0.011	2.073	Large

**Table 4**  
T-VALUES, P-VALUES AND EFFECT SIZE FOR EACH TEST ON SURFACE 1

Control group vs.	t-value	p-value	Significance	Cohen's d	Effect size
Resorcin	-0.516	0.62	Not Significant	-0.326	Small
Formic acid	-2.319	0.049	Significant	-1.467	Large
Phosphoric acid	1.94	0.088	Not Significant	1.228	Large
Ortho-meta-para-xylene	-0.201	0.846	Not Significant	-0.127	Small
Glacial acetic acid	0.449	0.665	Not Significant	0.283	Small
Dimethylformamide	2.382	0.044	Significant	1.506	Large

**Table 5**  
RESULTS OF TESTS CONDUCTED ON THE SECOND SURFACE

treated with resorcin ( $M=11.088$ ,  $SD=0.166$ );  $t(8)=8.470$ ,  $p < 0.001$ .

There was also a significant difference in the values for roughness of the control group ( $M=12.009$ ,  $SD=0.178$ ) and the roughness of the surface treated with:

- formic acid ( $M=11.042$ ,  $SD=0.189$ );  $t(8)=8.324$ ,  $p < 0.001$ ;

- phosphoric acid ( $M=11.334$ ,  $SD=0.328$ );  $t(8)=4.046$ ,  $p = 0.004$ ;

- ortho-meta-para-xylene ( $M=9.565$ ,  $SD=0.444$ );  $t(5.247)=11.418$ ,  $p < 0.001$ ;

- glacial acetic acid ( $M=9.581$ ,  $SD=0.661$ );  $t(8)=7.930$ ,  $p < 0.001$ ;

-dimethylformamide ( $M=11.425$ ,  $SD=0.357$ );  $t(8)=3.275$ ,  $p = 0.011$ ;

For each of the tests, Levene's test for equality of variances was conducted. The only test that had a significant difference in variances, and thus equal variances were not assumed, was for the surfaces treated with ortho-meta-para-xylene.

The obtained results clearly show that there is a significant difference between the roughness of the control (untreated) surface and each of the treated surfaces and thus the null hypothesis can be rejected.

Cohen's d was used to determine the effect size for each of the conducted tests and was done with an online tool (<http://www.uccs.edu/~lbecker/>). The results can be seen in table 4 along with the corresponding t-values and p-values for each test.

As can be seen from the table above, the effect size is large, exceeding Cohen's convention for large effects ( $d = 0.80$ ) for each of the tests.

In the case of the second surface the results are summarized in table 5.

The results are only significant for the samples immersed in formic acid and dimethylformamide. One reason for this is that the samples treated with formic acid and glacial acetic acid floated in the liquid, the density of the solution being higher than the density of the samples. Thus, the surfaces were not attacked correctly, leading to an insignificant change in roughness. Only the significant results had a large effect size, the positive sign meaning that the mean (of the dimethylformamide sample in this case) is larger than the mean of the control group.

In figure 3 (a, b, c, d, e) SEM images are displayed before and after treating the samples with different substances.

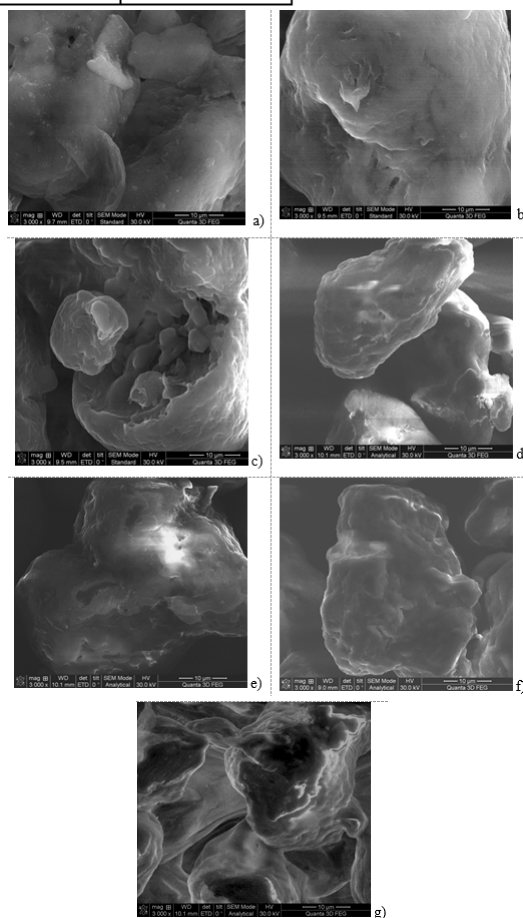


Fig. 3. SEM images obtained at 3000 x for:

- a) control sample at 10µm; b) sample treated with Ortho-meta-para-xylene at 10µm; c) sample treated with formic acid at 10µm; d) sample treated with glacial acetic acid at 10µm; e) sample treated with phosphoric acid at 10µm; f) sample treated with resorcin and ethylic acid at 10µm; g) sample treated with dimethylformamide at 10µm

It can be seen that there are changes in surface topography that will determine changes in roughness too.

The novelty of this study as compared to the literature in the field is fact that it was made a comparison between the changes occurred in surface roughness due to modifying the surfaces with various substances for the samples from PA 2200 material (manufactured by Electro Optical Systems - EOS GmbH) using DTM Sinterstaion 2000 Machine.

At present our research studies continue with cytotoxicity testing in vitro and in vivo of the new obtained surfaces in order to follow any appearance of bacterial or fungal colonization on the surface of the polyamide.

### Conclusions

The study conducted a review of the current state of research on modifying the quality of polyamide surfaces parts, made by Additive Manufacturing technologies. The determination of roughness and its modifying by immersion in various solvents (alcohol and resorcin, formic acid, phosphoric acid, ortho-meta-para-xylene, glacial acetic acid, dimethylformamide) of the PA 2200 parts produced by SLS process brings original approaches concerning the use of those procedures in the increase of the surfaces quality.

Scanning electron microscopy, roughness readings and statistical analysis using *t* test to compare averages obtained corroborates the results of research on different surfaces changes parts of PA 2200 according to the substance used for the attack. All the six substances used in the study gave statistically significant differences in roughness change of PA 2200 parts. On the second surface of the parts, phosphoric acid, glacial acetic acid and dimethylformamide influenced it by the decrease of the roughness values, while resorcin, formic acid and ortho-meta-paraxylene increased the roughness values. On the first surface of the parts, all the used substances led to the decrease of the roughness, starting from a higher roughness value of the control group ( $R_a = 12.009 \mu\text{m}$ ).

### References

1. BRYDSON J.A., 18- Polyamides and Polyimides, *Plastics Materials*, **7**, 1999, p. 478.
2. PODARU G., Studies on the behavior of flanged packing for pneumatic cylinder with rod made of polymeric materials, PhD Thesis, Galati, 2011.
3. \*\*\* EOS GMBH - Electro Optical Systems, Material Data Sheet, PA2200 Product.
4. ZHANG. J. C., LU. H. Y., LV G. Y., MOY A. C., YAN G., HUANG C., *Int. J. Oral Maxillofac. Surg.*, **39**, 2010 p. 469.
5. ABDAL-HAYA A., Tijingb D. L., Limc J. K., *Chem. Eng. J.*, **215-216**, 2013, p. 57.
6. JIE W., YUBAO L., *Eur. Polym. J.*, **40**, nr 3, 2004, p. 509.
7. MUELLERA A., PAYSANC P., SCHUMACHER R., *Br J Oral Maxillofac Surg*, **49**, nr 8, 2011, p. e67.
8. BORCIA G., DUMITRASCU N., POPA G., *Surf. Coat. Technol.*, **197**, nr 2-3, 2005, p. 316.
9. PAL S. J., MOHAN P. P., *ICTE2013, Procedia Eng.* **59**, 2013, p.59.
10. DE OLIVEIRA SETTI G., DE OLIVEIRA M. F., ALVES MAIA I., LOPES DA SILVA J. V. AND JOANNI E., *Rapid Prototyping J*, **20**, nr 4 , 2014, p. 280.
11. BACCHEWAR P. B., SINGHAL S. K., PANDEY P. M., *J. Eng. Manuf.*, **221** nr. 1, 2007, p. 35.
12. KIM G. D., OH Y. T., *J. Eng. Manuf.*, **222**, nr. 2, 2008, p. 201.
13. SCHMID M., SIMON C., LEVY G.N., *International Solid Freeform Fabrication Symposium (SFF)*, Austin, TX, 2009.
14. UPADHYAY D.J., CUI NAI-YI, ANDERSON C.A., BROWN N.M.D., *Colloid Surf A Physicochem Eng Asp*, **248**, nr 1-3, 2004, p. 47.
15. RIDZON M., ZAVACKA A., *Appl Mech Mater*, **421**, 2013, p. 329

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