RBAV Revista Brasileira de Aplicações de Vácuo https://doi.org/10.17563/rbav.v40.1193

Effects of vacuum exposure on mechanical properties of thermoplastic materials

Efeitos da exposição ao vácuo nas propriedades dos materiais termoplásticos

Tiago Rodrigues dos Santos[1,*], Isla Kalleny Marques Brandão[1], Mateus Silva Sant'Ana[1], Pedro Henrique dos Santos Alves[1], Rana Mayeli Piêgas Taborda[1], Paolo Gessini[1], Manuel Dias Nascimento Barcelos Junior[1]

1. Universidade de Brasília - Departamento de Engenharia Aeroespacial - Faculdade do Gama – Brasília (DF), Brazil.

Correspondence author: tiagorsantos97@gmail.com

Section Editor: Maria Lúcia P Silva

Received: Nov. 30, 2020 **Approved:** Jan. 26, 2021

ABSTRACT

The present paper proposes the study of the behavior of three thermoplastic materials: acrylonitrile butadiene styrene (ABS), poly(lactic acid) (PLA), and polyethylene glycol terephthalate (PETG), processed by additive manufacturing type fused deposition modelling (FDM) when exposed to low vacuum. The experiment was composed of three moments consisting of tridimensional modeling and manufacturing of the specimens, drying process and vacuum exposure for 24 hours, according to American Society for Testing and Materials (ASTM) D6653/D6653M standards, and bending test for the determination of mechanical properties, based on ASTM D790 standards. The vacuum chamber tests exposed oscillations in the pressure indicating gases releasing from the specimen, but none of the samples showed visible deformations. Subjecting the materials exposed to low vacuum to bending tests and comparing them to the unexposed material, we observed a significant increase in the calculated modulus of elasticity and a change in the slope of graphic force versus deflection in all materials. This behavior demonstrates that it is possible to submit polymeric materials to vacuum, and low vacuum exposure can be a treatment for thermoplastic materials. In the future, a study using a spectrometer will be necessary to verify which gases are present during pressure oscillation in the chamber, thus making it possible to understand which factor has increased the mechanical properties of the materials. In sequence, experiments will be necessary to validate the vacuum exposure as a form of treatment of materials and to verify the possibility of applying thermoplastics commonly used in additive manufacturing for low-impact space applications.

KEYWORDS: Thermoplastic materials, Low vacuum, Mechanical properties.

RESUMO

O presente trabalho propõe o estudo do comportamento de três materiais termoplásticos: Acrilonitrila Butadieno Estireno (ABS), Poli (ácido lático) (PLA), Politereftalato de Etileno Glicol (PETG), processados por manufatura aditiva do tipo *Fused Deposition Modelling* (FDM) quando expostos ao baixo vácuo. O experimento foi composto de três momentos: modelagem 3d e fabricação dos corpos de provas, um processo de secagem e exposição ao vácuo por vinte e quatro horas cada um dos processos, conforme as normas ASTM D6653/D6653M, e ensaio de flexão para a determinação das propriedades mecânicas, baseado na norma ASTM D790. Os testes na câmara de vácuo mostraram oscilações na pressão indicando uma possível escapa de gases dos corpos de prova, mas nenhuma das amostras apresentou deformações visíveis. Submetendo os materiais expostos ao baixo vácuo à testes de flexão e comparando-os ao material não exposto, notou-se um aumento significativo no módulo de elasticidade calculado e uma mudança na inclinação da força por flecha em todos os materiais. Isso demonstra ser possível submeter os materiais poliméricos ao vácuo, e que a exposição ao baixo vácuo pode ser um tratamento para o termoplástico. Futuramente, será necessário um estudo com uso do espectrômetro para verificar quais gases estão sendo expelidos durante a oscilação da pressão na câmara, possibilitando, dessa forma, a compreensão de qual fator aumentou as propriedades mecânicas dos materiais. Em seguida, será realizado experimentos para validar a exposição do vácuo como uma forma de tratamento dos materiais, assim como, verificar a possibilidade de uso dos termoplásticos de uso comum na manufatura aditiva para aplicações espaciais de baixo impacto.

PALAVRAS-CHAVE: Materiais termoplásticos, Baixo vácuo, Propriedades mecânicas.

INTRODUCTION

Additive manufacturing, also known as tridimensional (3D) printing, proposes an innovative mode of production, which allows a high level of customization of objects[1]. It is remarkable how quickly the technique of additive manufacturing has evolved, with applications in several areas of engineering available[2]. Tridimensional printing has proved to be a very applied technique in the production of final parts. So that, currently, it is not only used as a tool for prototype production. The advantages of 3D printing over traditional processes include reduced cost prototype production and less manufacturing time, significant reduction in raw material waste, the ability to make complex geometries in a single manufacturing process and the affordability of table machines and materials[3].

The most commonly used materials in this additive manufacturing scenario are the thermoplastic filaments of acrylonitrile butadiene styrene (ABS), poly(lactic acid) (PLA), polyethylene glycol terephthalate (PETG), polycarbonate (PC) and nylon[4]. According to Tanikella et al.[5], PLA, besides being very popular, is easier to print when compared to ABS, having more efficient thermomechanical properties, better mechanical resistance and lower thermal expansion coefficient. PETG is considered a filament that has similar qualities to ABS, being ductile and resistant, combined with the ease of printing PLA.

According to Divyathej et al.[6], 3D printing has the quality defined by the thickness of the layers, nozzle and bed temperature, orientation, and support, besides considering particularities between different types of equipment. We define these parameters through slicing software, such as the Simplify3D. In 3D printing, a 3D computer aided design (CAD) software is used to design the objects[7]. At this juncture, the specimens used in the experiments performed to compose this article were designed with a CAD software aid and sliced in the Simplify3D software. The 3D printer used is the Graber i3 model, built in medium density fiberboard (MDF) structure.

Vacuum technology also has contributed significantly to scientific research and industry in recent years. According to Hara et al.[8], this is due to the use of vacuum in studies that analyze rarefied and controlled atmosphere. Problems of suspended particles control, tools and prototypes fixation, molecular deposits and gases removal are some of the examples that can be solved with the help of this technology[9]. Thus, it is necessary to research the effect of vacuum on the mechanical properties of materials under these conditions.

In this research, we have chosen a mechanical vacuum pump capable of generating low vacuum, because it meets the analysis requirements and contributes to low cost and complex apparatus. The vacuum pump aims to produce a difference in pressure inside the vacuum chamber and the piping about the pump's inlet. The pressure at the inlet is lower than at other points[10]. The vacuum technology pays attention to the pressure difference for low-pressure situations, being irrelevant to the gas flow and the molecules' disposition. We define a low vacuum between 10E5 and 10E-1 mbar[11].

One can improve a polymer by vacuum exposure at a high temperature. Previous experimental work has determined that rupture stresses increase when exposing a polymer to high vacuum and high temperatures[12]. This is because the polymeric material invariably contains mold lubricants, fire retardant additives, antioxidants, and plasticizers. Such additives are removed from the material when exposed to vacuum, making it purer and modifying its mechanical properties.

As the study is about basic materials used in 3D printing, the preference for thermoplastic materials ABS, PLA, and PETG in this research area is due to their versatility and accessibility. The article seeks to consider the analysis of the mechanical behavior of the specimens manufactured by a 3D fused deposition modelling (FDM) printer, when submitted to a low vacuum, using the mechanical bending test to generate data of the effects on the mechanical properties. We based the experiments on American Society for Testing and Materials (ASTM) D790 (used for destructive mechanical bending tests on polymers with and without reinforcement) and ASTM D6653/D6653M, which substantiates the experiment of exposure to vacuum with mechanical pumps[12-14]. In the experiments performed, the thermoplastics ABS, PLA, and PETG showed potential for applications at high altitudes. The exposition of these materials to vacuum evidenced the treatment of thermoplastics to modify mechanical properties by using the vacuum. This technique is beneficial for several applications.

METHODOLOGY

The experiment's development was composed of three stages: the manufacture of bending specimens through additive manufacturing; the drying and exposure to vacuum, a part of the specimens; and the mechanical testing and data analysis[15,16].

For the development of the experiment, we manufactured the specimens with three different thermoplastic materials: PLA, ABS, and PETG. Eighteen specimens of each material were manufactured – half would be exposed to vacuum, and the other part would serve as the control sample. The first step for manufacturing was to prepare the CAD of the specimens using the SolidWorks software, following the guidelines of ASTM D790, which is the technical standard that bases the destructive mechanical bending test for polymers with and without reinforcement. Afterwards, from the CAD of the specimens, it was performed the slicing of the specimens using the software Simplify3D, applying the following parameters: the layer height of 0.100 mm, the print speed of 30 mm/s, the tracking angle of 0/90 degrees, 100% filling, the overlap edge of 60%, 0.4 nozzle and the wall thickness of 1.2 mm. The specimens were made using 3D Lab's filaments whose id numbers are L.9AC3, L.9AC4 and L.9AC5. Each filament has 1.75 mm in diameter and the setting parameters used for printing were recommended in the following Table 1[17].

Table 1: Recommended printing parameters to tridimensional lab filaments according to the provider.

Material	Printing temperature [°C]	Table temperature [°C]	Printing speed [mm/s]
PLA	200–220	< 70	up to 150
ABS	200–240	100–120	up to 150
PETG	230–255	< 85	up to 120

PLA: poly(lactic acid); ABS: acrylonitrile butadiene styrene; PETG: polyethylene glycol terephthalate.

We have manufactured the specimens using the 3D printers of the Laboratory of Aerospace Structures (LAE) of the Universidade de Brasília (UnB), Campus UnB Gama. The printer used was a Graber model i3 in medium density wood structure (medium density particleboard – MDF) with simple extrusion, whose print dimensions were 200-mm wide and 200-mm high and thermally insulated in an MDF box with aluminum and glass doors.

We divided the specimens of each material into two sets; each set consisted of nine samples. We submitted one set to vacuum and performed all the necessary procedures for this exposure, and the other set became the reference for the comparison. We measured the weight and the geometry of all specimens four times. The sets submitted to the vacuum went through this process before and after the vacuum exposure. We employed a SHIMADZU precision scale model ATC224 with four decimal places precision, and a VONDER digital caliper with two-decimal places precision was used to measure the mass of the specimens[16].

We used the apparatus of the Space Systems Laboratory (LASE) of the UnB, Campus UnB Gama, for the experimental vacuum procedure. We based the vacuum procedure on D6653/D6653M[15], and the equipment used was the Drystar® GV80 dry vacuum pumps. The vacuum chamber had the diameter of 755 mm and length of 1,040 mm, according to Figures 1, 2, and 3, connected to a mechanical type vacuum pump. Due to the pump's suction capacity and the volume of the vacuum chamber, it was only possible to reach the minimum pressure of 0.1 Pa. This was enough for this research, since the objective was to perform a test to understand thermoplastics' behavior processed by additive manufacturing when exposed to low vacuum.

The standard D6653/D6653M requests that the specimens, before being exposed to vacuum, stay at a temperature of 5°C for 24 hours, or stay for 24 hours at 25°C. For this experiment's development, we have chosen to leave the specimens for 24 hours inside a kiln with temperature control at 25°C ± 0.5°C. So, after 24 hours, the specimens were removed and placed in a sealed container to avoid absorption of moisture, in sequence taking them to the vacuum exposure apparatus.

We have captured internal chamber pressure data utilizing a Pirani-type pressure sensor with 24 hours of exposure. We have chosen the Pirani type sensor, because it allows the reading of pressure up to a low vacuum limit required by the research. We distributed the three different materials' specimens at a short distance inside the vacuum chamber (Fig. 3), immediately after leaving the kiln.

Figure 1: Vacuum chamber.

Figure 2: Vacuum chamber computer aided design.

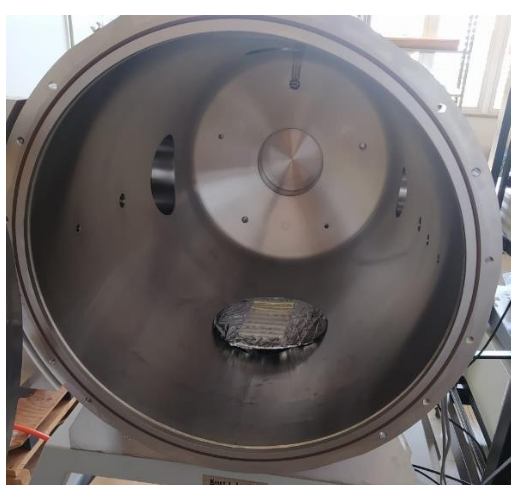


Figure 3: Specimens inside the chamber.

After the allocation of the specimens, the vacuum suction procedure was initiated with a 24-hour exposure duration. The specimens were removed after the period the bending tests were performed. The bending test was performed on the INSTRON 8801 (100KN) (Fig. 4) machine according to the ASTM D790 standard. The three points bending method was adopted, with a descent speed of 5 mm/s, velocity provided by the standard. A distance of 102.4 mm between the supports was used. The specimens have dimensions of 127 ± 2 mm long, 12.7 ± 0.5 mm wide and 3.2 ± 0.2 mm high. The test was performed at room temperature and at 24°C, obeying the standard, which specifies that the temperature must be between 23 and 25°C.

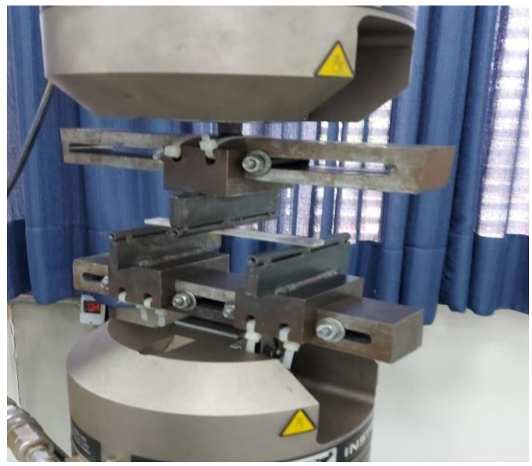


Figure 4: Bending test.

RESULTS AND DISCUSSION

From the Pirani sensor connected to the computer, it was possible to capture the pressure in the time interval of the experiment execution and generate the corresponding vacuum curve, along with the vacuum curve with the empty chamber (Fig. 5), for the analysis. The pressure stabilized from 0.5 Pa, which corresponds to an altitude of approximately 85 km, i.e., beginning from the ionosphere. The altitude was defined from the U.S. Standard Atmosphere[18], and the graph of pressure by altitude can be observed in Fig. 6.

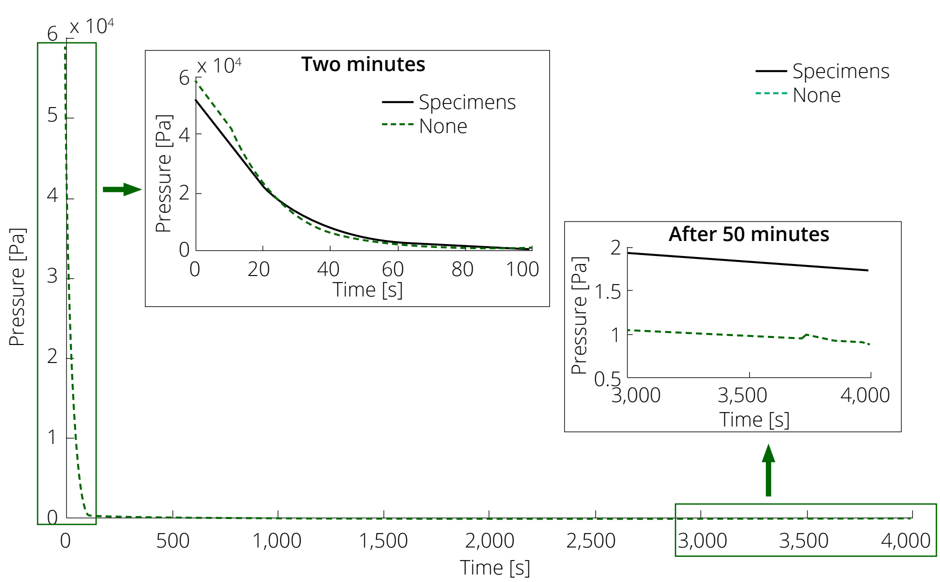


Figure 5: Pressure curve.

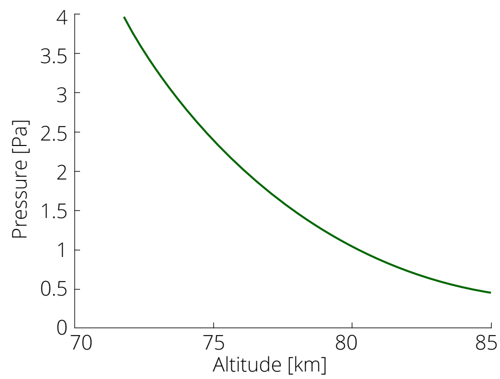


Figure 6: Pressure by altitude.

Figure 5 shows a faster descent at the beginning and, after 20 seconds, the pressure of the chamber with the specimens was higher than the pressure of the empty chamber, indicating a probable sublimation of the thermoplastic material or the rupture of air pockets in the structure of the specimen. It was noted that the pressure of the chamber with the specimens has stabilized above the pressure without the specimens, which is justified by the release of pockets of gases, which are trapped inside the materials. The releasing of those gases has some noticeable effect on mechanical properties; we can observe this in Tables 2 and 3. Besides the gases releasing, some authors suggest that the sublimation may occur by additives aggregate during the polymers manufacturing process, as mold lubricants, flame retardant, plasticizers, and others. Those additives tend to sublimate first than the polymeric material, considering that the concentration of both is undermost when compared to the polymer mass, justifying so the sublimation without any significant change in specimens' mass[12].

The three-point bending test provides the average force curves per arrow, as shown in Figs. 6, 7, 8 and 9, from which it was possible to determine the maximum forces, maximum stresses and maximum deflections presented in Table 2. The curves presented also serve to determine the modulus of elasticity to bending presented in Table 3.

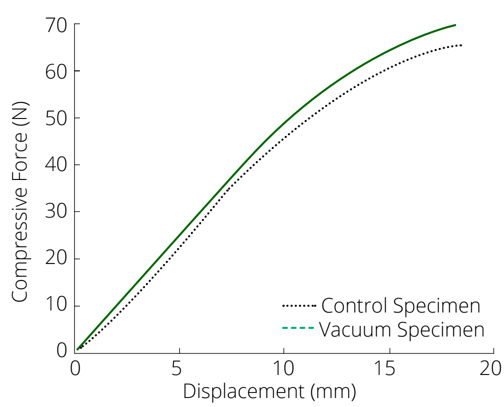


Figure 7: Poly(lactic acid) force by deflection graph.

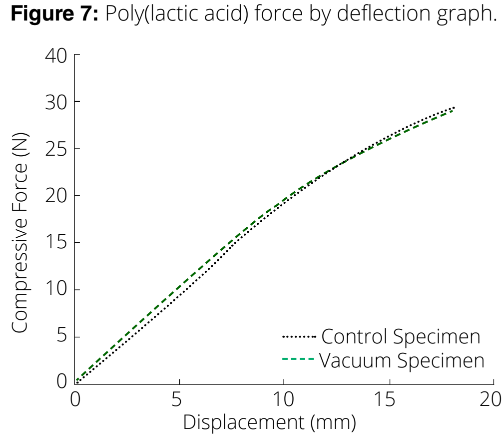


Figure 8: Acrylonitrile butadiene styrene force by deflection graph.

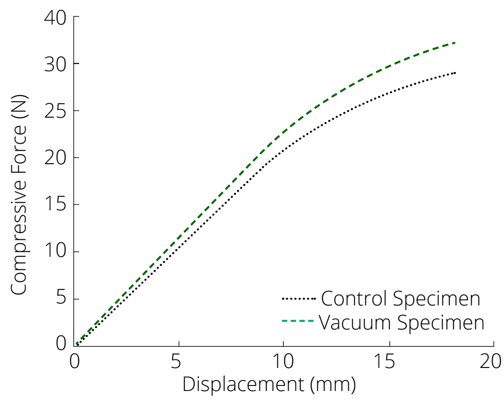


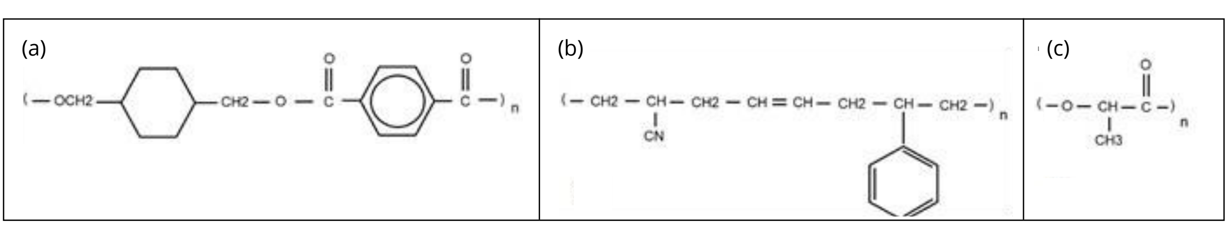
Figure 9: Polyethylene glycol terephthalate force by deflection graph.

Table 2: Bending test results.

Material	Maximum force [N]	Maximum stress [MPa]	Maximum arrow [mm]
PLA without vacuum exposure	75.5012 ± 2.5206	285.36	22.1737 ± 2.3552
PLA with vacuum exposure	77.9547 ± 2.5097	294.63	2.9538 ± 1.6455
ABS without vacuum exposure	41.7990 ± 4.7708	157.98	22.0285 ± 2.3723
ABS with vacuum exposure	45.7555 ± 2.5208	172.93	21.4293 ± 1.6104
PETG without vacuum exposure	39.7376 ± 3.1674	150.20	25.4942 ± 2.3467
PETG with vacuum exposure	38.9010 ± 3.5284	147.03	25.5478 ± 1.7154

PLA: poly(lactic acid); ABS: acrylonitrile butadiene styrene; PETG: polyethylene glycol terephthalate.

It is noted in Table 2 that the PLA after exposure to vacuum endured 3.24% more load than evidence bodies that were not exposed to vacuum. The same happened for ABS, which endured 9.46% more load. However, PETG showed an inverse behavior in which a load 2.10% lower when compared to specimens that were not exposed to vacuum. The divergence in behavior between PLA and PETG polymers, which are semi-crystalline, indicates that the crystallinity of the polymers does not have much influence on their behavior under vacuum. However, Frankel[12] demonstrates in his work that the chemical binding energy in the composition of polymers has an influence on their behavior when exposed to vacuum, with materials containing C-F bonds showing little influence from vacuum exposure on their mechanical properties. ABS was the polymer that suffered the least effects from vacuum exposure, which is justified because of the three polymers, it has the strongest bonding energy. This becomes evident when analyzing the results of Table 3. The PLA was the material that suffered most from the effects of vacuum exposure, having an increase in its modulus of elasticity to the flexure of 7.76%, and PETG suffered an increase of 7.08% of its modulus of elasticity to the flexure. PETG is a copolymer that has in its structure glycol, in order to reduce the crystallization speed, so that the material is translucent without losing its mechanical properties[19,20]. In Fig. 10, it is possible to see the molecular structure of PLA, PETG and ABS[19,20].



PLA: poly(lactic acid); ABS: acrylonitrile butadiene styrene; PETG: polyethylene glycol terephthalate.

Figure 10: (a) PETG molecular structure; (b) ABS molecular structure; (c) PLA molecular structure.

Table 3: Calculated modulus of elasticity.

Material	Bending modulus of elasticity [MPa]		Modulus of elasticity percentual raise after the exposure to vacuum [%]
	Without exposure to vacuum	With exposure to vacuum	
PLA	3,088.60	3,328.40	7.76
ABS	1,662.29	1,767.77	6.62
PETG	1,130.06	1,209.57	7.08

PLA: poly(lactic acid); ABS: acrylonitrile butadiene styrene; PETG: polyethylene glycol terephthalate.

The increase in the modulus of elasticity to bending of all materials tested demonstrates, along with the increase in maximum stress, that the exposure of polymers to vacuum tends to be a method of post-manufacturing treatment for polymers. According to Frankel[12], a polymer can be improved by post-curing in vacuum at a high temperature. It has been experimentally determined that rupture stresses are increased when a polymer is exposed to vacuum at high temperatures. This can be justified because the polymeric material invariably contains mold lubricants, fire retardant additives, antioxidants, plasticizers, among others. Such additives are removed from the material when exposed to vacuum, making it purer and, consequently, modifying its mechanical properties, so that the results obtained corroborate the research made by the referred author. However, the results obtained indicate that the same behavior occurs at room temperature, probably with less intensity[20].

The curves obtained through the bending test confirmed the behavior analyses, since it is possible to see the inclination of the elastic region used to determine the modulus of elasticity to bending, which in turn increases the modulus of resistance to bending of the materials, as well as the maximum forces and displacements of the material indicating that the material becomes less ductile.

CONCLUSION

The result obtained in the paper showed that the exposure of polymers to vacuum can be a method of purification of thermoplastic materials, removing impurities and additives from them. Consequently, the mechanical properties suffer significant increases, such as the variation in the modulus of elasticity of polymers exposed to vacuum, being possible to notice the influence of atomic bond energy on the behavior of exposed materials as present in the literature. However, further studies are still needed to better understand the observed behavior. In addition, the results indicate a possibility that low-cost polymers can be used in aeronautical and aerospace applications up to 85 km in altitude. To confirm these results, some complementary analyses are required, such as radiation degradation analysis, tensile testing, impact, microscopy analysis and the use of a mass spectrometer to better understand the mechanical properties of the material.

ACKNOWLEDGMENTS

We would like to thank the professors involved in the research and the laboratories of the Universidade de Brasília for their technical support.

REFERENCES

1. Conner BP, Manogharan GP, Martof AN, Rodomsky LM, Rodomsky CM, Jordan DC, et al. Making sense of 3-D printing: Creating a map of additive manufacturing products and services. Addit Manuf. 2014;1-4:64-76. https://doi.org/10.1016/j.addma.2014.08.005

2. Haeusler MH, Muehlbauer M, Bohneberger S, Burry J. Furniture Design Using CustomOptimised Structural Nodes. In: 22nd International Conference of the Association for Computer Aided Architectural Design Research, Hong Kong; 2017. p. 841- 851.

3. Song C, Lin F, Ba Z, Ren K, Zhou C, Xu W. My smartphone knows what you print: exploring smartphone based side-channel attacks against 3D printers. In: Conference on Computer and Communications Security, Vienna; 2016. p. 895-907. https://doi.org/10.1145/2976749.2978300

4. Cicala G, Latteri A, Del Curto B, Lo Russo A, Recca G, Farè S. Engineering thermoplastic for additive manufacturing: a critical perspective with experimental evidence to support functional applications. J Appl Biomater Funct Mater. 2017;15(1):10-e18. https://doi.org/10.5301%2Fjabfm.5000343

5. Tanikella NG, Wittbrodt B, Pearce JM. Tensile strength of commercial polymer materials for fused filament fabrication 3D printing. Addit Manuf. 2017;15:40-7. https://doi.org/10.1016/j.addma.2017.03.005

6. Divyathej MV, Varun M, Rajeev P. Analysis of mechanical behavior of 3D printed ABS parts by experiments. Int J Eng Res. 2016;7(3):116-24.

7. Berman B. 3-D printing: the new industrial revolution. Bus Horiz. 2012;55(2):155-62. https://doi.org/10.1016/j.bushor.2011.11.003

8. Hara D, Ferreira DA, Degasperi FT. Cálculo E determinação experimental da taxa de desgaseificação de materiais poliméricos em vácuo. São Paulo: FATEC-SP; 2011.

9. Paiva JA. Aplicações da tecnologia do vácuo em engenharia mecânica. Paraíba; 2010.

10. Moutinho AMC, Silva ME, Cunha MA. Tecnologia do vácuo. Portugal; 1980.

11. Paiva JA. Aplicações da tecnologia do vácuo em projeto de engenharia de precisão. Paraíba; 2010.

12. Frankel HE. Effect of vacuum on materials. Maryland: NASA-Goddard Space Flight Center; 1969.

13. American Society for Testing and Materials. Standard Test Method for Total Mass Loss and Collected Volatile Condensable Materials from Outgassing in a Vacuum Environment. American Society for Testing and Materials; 1993.

14. American Society for Testing and Materials. Standard Test Method for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials. American Society for Testing and Materials; 1997.

15. American Society for Testing and Materials. Standard Test Methods for Determining the Effects of High Altitude on Packaging Systems by Vacuum Method. American Society for Testing and Materials; 2001.

16. Bitzer T. Honeycomb technology: materials, design, manufacturing, applications and testing. Dublin: Springer Science Business Media; 1997.

17. Callister WD. Ciência e engenharia de materiais: uma introdução. 5ª ed. Rio de Janeiro: LTC; 2002.

18. NASA-TM-X-74335. U.S. Standard Atmosphere. United States: NASA; 1976.

19. Baranowski M, Woźniak-Braszak A, Jurga K, Jurga J, Hołderna-Natkaniec K. Molecular Dynamics in Poly(Ethylene Terephthalate) (PET) and Poly(Ethylene Terephthalate)-Glycol (PETG). 2009.

20. Canevarolo Jr. SV. Ciência dos polímeros: um texto básico para tecnólogos e engenheiros. 2ª ed. São Paulo: Artliber; 2006.