EFFECTS OF VACUUM EXPOSURE ON MECHANICAL PROPERTIES OF THERMOPLASTICS MATERIALS

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Abstract

The present work 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 (Fused Deposition Modelling - FDM) and exposed to low vacuum. The study is about these three materials due to accessibility of these thermoplastics and the possibility of applying them to prototypes used at low pressure. The experiment was composed of three moments consisting of 3D modeling and manufacturing of the specimens, drying process, and vacuum exposure for twenty-four hours, according to ASTM D6653/D6653M 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 verify the possibility of using thermoplastics commonly used in additive manufacturing for low-impact space applications.

1. Introduction

Additive manufacturing, also known as 3D printing, proposes an innovative production model, which allows a high level of customization of objects. [1] It is remarkable how quickly the additive manufacturing technique has evolved, with applications in several engineering areas available [2]. 3D 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, a 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], besides being very popular, PLA is easier to print than ABS, having more efficient thermomechanical properties, better mechanical resistance, and lower thermal expansion coefficient. PETG is considered a filament with 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 three-dimensional printing, one can employ a 3D computer-aided design (CAD) software 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 has also contributed significantly to scientific research and industry in recent years. According to Hara, Ferreira, and Degasperi [8], this is due to vacuum use in studies that analyze rarefied and controlled atmosphere. Problems of control of suspended particles, fixation of tools and prototypes, molecular deposits, and gas removal are examples that one can solve with this technology's help [9]. Thus, it is necessary to research the effect of vacuum on materials' mechanical properties under these conditions.

In this research, we choose a mechanical vacuum pump capable of generating a 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-

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pressure situations, being irrelevant to the gas flow and the molecules' disposition. We define a low vacuum between 105 and 10-1 Pa [11].

One can improve a polymer by vacuum exposure at a high temperature. Previous experimental work determined that rupture stresses increase when exposing a polymer to high vacuum and high temperatures [12]. 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 simple materials used in 3D printing, the preference for thermoplastic materials ABS, PLA, and PETG in this research area 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 printer (FDM), 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 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.

2. Methodology

The experiment's development was composed of 3 stages: the first was the manufacture of bending specimens through additive manufacturing; the second stage was the drying and exposure to vacuum, a part of the specimens; the third stage was the mechanical testing and data analysis.

For the development of the experiment, we manufactured the specimens with three different thermoplastic materials: Lactic Polyacid (PLA), Acrylonitrile Butadiene Styrene (ABS), Polyethylene Glycol Terephthalate (PETG), where was manufactured 18 specimens of each material - half would be exposed to vacuum, and another part will serve as the control sample. The first step for manufacturing is to prepare the computer-aided design (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. After, from the CAD of the specimens, it was performed the Slicing of the same 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, the 100% filling, the overlap edge of 60%, the nozzle 0.4 and the wall thickness of 1.2mm. The filaments used for the specimen production are from the manufacturer 3Dlab of L.9AC3, L.9AC4, and L.9AC5 numbers of a 1.75 mm diameter recommend the printing parameters of table 1 [17].

Table 1. *Recommended Printing Parameters to 3D Lab filament according to the provider.*

Recommended Printing Parameters			
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

We manufactured the specimens using the 3D printers of the Laboratory of Aerospace Structures (LAE) of the University of Brasilia, Campus UnB Gama. The printer used was the Graber model i3 in medium density wood structure (MDF - Medium Density Particleboard) with simple extrusion, whose print dimensions are 200 mm width and length, and 200 mm hight 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 9 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

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precision scale model ATC224 with four decimal places precision and a VONDER digital caliper with two decimal places precision used to measure the specimens' mass [16].
We used the apparatus of the Space Systems Laboratory (LASE) of the University of Brasilia, 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 has a diameter of 755 mm and a length of 1040 mm, according to Figures1, 2 and 3, connected to a mechanical type vacuum pump. Due to the pump's suction capacity and the vacuum chamber's volume, it is only possible to reach a minimum pressure of 0.1 Pa. It is enough for this research since the objective is to perform a test to understand thermoplastics' behavior processed by additive manufacturing when exposed to low vacuum.
The ASTM D6653/D6653M requests that before exposure to vacuum, specimens stay at a temperature of 5°C for 24 hours, or stay for 24 hours at a temperature of 25° C. For this experiment's development, we choose 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.

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Fig. 1. *Vacuum Chamber.*

Fig. 2. *Vacuum Chamber CAD.*

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

Fig. 3. *Specimens inside the chamber.*

After the allocation of the specimens, we initiated the vacuum suction procedure with 24-hour exposure duration.

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We removed the specimens, and after this period, we performed the bending tests. We used the INSTRON 8801 (100KN) machine to perform the bending test according to the ASTM D790 standard. The 3 points bending method was adopted, with a descent speed of 5 mm/s, velocity provided by the standard. We employed a distance of 102.4 mm between the supports. The specimens are 127.00 ±2.00 mm long, 12.7 ± 0.5 mm wide, and 3.2 ± 0.2 mm high. The test was performed at room temperature and 24 °C, obeying the standard, which specifies that the temperature must be between 23°C and 25 °C.

Fig 4. *Bending test.*

3. Results and Discussions

From the Pirani sensor connected to the computer, it was possible to capture the pressure in the experiment execution time interval and generate the corresponding vacuum curve, together with the vacuum curve with the empty chamber, Figure 5, for the analysis. The pressure stabilized from 0.5 Pa, which corresponds to an altitude of approximately 85 km, i.e., the ionosphere's beginning. We defined the altitude from the U. S. Standard atmosphere [18], and we present the graph of pressure by altitude in Figure 6.

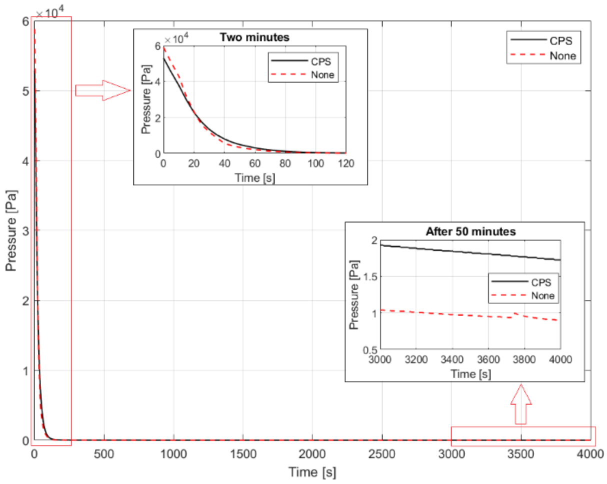

Fig 5. *Pressure curve.*

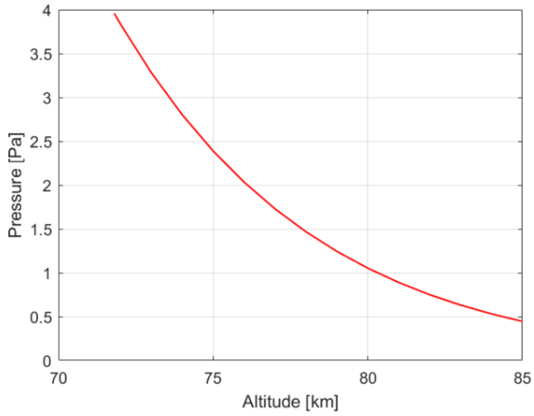

Fig 6. *Pressure by altitude.*

Figure 5 shows a faster descent at the beginning. After 20 seconds, the chamber's pressure with the specimens is higher than the pressure of the empty chamber, indicating a probable sublimation of the thermoplastic material or the rupture of air pockets in the specimen's structure. We noticed that the chamber's pressure with the specimens has stabilized above the pressure without the specimens due to releasing pockets of gases 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, 25].

The 3-point bending test provides the average force curves per arrow, shown in Figures 6, 7, and 8. It was possible

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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.

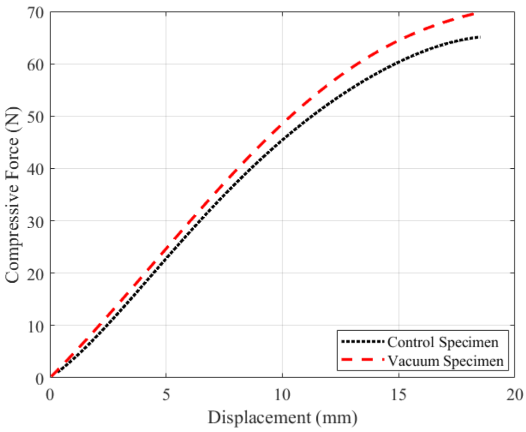

Fig. 7. *PLA force by deflection graph*

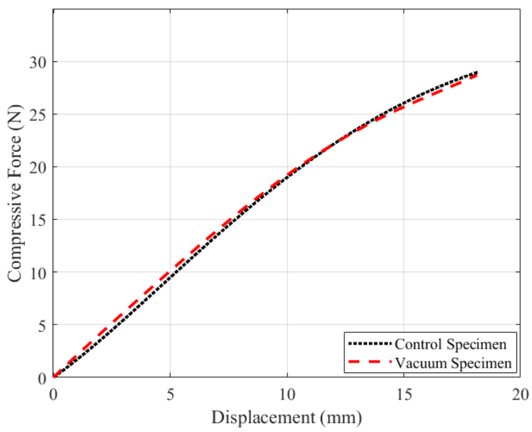

Fig. 8. *ABS force by deflection graph.*

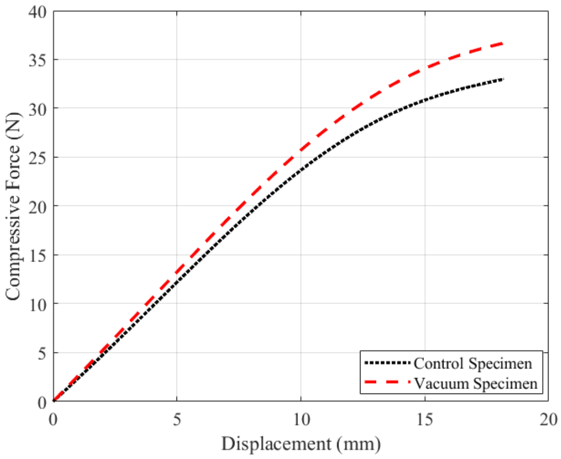

Fig. 9. *PETG force by deflection graph.*

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	22.9538 ± 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

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One can notice in table 2 that after exposure to vacuum, the PLA endured about 3.24% more load than testing specimens that we did not expose to vacuum. The same happened for ABS, which endured about 9.46% more load. However, PETG showed an inverse behavior in which a load was 2.10% lower than specimens that we did not expose to vacuum. The divergence in behavior between PLA and PETG polymers, which are semi-crystalline, indicates that the polymers' crystallinity does not influence their behavior under vacuum. However ,Frankel [12] demonstrates in his work that the chemical binding energy in the composition of polymers influences 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. This because, among the three polymers, it has the strongest bonding energy. It becomes evident when analyzing the results of table 3. The PLA was the material that suffered most from the effects of vacuum exposure. The PLA had an increase in its modulus of elasticity of about 7.76%. The PETG suffered an increase of 7.08% of its modulus of elasticity. PETG is a copolymer that has in its structure a glycol in order to reduce the crystallization speed so that the material is translucent without losing its mechanical properties [19,20]. In figure 10, it is possible to see the molecular structure of PLA, PETG, and ABS [19,20,24].

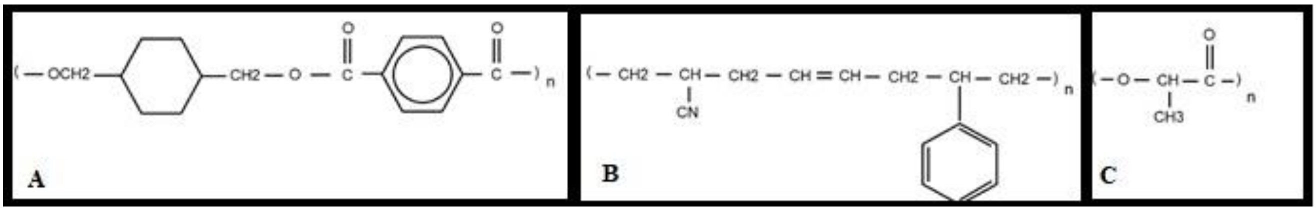

Fig 10. (A) Molecular structure PETG ; (B) Molecular structure ABS; (C) Molecular structure PLA.

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	3088.60	3328.40	7.76
ABS	1662.29	1767.77	6.62
PETG	1130.06	1209.57	7.08

The increase in the modulus of elasticity to bending of all materials tested demonstrates, along with the increase in maximum stress, that polymers' exposure to vacuum tends to be a post-manufacturing treatment method for polymers. According to Frankel [12], a polymer can be improved by post-curing in a vacuum at a high temperature. He could experimentally determine that rupture stresses increased when he exposed polymers to vacuum at high temperatures. The polymeric material invariably contains mold lubricants, fire retardant additives, and antioxidants plasticizers, among others. Such additives are removed from the material when exposed to vacuum, making it purer and, consequently, modifying its mechanical properties. 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 [20-22].
The curves obtained through the bending test confirm the behavior observed. By the elastic region's slope, it is possible to see that the modulus of elasticity due to bending increases, augmenting the material resistance to bending and the maximum force and displacement pair achieved, indicating that the material becomes less ductile [24-26].

4. Conclusion

The result obtained in the paper showed that the exposure of polymers to vacuum could 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 polymers' elasticity after vacuum exposure. It is possible to notice the influence of atomic bond energy on exposed materials' behavior as present in the literature. However, further studies are still needed to understand the observed behavior better.

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The results also indicate that low-cost polymers can be used in aeronautical and aerospace applications up to 85 km in altitude. However, some complementary analyses are required to confirm these results, such as radiation degradation analysis, tensile testing, impact, microscopy analysis, and a mass spectrometer to understand the material's mechanical properties better.

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