Analysis of the Exposure of PLA Surfaces to Ozone Gas, Ozonated Water, and Ultraviolet Radiation, Preliminary Evaluation

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Abstract. 3D printing, also known as additive manufacturing (AM), has been used in automobiles, aerospace, mechanical systems, medicines, and biological systems, among other environments. The present study aimed to evaluate possible alterations induced after exposure to ozone (O_3), both in the gaseous form and dissolved in water, and ultraviolet (UV) radiation, in materials that are used in three-dimensional (3D) printing, since they have a great potential for use in health. The material analyzed as polylactic acid (PLA), is the filament most commonly used. To evaluate the degradation of this material, objects were printed on a 3D printer, and the samples were divided into 3 groups Ozone Gas (O_3), Ozonated Water, and UV light, and monitored in two cycles of 90 min of exposure. Optical microscopy was used to evaluate the alterations of the surfaces exposed to the different treatments. The tested materials showed resistance to exposure to O_3 in the gas and liquid phases, but UV exposure showed that PLA was degraded. The data obtained suggest that this material can be used to manufacture parts to be used and exposed to O_3 gas, as well as ozonated water. In this sense, the use of PLA is promising in health equipment and instruments, such as components for ozone therapy, and/or disinfection equipment that uses ozone or ozonated water.

Keywords: Ozone · PLA · Surface modification · UV radiation

1 Introduction

3D printing, also known as additive manufacturing (AM), has been used in automotive, aerospace, mechanical systems, medicines, and biological systems, among other environments [1, 2]. The main advantage of 3D printing is the ability to build complex shapes economically using a wide variety of materials. By using this technology, consumers and industries can quickly prototype early-stage product designs [3].

J. L. B. Marques et al. (Eds.): CLAIB 2022/CBEB 2022, IFMBE Proceedings 101, pp. 253–262, 2024.
https://doi.org/10.1007/978-3-031-49410-9_25

Medical applications for 3D printing have expanded greatly in recent years and it is expected to revolutionize health, as the application of 3D printing in medicine can provide many benefits, including customization and customization of medical products, medicines, and equipment; increasing the effectiveness of known procedures and increase the reproduction of innovative techniques [4].

Among the main processes of 3D printing is the casting modeling (FDM) or manufacture of molten filaments (FFF), which belongs to the process of extrusion of materials, and is becoming the most popular due to its extrusion systems presenting lower cost and flexible, including thermoplastic materials [5]. However, the phenomena of chemical, photodynamic, and thermal degradation of 3D printed thermo-plastics are an inevitable problem for long-term reliability.

Components created through 3D printing technology come into contact with different environments in common practice, especially in the case of engineering, where there is a high probability that they will be exposed to considerably adverse effects, one of which is contact with agents causing chemical degradation, these can then have a fundamental impact on the properties and durability of these components [6].

Ozone stands out for its high oxidation potential, being the second strongest oxidizing agent, second only to fluoride [7]. The water solubility of O_3 is higher than in oxygen, so when dissolved in water, ozone decomposes much faster than in oxygen or air [8].

Both O_3 and UV radiation quickly damage unprotected polymers, which can considerably reduce their service life. In particular, highly unsaturated polymers (i.e., rubbers) are known to undergo a major degradation by O_3, due to their double bonds, while saturated polymers also react, but much more slowly [9].

UV treatment can mainly affect the properties of the surface region with minimal influence on volume properties depending on the choice of UV lamp and optical geometry [10].

The objective of this study was to perform the analysis of the surfaces of parts constituted of PLA after exposure to ozone gas, ozonated water, and UV separately, and thus, later, to verify whether or not there was a degradation of the material.

2 Materials and Methods

2.1 Fused Deposition Modeling

The test samples were manufactured using Fused Deposition Modeling (FDM) technology, using thermoplastic Poly Lactic Acid (PLA). PLA samples were designed using the Inventor® Professional 2020 CAD Software and printed using the 3D printer (MakerBot Replicator+), in association with your printing software (MakerBot Print, version 4.10.1.2056). The experiment was carried out in sample pieces of connectors to flow liquids and gases so that each part produced is composed of half of the connector already mentioned, in this sense the final sample was assembled by the junction of the two pieces printed by the system, Fig. 1.

The print fill density has been adjusted to 100% to inhibit leaks. To join the two pieces and ensure a better seal, Polytetrafluoroethylene (PTFE) tape was used.

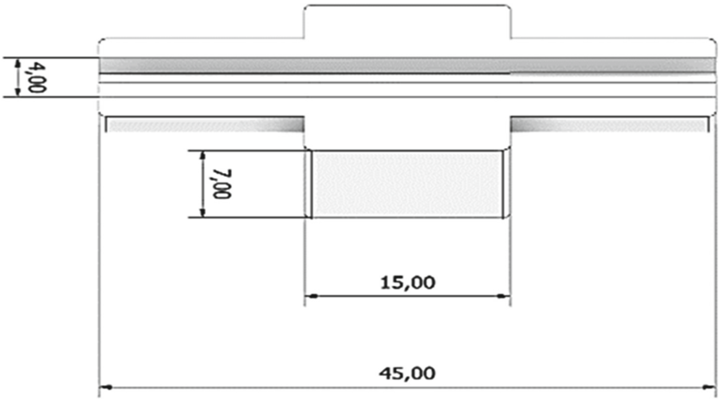

Fig. 1. The three-dimensional design of the connector is composed of two symmetrical parts, to obtain the sample with flat internal surfaces, and to perform exposures to O_3, UV, and ozonized water.

The samples were divided into 3 groups O_3 (gas), Ozonated Water, and UV, and monitored in two cycles of 90 min of exposure, with an interval of 90 min between them. Each test was performed considering two exposure surfaces.

2.2 Exposure to Ozone Gas

To perform the ozonation of the printed parts, an ozone generator (Ozone & Life, O&L 1. 5RM), at its inlet was connected to an oxygen cylinder in conjunction with a pressure-reducing valve, and flow regulator, specifically adjusted in 1/4 L/min. At the outlet of the ozone generator, the PLA part was connected to a flexible silicone duct as shown in Fig. 2. Ozonation occurred within a chapel with exhaustion in two cycles of 90 min of exposure to a concentration of 48 mg.

2.3 Exposure to Ozonated Water

A hydraulic apparatus containing a reservoir for storing distilled water was developed. This reservoir has an outlet where a pump of the centrifugal type was coupled, and to this was connected a three-way valve (Venturi). The entry of hollow zone gas through the third access route of this valve, thus produces the mixture with pumped water, after passing through the Venturi the ozonized water will drain the two surfaces that make up the PLA connector, which returns by draining the reservoir, thus closing the hydraulic circuit. The excess ozone gas during this process is collected through a flexible tube, from the reservoir cover, the surplus O_3 was processed and discarded to the external medium through the exhaust system as shown in Fig. 3. A sensor that instantly obtains the dissolved ozone value was used to perform the analysis of ozone concentration in water using the tri-electrode measurement method (DOZ3O, Clean®).

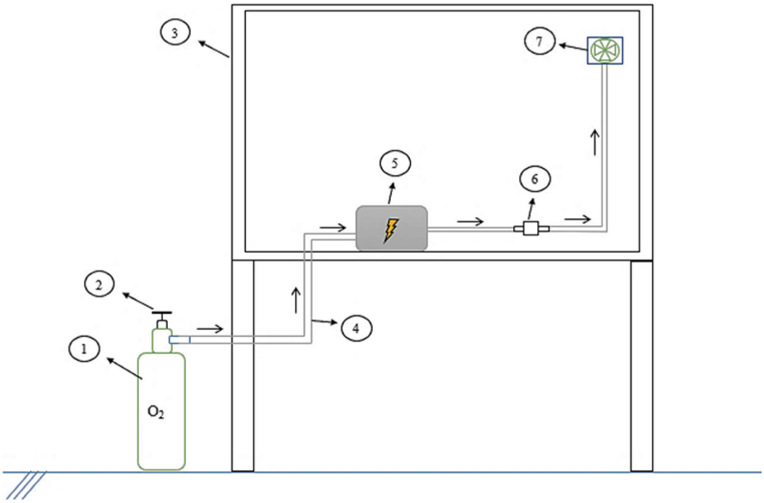

Fig. 2. Mounting equipment for the exposure of electrical parts to ozone gas. (1) Oxygen cylinder, (2) Pressure reducing valve and flow control, (3) Chapel with exhaust, (4) Silicone hose, (5) generator O_3, (6) PLA printed connector, (7) Overall disposal exhaust fan

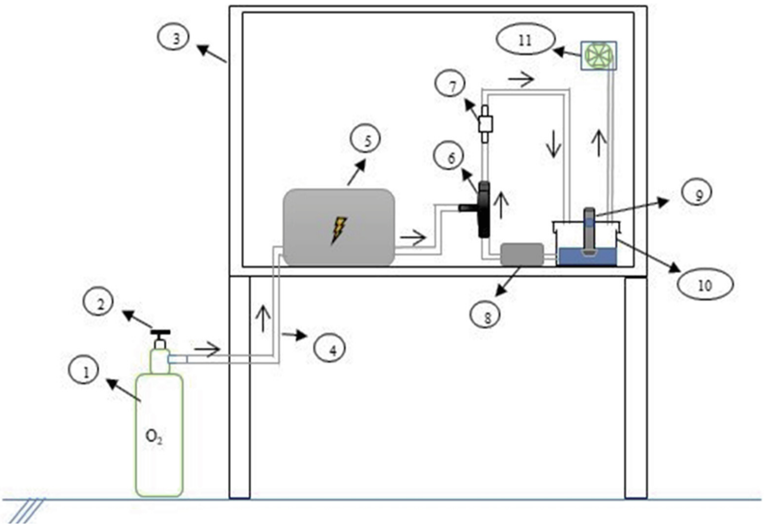

Fig. 3. Assembly was performed for the experimentation of exposure of parts containing flat surfaces of PLA, to ozonized water in a fluid dynamic situation. (1) Oxygen cylinder, (2) Pressure reducing valve and flow regulator, (3) Exhaust chapel, (4) Silicone hose, (5) O_3 generator, (6) Venturi valve, (7) sample connector printed in PLA, (8) Water pump, (9) Ozone sensor (10) Water tank, (11) Exhaust fan for the ozone not used.

2.4 Exposure to Ultraviolet (UV)

This stage was carried out in the Optical Diagnosis laboratory at the Center for Innovation, Technology, and Education (CITÉ) Technological Park of São José dos Cam-pos/SP. To perform the exposure of the PLA part to the UV, a chamber constructed with medium-density fiber panels was used, in this, there are mercury gas lamps of the "germicidal" type, which emit light radiation in the spectral bands UV-A + UV-B, (26 W, Zoo Med, CA, USA, 2 units; 26 W, Exo Terra, MA, USA, 2 units; and 15 W, Sylvania, Bavaria, Germany, 1 unit) (Fig. 4). Two cycles for each time 90 min of exposure were performed.

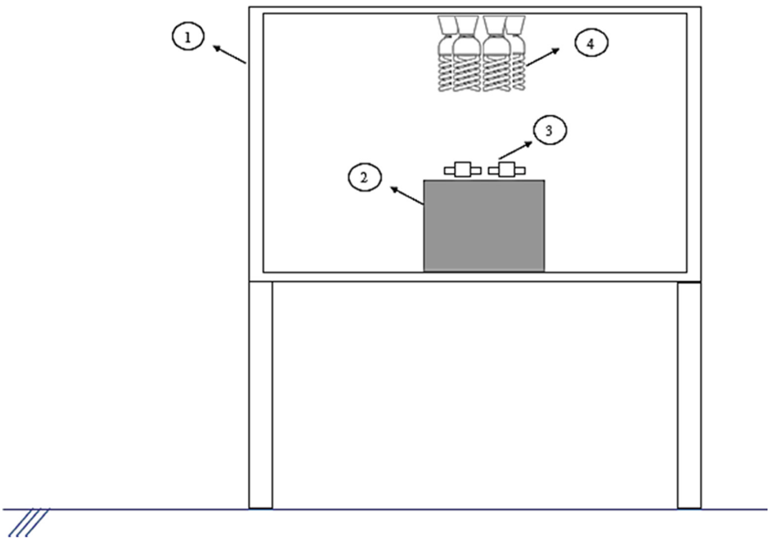

Fig. 4. Schematic representation of assembly for the exposure of sample parts constituted of PLA before UV radiation. (1) Reflective chamber for exposure, (2) Base with 40 cm height (3) PLA samples with separate symmetrical parts to allow the incidence of radiation, (4) UV lamps - A + UV - B.

2.5 Analysis of Parts Using an Optical Microscope

The images of microscopic optics were obtained in the Biomedical Instrumentation laboratory at the Center for Innovation, Technology, and Education (CITÉ) of the Technological Park of São José dos Campos/SP, through the optical microscope (Opton TNB-01T). The microscope is equipped with a set of lenses that offer magnifications of × 10, × 40, × 100, and × 1000 and a digital camera coupled to a computer for capturing images.

Optical microscopy was used as a non-destructive technique to investigate the surface of the parts. A more detailed analysis was performed in × 40 magnification with the change of focus depth/microscope position, to also visualize surface reliefs.

3 Results

Through the data collected from the ozone sensor, the curve of dissolved ozone concentration in the reservoir water was obtained, where it was verified that the maximum concentration reached 7.73 mg.L^{-1}. The data comprise the average of the two ozonation tests using distilled water for each 90 min cycle. The second curve indicated by the dashed line represents the average curve of the measurement points according to the polynomial equation representing the correlation coefficient (R2). This mathematical function, shown in Fig. 5, allows the calculation of ozone concentration in water as a function of ozonation time.

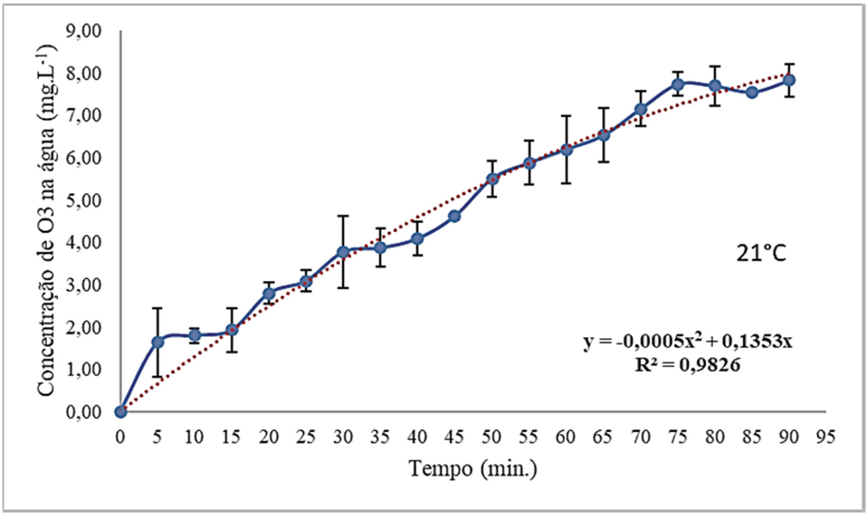

Fig. 5. Determination of the ozone concentration (mg.L^{-1}) dissolved in the water according to time.

When evaluating through the optical microscope it was possible to visualize that even after the second 90-min exposure cycle to the ozone gas in high concentration there was no degradation of the PLA part (Fig. 6).

After exposure of PLA pieces to ozonated water, it was observed that there was no degradation even after exposure to the second cycle of 90 min (Fig. 7).

When performing the analysis through the optical microscope it was possible to observe that after the second cycle of exposure of 90 min to the UV there was the degradation of the PLA part, with a reduction of the material, even eliminating parts and increasing the depth of the grooves as it is possible to observe through the indications in Fig. 8.

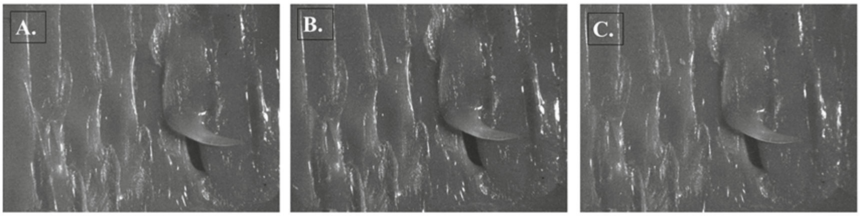

Fig. 6. Images were obtained from surfaces exposed to the flow of ozone gas, using the optical microscope with an x40 lens. (A) Before exposure to ozone gas. (B) After the first 90 min cycle of ozone gas actuation. (C) After the second cycle of 90 min of exposure to O_3.

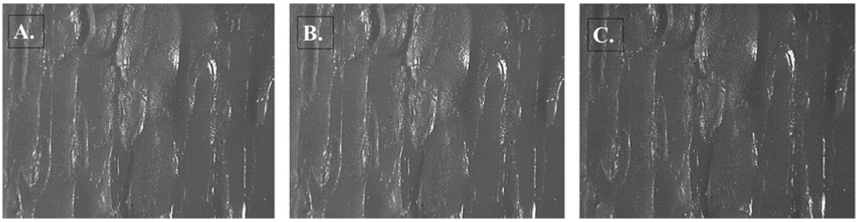

Fig. 7. Images were obtained from samples exposed to the ozonized water in fluid dynamic conditions, using an optical microscope with an x40 lens. (A) Before exposure to ozone water. (B) After the first 90 min cycle. (C) After the second cycle of 90 min.

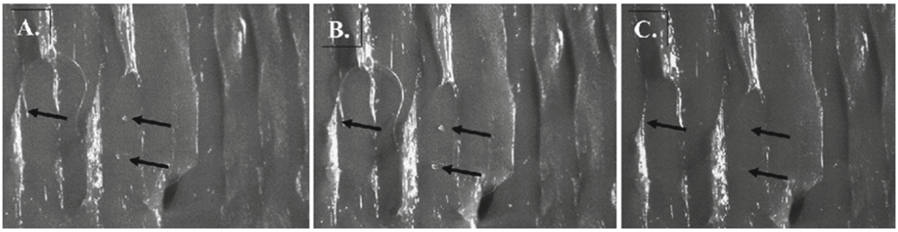

Fig. 8. Images were obtained through the microscope with an x40 lens, before exposure to UV light. (A) Before UV exposure. (B) After the first 90 min cycle of UV exposure. (C) After the second cycle of 90 min of UV exposure. The Arrows indicate where the material was degraded.

4 Discussion

3D Printing is an area of manufacturing engineering that is characterized by stages of building parts by automatic deposition layer by layer from a virtual model controlled by computer programs [3]. Recently due to the critical lack of personal protective equipment that occurred during the COVID-19 pandemic, the researchers [11], after analyzing the possibility of using 3D printing for the development of masks, found that despite the porosity, PLA can be considered appropriate material for this use.

Metal/mechanical machining and forming technology demand machines, devices, tools, and molds in the course of relatively high time and cost. The advantage of using part printing systems, with the use of 3D printers, is to obtain low production cost parts with different geometries and details without the organizational need for machining and assembly [12].

The manufactured parts are macroscopic objects, and the current study was focused on their ability to resist exposure to high ozone concentration both in their gaseous phase and dissolved in water and UV radiation, due to the use of these agents in health. Knowing that these agents cause the degradation of organic materials and polymers in general, this study aimed to evaluate the degree of damage due to the actions of the agents already mentioned. The results of optical microscopy showed that ozonized water and ozone gas did not degrade the surfaces of PLA parts.

According to Madrid Declaration on Ozone Therapy [13], the estimated time of ozonation of the water (double-distilled) is from 5 to 10 min for the volume used, since the time of exposition of wounds to O_3 gas is used periods of 5, 10, and 20 min [13]. In the present study, cycles with longer periods were carried out, aiming at greater exposure of the parts to oxidizing agents.

Ozonation is a promising technology, but it presents certain challenges because the materials used to produce this gas and its use systems must present characteristics of resistance to the degradation of this agent [14, 15]. Stainless steel, glass, and Teflon have good resistance to ozone when in moderate concentrations. Copper alloys are susceptible to oxidation, and polyvinyl chloride (PVC) and polyethylene (PE) are generally resistant at low concentrations [14]. In the case of natural rubber, rapid disintegration may occur [14, 15], while silicone has short-term resistance, but oxidizes in prolonged exposure [15].

The preliminary results of this study showed that PLA is a compatible material for the development of parts that act in systems in which the environment has ozone in the gas phase or diluted in water. Thus, due to the ease of obtaining different geometries of parts via 3D printing technology, it has become a viable alternative to the traditional machining and forming machine for the development of parts to be used in health, such as components for ozone therapy or disinfection equipment that use ozone or ozonized water as the main agent.

As can be seen in Fig. 8 there was a degradation of the surface of the PLA piece after the second cycle of UV exposure, corroborating the study conducted by [16]. This work performed by the author already mentioned, it was analyzed the photochemical action that UV-B radiation could cause in the mechanical properties of 3D printed parts made of PLA. After mechanical tests, the authors verified that the resistance decreased slightly for PLA samples submitted to a 24-h exposure, as well as post-exposure to UV-B radiation, which simulates the effect of the SUN's UV action, and the tested parts darkened, instating an increase in reflectivity.

It has been reported that UV radiation, O_3, and other oxygen-related species can oxidize the polymer surface and shorten its shelf life. According to [17] the intensity of UV radiation and the longer exposure time led to gradual pho-to-oxidation of the PLA surface, which results in visible surface deformation. The longer effect of O_3 concentration, atomic oxygen, and UV radiation causes the disintegration of the ester bonds that make up the material, with PLA samples becoming hydrophilic [10].

In a study carried out by [18], where the possibility of using 3D printing materials for applications in active particle generators, O_3 and UV radiation from electrical discharges was investigated, they concluded that from a macroscopic point of view, PLA and ABS could be used, at least on the experimental use scale, despite surface damage due to UV exposure.

5 Conclusion

In the present study, the possibility of using 3D printing materials for health applications related to exposure to ozone gas and ozonized water was evaluated. As test samples, PLA parts were used, which were integrated into the ozonation system with the potential to replace stainless steel connectors, for example, becoming a viable alternative with lower production cost and customizable, so that they can be used in health. The analysis of the surface by optical microscopy, after exposure of the groups to O_3 and ozonized water, leads to the conclusion that the use of PLA in parts that will be exposed to ozone gas and ozonized water is promising. The pieces printed in PLA showed mechanical stability and potentially high sealing, also corroborating the ecological aspects, the PLA is biodegradable and free of petroleum derivatives. Another advantage is the possibility of customizing and creating parts through 3D printing as needed in protocols involving ozone.

Acknowledgment. This study was financed in part by the Coordination for the Improvement of Higher Education Personnel - Brazil (CAPES) - Finance Code 001.

Conflict of Interest. The authors declare that they have no conflict of interest.

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