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# SURFACE CHARACTERIZATION OF COPPER-BASED BACTERICIDAL SEALANT FOR ADDITIVE MANUFACTURED PERSONAL PROTECTIVE EQUIPMENT

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**Abstract.** *This work aimed to obtain properties of the polymer surface based on polylactic acid (PLA) used in the manufacture of facial protectors (face shields) made by additive manufacturing (3D printing), in the uncoated and coated situation with an inorganic sealant based on copper, which is expected to provide bactericidal activity. The methodology included the manufacture of PLA polymeric plates through additive manufacturing, which were coated with a copper sulfate-based sealant. Techniques of visual inspection, optical microscopy (OM), scanning electron microscopy (SEM), semi-quantitative chemical analysis by energy-dispersive spectroscopy (EDS), surface roughness measurements and digital image analysis and processing (DIP) were used. The results showed that it was possible to reach 17% surface coverage and that the copper sulfate was encapsulated by the varnish, which was used as a matrix for the sealant.*

**Keywords:** *PLA, 3D printing, roughness, bactericidal inorganic sealant*

## 1. INTRODUCTION

The capacity of a substance to exterminate or render inactive microbes such as bacteria, fungi, and viruses endows it with the designation of being an “antimicrobial surface”. Numerous studies have showcased copper’s superior antimicrobial efficacy when compared with materials such as aluminum, stainless steel, PVC (polyvinyl chloride), and polyethylene, for instance. The antimicrobial effect of copper is dependent on a variety of system-related factors including temperature, acidity or alkalinity of the environment, and the presence of organic matter, among others. Furthermore, attributes related to the material’s surface, such as morphological aspects, roughness, chemical composition, and surface tension, are found to influence the adhesive ability, survival, and reproduction of microorganisms (Canabarro *et al.*, 2008; Azam *et al.*, 2012; Amousoltani *et al.*, 2019; Casey *et al.*, 2011; Cioffi *et al.*, 2005).

Copper is recognized for its antimicrobial properties against a broad spectrum of microorganisms that are important in both industry and the environment. However, it is particularly effective against pathogens affecting humans and animals, as these are rapidly neutralized when they come into contact with copper. The pathogenic bacteria that are notably affected include *Listeria monocytogenes*, *Campylobacter jejuni*, *Salmonella Enteritidis*, *Legionella pneumophila*, *Enterobacter spp.*, *Staphylococcus aureus*, *Proteus spp.*, *Escherichia coli*, *Group D Streptococcus*, *Pseudomonas aeruginosa*, and *Mycobacteria* (Jorgensen and Pfaller, 2015) linked to tuberculosis. In the case of pathogenic fungi, copper has a confirmed efficacy against *Aspergillus niger* and *Candida albicans* (Carlile *et al.*, 2001). Furthermore, its antiviral activity has been confirmed against the Poliovirus, which causes poliomyelitis, and the Influenza virus, which leads to the H1N1 flu (Delgado *et al.*, 2011; Diniz *et al.*, 2002).

The antimicrobial mechanisms of copper are intricate and transpire in various forms, both within cells and in the interstitial spaces between cells. A critical factor accountable for the antimicrobial properties of copper is its high reduction potential. This chemical characteristic allows copper ions to modify the proteins within microbial cells in such a way that

they can no longer perform their normal functions. It has also been noted that copper is responsible for inhibiting electron transport in cell wall interactions, by binding to DNA (deoxyribonucleic acid) and disrupting helical structures. Through these mechanisms and others, copper effectively inactivates numerous types of bacteria, fungi, and viruses (Cioffi *et al.*, 2005; Delgado *et al.*, 2011).

Given that the deployment of copper-based hospital equipment and personal protective equipment (PPE) would not be feasible due to the associated costs and other design issues, the application of copper-based coatings (such as varnishes, paints, or sealants) could introduce antimicrobial benefits in the hospital environment. Sealants are either organic or inorganic coatings that can be applied to various types of surfaces as part of a paint scheme. These sealants can be resin-based (epoxy, polyester, or polyurethane) or wax-based, and may or may not incorporate metallic pigments. However, in order to ensure their optimal performance, these sealants must have a low ratio of solids by volume. The solid pigments should be small and compatible with the surface to be coated. Moreover, the sealant should have low water absorption, be compatible with the work environment, and have a thin layer, typically 75 micrometers or less (International Organization for Standardization, 2011; Jiao *et al.*, 2017).

In this context, the objective of this study (de Souza *et al.*, 2020) was to characterize the surfaces of PLA-based (polylactic acid) polymers used in the fabrication of face shields produced through additive manufacturing (3D printing), both uncoated and coated with a copper-based inorganic sealant at varying copper proportions. It is anticipated that this sealant could be manually and simply applied onto face shields and other materials used in a hospital setting, in order to inhibit bacterial and viral proliferation.

## 2. METHODOLOGY

A total of 100 PLA plates, each with dimensions of 2.5 X 2.5 X 0.5 cm, were fabricated using the additive manufacturing process with a Sethi printer, model BB, possessing a bed of 400 x 400 x 400 mm. The production process of these plates employed the same parameters typically used for constructing the support structure of transparent acetate face shields used in hospital settings. The specific parameters include a nozzle temperature of 210 °C, a non-heated bed, a nozzle speed of 17.5 mm/s on the outer layers, a nozzle speed of 35 mm/s on the inner layers, and a layer height of 0.3 mm. The PLA was sourced from a single supplier.

The roughness measurements of the plate surfaces, both before and after being coated with an inorganic sealant, were conducted using a Mitutoyo SurfTest SJ - 210 roughness meter, equipped with ST Communication Tool software. Twenty measurements were taken in each of two mutually perpendicular directions, maintaining the formal and scientific tone of the investigation.

The sealant used to coat one side of the plate surfaces was prepared by mixing solid copper sulfate particles with diameters ranging between 0.5-200 µm and a varnish. Mixtures containing between 0.1 - 0.001 g of copper sulfate and 1 mL of varnish were manually applied to the plate surfaces using a Tigre brand number 267-6 brush. After 24 hours of curing, the mixtures were considered to be adequately adhered, as confirmed by visual inspection. Figure 1 shows an example of an uncoated printed plate and a printed plate coated with the inorganic sealant.

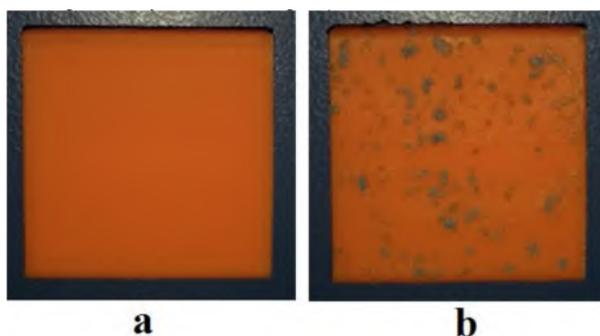


Figure 1. 3D printed PLA plates. a - without sealant; b - coated with a copper-based sealant containing 0.01g of copper sulfate per mL of varnish. Magnification of 3.5 X.

The surfaces of the plates, both with and without sealant, across various tested compositions, were scrutinized via stereo microscopy, optical microscopy (OM) (Pimenta *et al.*, 2020a,b), and scanning electron microscopy (SEM) (Pimenta *et al.*, 2020a,c). This was accomplished through the use of Olympus model 8ZX16, Zeiss model M2m, and Hitachi model TM3000 microscopes, with the latter operating at 15kV. Analysis and mapping of present chemical elements (de Castro Braga *et al.*, 2019; de Campos *et al.*, 2020) were conducted through Energy Dispersive Spectroscopy (EDS) (Freitas *et al.*, 2016b; Ribeiro *et al.*, 2016; Freitas *et al.*, 2016a; Pereira *et al.*, 2021; Felix *et al.*, 2018) employing an X Flash MIN SVE detector, manufactured by Bruker, integrated with the SEM.

Analysis and digital image processing (DIP) (Gonzalez, 2009; Paciornik and Mauricio, 1989) on a macro scale (10

images for each condition at a magnification of 3.5 X) of surfaces covered with sealant were carried out using FIJI Image J software version 2.0.0-rc-66/1.52b. Techniques of color segmentation in the Red-Green-Blue (RGB) system were employed to determine the percentage area fraction covered with copper sulphate for each tested mixing condition.

### 3. RESULTS AND DISCUSSION

Figure 2 displays examples of roughness profiles obtained for the surface of the Polylactic Acid (PLA) fabricated through additive manufacturing, where pronounced anisotropy or variation of the property as a function of direction could be observed. This situation is connected to the manner in which the polymer layers were deposited during the production of the plates and to their manufacturing process (Duty and Love, 2015; Ashby, 1987).

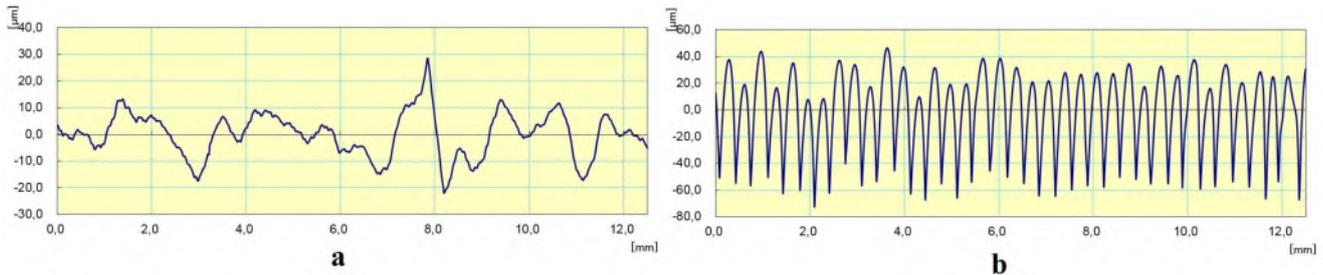


Figure 2. Roughness profile of uncoated PLA. (a) - parallel to the deposition lines of the print. (b) - perpendicular to the deposition lines.

The average roughness values ( $R_a$ ) obtained were  $22.51 \pm 8.40 \mu\text{m}$  in the direction parallel to the preferential orientation lines generated by the print, and  $8.72 \pm 3.49 \mu\text{m}$  in the direction perpendicular to these lines. The presence of the sealant with the lowest concentrations of copper sulfate tested resulted in a mild reduction in  $R_a$  values, for both directions. This effect was expected, as the varnish filled the grooves' cavities and smoothed the disparities between surface peaks and depressions. The  $R_a$  values obtained for 0.001g of copper sulfate / mL of varnish were  $18.10 \pm 0.67 \mu\text{m}$  and  $4.36 \pm 0.81 \mu\text{m}$ , for the directions parallel and perpendicular to the print lines respectively. For the highest concentrations of copper sulfate in the sealant, it was not possible to assess roughness profiles, as copper sulfate particles formed clusters of small agglomerates on the PLA. This smoothing of the troughs can be observed in Figure 3, which presents the images of the sample surface as observed by SEM under conditions with and without sealant. Figure 4 provides more detail, depicting the terrain features and the copper sulfate particles encased by the varnish using MO technique. The MO technique alone did not allow us to determine whether the particles were completely encapsulated by the varnish. In Figure 3, it is observable that the additive manufacturing process resulted in approximately 3 filaments per millimeter, which is consistent with the roughness profile in Figure 2b.

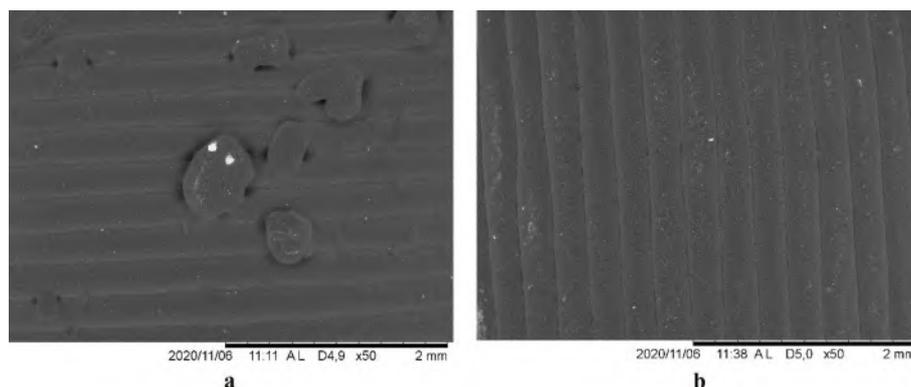


Figure 3. Surface of PLA with sealant (a) and surface of PLA without sealant (b). SEM, 50X magnification.

Figure 5 showcases: (a) a SEM image focused on a region with a copper sulfate particle, (b) the EDS-derived color map indicating the chemical elements present in the region, and (c) the characteristic energy spectrum profile associated with the detected elements. Micro-chemical analysis of the PLA via EDS revealed indications that the copper sulfate particles were effectively encapsulated by the varnish. Notably, even though copper sulfate particles were present in the analyzed region, the EDS technique was not able to detect it. This is likely attributed to the varnish encapsulation, predominantly consisting of carbon and silicon, as these elements displayed the most pronounced energy peaks in Figure 5(c). The thickness of the varnish encapsulation, on the scale of one millimeter, might have obstructed the beam, preventing the EDS from detecting the copper. Figure 5(c) also illustrates minor peaks for aluminum and oxygen, commonly observed in

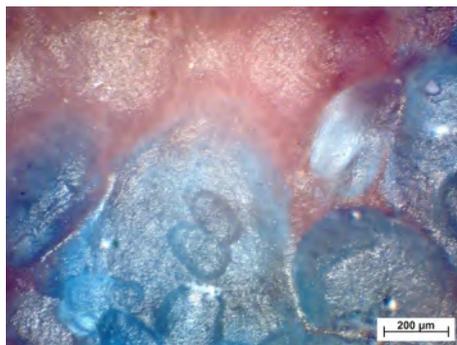


Figure 4. Copper sulfate particles (bluish regions) adhered to the surface of PLA. Magnification: 10X, using a microscope objective.

such samples. A trace amount of sulfur was also identified, presumably residual in nature. Such encapsulation enhances the durability of copper sulfate in PPEs. In addition, the bactericidal and antiviral effectiveness of the system depends on this encapsulation (Diniz *et al.*, 2002; Nordstrom *et al.*, 2012; Sanin *et al.*, 2003).

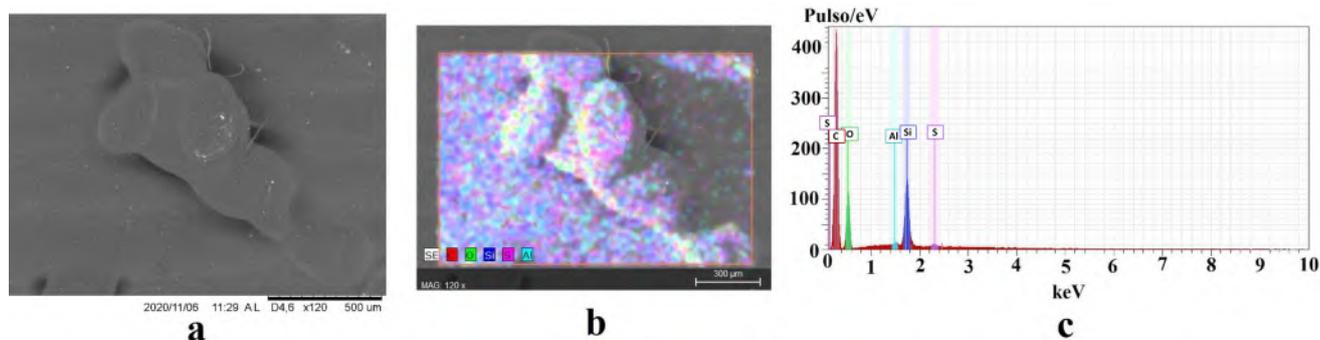


Figure 5. Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS) were employed to examine a cluster of copper sulfate particles deposited on PLA. Figure (a) displays a SEM image at a magnification of 120X, while Figure (b) represents the EDS mapping of the chemical elements present. Figure (c) exhibits the results of EDS through characteristic energy spectra.

The Particle Distribution Index (PDI) established that the manual process of sealant application resulted in copper sulfate coating on PLA surfaces, varying in coverage from 1 - 17% of the plate's total surface area. This range corresponds to the relative absence or abundance of the said compound. Figure 6 provides a representative illustration of one such outcome, based on the analyzed images and quantification of the surface area fraction occupied by the copper-based reactant, visible in various blue hues.



Figure 6. Copper sulfate particles, comprising approximately 17% of the coated surface, as determined by Particle Size Distribution (PSD) measurements.

Taking into account that the features and parameters associated with the surface will strongly impact the adhesion mechanisms, survival, and proliferation of bacteria and viruses on the material, such as the average roughness (Ra),

morphological aspects, and chemical composition, these must be determined so that they can be correlated with the biological mechanisms of the contacting cell cultures (Canabarro *et al.*, 2008; Diniz *et al.*, 2002).

#### 4. CONCLUSIONS

In light of the employed characterization methodologies, it was inferred that the sealant under consideration, integrated with copper sulfate particles, designed to provide a coating for components made from Polylactic Acid (PLA) via additive manufacturing for hospital-grade face shields, demonstrated significant anisotropic properties in relation to the mean surface roughness (Ra). This observation is linked to the layer-by-layer deposition process of PLA during additive manufacturing. Clusters were formed by the copper sulfate particles, which covered areas varying from 1-17% of the coated surfaces for copper sulfate amounts between 0.1 - 0.001g per milliliter of sealant, and were firmly attached after a curing period of 24 hours. Despite the sealant's presence, even with the maximum concentrations of copper sulfate, the surfaces primarily exhibited carbon and silicon, suggesting a thorough encapsulation and envelopment of the particles, as no traces of copper were observed. While copper sulfate is recognized as harmful when ingested, its application in face shields is expected to hinder bacterial growth without posing any risks to the users. Future studies will correlate morphological, qualitative, and quantitative assessments of the material's surface and the inorganic compound with both qualitative and quantitative evaluations of cell cultures to gauge the bactericidal impacts of the surface coated with the suggested sealant.

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