

## COB- 2023-1813

# EVALUATION OF 3D-PRINTABILITY OF COPPER METAL PASTES

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**Abstract.** Among the Additive Manufacturing (AM) technologies, 3D extrusion of viscous pastes has been highlighted because of its great flexibility of materials that can be processed, high material utilizations and enabling to produce parts with complex-shaped geometries and isotropic properties. However, there is a lack in the investigation of manufacturing metals by 3D extrusion of viscous pastes published in the literature. In this context, the focus of this study was on evaluating the printability of copper pastes. The pastes were fabricated using two water-based binder systems. By systematically varying the powder load and binder composition, we aimed to identify the binder composition that yielded the desired viscosity and printability characteristics. This information is crucial for ensuring successful additive manufacturing processes. Overall, this investigation provided valuable insights into the development of copper pastes for 3D extrusion, highlighting the importance of binder selection in achieving the desired material properties and process performance.

**Keywords:** Copper pastes, Rheology, 3D-extrusion, Printability.

## 1. INTRODUCTION

For the purpose of enhancing manufacturing efficiency and cost reduction, the concept of design for additive manufacturing (AM) has been introduced. Current design methodologies for AM predominantly rely on surrogate models (Zang et al., 2020). However, with the abundance of available data in recent times, machine learning (ML) techniques have been employed in various fields such as medical diagnosis, image processing, prediction, classification, and learning associations. Consequently, numerous studies have been conducted to explore the utilization of machine learning in optimizing the process parameters of AM, aligning them with specific objectives (Parenti, 2021).

Additive manufacturing (AM), initially introduced as rapid prototyping in the 1980s, revolutionized the creation of three-dimensional objects through computer-aided design (CAD). Originally intended for engineers to materialize their ideas, rapid prototyping has emerged as one of the early forms of additive manufacturing processes. Unlike traditional methods, this technology enables the production of functional parts, not just mere models. Its impact on product development has been significant, as it offers advantages such as reduced time and cost, enhanced human interaction, and shortened product development cycles. Additionally, AM provides the flexibility to fabricate complex shapes that would otherwise be challenging to machine. Although its adoption in the manufacturing sector is still evolving, it has found extensive use among scientists, medical professionals, students, professors, market researchers, and artists. Scientists and students can swiftly construct and analyze models for theoretical comprehension and studies, doctors can create replicas of damaged body parts to aid in analysis and surgical planning, market researchers can gather insights on consumer perception of new products, and artists can explore their creativity more freely with the aid of rapid prototyping (Wong et al., 2019).

In the last decades, new AM technologies enabling printing ceramic and metallic components have emerged. Among these technologies, 3D printing technologies based on past/ink extrusion has been highlighted because of its low cost, similarity with fused filament fabrication, great flexibility of materials that can be processed, high material utilization, and for enabling to produce parts with complex-shaped geometries and isotropic properties. These extrusion-based technologies have been widely investigated for ceramic production (Ang, 2023). However, there is a lack in the investigation on manufacturing metals and metal matrix composites by 3D extrusion of pastes published in the literature. Developing metal pastes with suitable printability, is a key for the application 3D extrusion of pastes for metal fabrication.

The printability of a material in additive manufacturing is significantly influenced by various viscosity parameters. Flowability refers to the material's ability to flow smoothly and evenly during the printing process, ensuring uniform layer

deposition. Extrudability is crucial for proper material extrusion through the nozzle, allowing for accurate part formation. Open time refers to the duration during which the material remains workable and printable, affecting the overall printing speed and build quality. Buildability relates to the material's ability to maintain its shape and structural integrity during layer stacking, ensuring dimensional accuracy. Green strength is a measure of the material's initial strength after printing, indicating its ability to support subsequent layers and resist deformation. Hydration plays a role in materials that require curing or drying, affecting their setting and hardening processes. Compressive strength reflects the material's resistance to compression forces, determining its load-bearing capacity. Finally, air void content and distribution are critical to assess the presence of air bubbles or defects within the printed structure, as they can impact its overall strength and integrity. Careful control and optimization of these viscosity parameters are essential for achieving desirable printability, ensuring successful fabrication of high-quality and reliable printed components (Chen et al., 2020a).

Direct ink writing (DIW) technology is an extrusion-based printing technique that allows for the precise customization and printing of 3D structures at meso- and microscales. It involves the deposition of a viscoelastic ink through a fine nozzle in a layer-by-layer fashion. The process requires 3D modeling, generating movement paths for the nozzle, and ink deposition. Machine parameters like nozzle size and printing speed influence printing accuracy and resolution. Smaller nozzles improve resolution but require higher pressure and longer build time. DIW can extrude continuous filaments at room temperature based on ink's rheological properties. Optimizing the ink's rheology is critical and can be achieved through chemical modification and the addition of modifiers. After deposition, the ink solidifies naturally or with external assistance. DIW technology minimizes post-processing and material waste, making it an economical and sustainable manufacturing process. The printability and shape fidelity of the ink are crucial, requiring shear-thinning behavior for smooth flow through nozzles. The viscosity of DIW ink typically ranges from 102 to 106 mPa s at a shear rate of approximately  $0.1\text{s}^{-1}$  (Saadi, 2021).

Zhang et al. (2017) fabricated WC-20Co components by 3D printing of WC-20Co ink, the process involved slicing the 3D model into 2D-slices and printing an ink composed of a slurry of WC-20Co powder dispersed in an organic monomer solution. The slurry is delivered to a screw extruder under pressure, along with the initiator and catalyst. In their process, the materials were blended, extruded through a nozzle, and deposited layer by layer on a printing platform. The organic monomer cross-links and polymerizes, fixing the solid powder in place. The resulting green body is then dried, debound, and sintered. The 3D printing equipment allowed flexible forming, simple structure, and accurate control. WC-20Co slurry is used as the printable ink in this study, aiming to fabricate high-density WC-20Co components with excellent mechanical properties.

Copper metal pastes, renowned for its excellent electrical and thermal conductivities, has become widely utilized in engineering applications. However, copper exhibits poor mechanical properties, particularly at elevated temperatures. To overcome this limitation, researchers have explored the incorporation of suitable fillers or reinforcements with copper, such as carbon fibers/nanofibers, graphite (nano) platelets, and single or few-layer graphene. These fillers possess desirable attributes including high thermal conductivity, impressive mechanical strength, and electrical properties (Elsayed, 2019).

Graphene-reinforced metals have a high specific strength, which makes them promising material for construction of lightweight structures for aerospace and electric vehicles applications. However, its industrial implementation comes up against technological problems related to its production. In recent studies, graphene and its derivatives have been extensively investigated as reinforcements within a copper matrix. Graphene and its derivatives are particularly suited for copper composites due to their outstanding in-plane thermal conductivity values (4000-5000 W/m.K) as well as through-plane thermal conductivity (10-20 W/m.K), excellent mechanical strength, electrical conductivity, and large specific area (SSA-500-1200 m<sup>2</sup>/g).

The low ductility of graphene-reinforced metals makes it difficult to fabricate complex-shaped parts using traditional metal forming and machining routes, so that its large-scale use has been limited by the high cost of manufacturing. One solution, especially advantageous for the fabrication of low ductility metals and metal matrix composites (as the graphene reinforced metals), is additive manufacturing (AM). The integration of graphene-based materials with copper through additive manufacturing techniques holds great potential in advancing the development of high-performance materials for aerospace applications, where efficient heat dissipation and mechanical reliability are of paramount importance (Nazeer et al., 2019). Given that this is an emerging subject, in the present study we evaluated the printability of copper pastes and in our ongoing this study, we will evaluate the printability of graphene-reinforced metals by using a 3D extrusion-based system.

Copper and graphene have gained prominence in material extrusion techniques that utilize filament and pellet-based feedstocks. MatEx involves the layer-by-layer fabrication of three-dimensional objects guided by computer-aided design (CAD) files. In this context, the rheological behavior of copper and graphene-based materials becomes crucial to the physics of the melt flow, as it significantly influences the extrusion process. The study highlights the importance of understanding shear and temperature-dependent viscosities to ensure consistent extrusion through the print nozzle and in the standoff region between the nozzle and the printing bed. Moreover, the investigation examines the impact of shear and/or extensional viscosities and the extent of die swell experienced by the materials under material extrusion processing parameters. Once deposited on the print bed, the rheological properties of the viscous copper and graphene melt during cooling play a vital role in determining interlayer welding and subsequently affect the mechanical performance of the

printed parts. Therefore, it is essential to control and monitor key rheological properties such as zero-shear viscosities and shear moduli of the melt in this region to ensure the desired mechanical robustness and shape integrity of the deposited layers (Art, 2019).

## 2. EXPERIMENTAL

Various tests were conducted to evaluate the successful production of 3D-printed paste filaments and their subsequent thermal debinding and sintering. Four compositions of copper pastes were produced. The past was composed of binder solution and copper particles. Copper particles used have an average size of 50  $\mu\text{m}$  and were provided by Brutt Metal. Water soluble polymers were used as binder: were used carboxymethyl cellulose (CM,) polyvinyl alcohol (PVA) and 3.5 polyethylene glycol (PEG). The compositions of the pastes were chosen from a previous study conducted in our research group (Signor, 2023).

First the binder solutions were prepared. The binder solutions were prepared by dissolving the polymeric binder in distilled water at 90 °C under magnetic stirring. Thun the copper was added in the binder solution. In addition, a pasta using copper particles coated with oleic acid (Sigma Aldrich) was prepared (Ren, 2016). For that the copper powder was mixed in alcohol solution with 1 wt.% of oleic acid for 20 hours in a ball mill and dried. The composition the binder solution and pastes are shown in Table1.

Table 1. Paste composition.

Paste Label	Starting Powder	Binder	Binder/Water (wt.%)	Powder load (wt%)
Cu_CMC_i	Copper	CMC	2	58
Cu_CMC_ii	Copper	CMC	2	60
Cu_CMC_iii	Copper	CMC	2	65
Cu_OA_P_i	Copper coated with OA	PVA + PEG	7.5 + 3.5	65

The printability was conducted using a commercial 3D paste extrusion printer (Duraprinter C01). This 3D printer operates similar to the fused filament fabrication (FFF) technology. It works by extrusion of a paste, and depositing it layer by layer to build three-dimensional objects. This printer has two mini helicoidal extruder that work with nozzle varying from 0.2 to 4 mm; and a layer resolution of 0.1 mm. In this work, only one extruder was utilized, as we worked with only one type of material at a time during the printing process. It utilizes a nozzle that moves along the X, Y, and Z axes, precisely controlling the extrusion of the molten filament. We utilized a nozzle with a 3 mm diameter, printed a single layer, and maintained consistent extrude and move speeds at 3.33mm/s. The layer height was set at 3mm, resulting in an estimated print time of 3.33 minutes. Notably, neither the print bed nor the nozzle were preheated, operating at room temperature throughout the process. Additionally, we achieved a solid 100% infill for this particular print, ensuring a robust and densely packed final product. A schematic of the printer is shown in Figure 1.

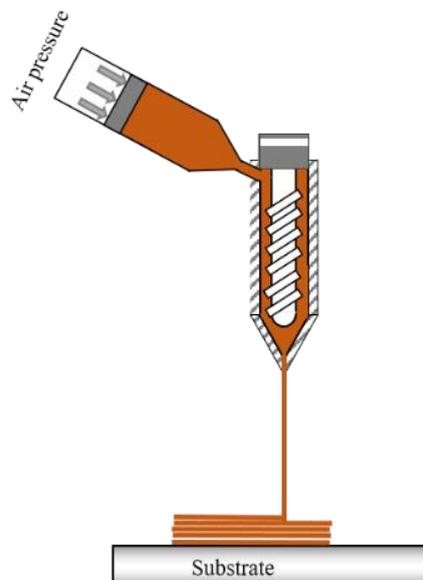


Figure 1. Schematic of 3D Printer.

The objective of this study is to analyze the printability of the produced pastes based on the parameters required for achieving a satisfactory printing outcome. Viscosity parameters such as flowability, extrudability, open time, buildability, green strength, hydration, compressive strength, and air void content significantly impact the printability of materials in additive manufacturing. These parameters affect the material's ability to flow smoothly, extrude accurately, maintain shape integrity, resist deformation, and achieve desired strength. Careful control and optimization of these parameters are crucial for successful and high-quality 3D printing (Chen et al., 2020b).

Printing parameters were adjusted in 3D Slice software (Ultimaker Cura, 2010) and directly on the printer to improve print quality and geometrical accuracy between the modeled and printed object:

- Line width: controls the width/thickness of the line/filament. Since the inner diameter of the nozzle is approximately 3mm, it is recommended to use this value. For thinner line widths, the nozzle should be changed.
- Layer height: the layer height affects the "flattening" of the printed object. Smaller layer heights for a given line thickness result in a more flattened shape as the layers are deposited.
- Flow: The flow was set to 150% in the Slice software, and in the printer was set to 100%. However, it was observed during initial tests that a higher value was required for improving material flow. This parameter also affects filament thickness. With a flow of 100% displays more spaced-out lines. Increasing it to 150% brings the lines closer together, which can be beneficial for controlling the density of the print and the bond between layers. On the printer, the ideal flow has been found to be 80.
- Infill pattern and Top/Bottom pattern: These parameters determine the filling pattern. For these tests, line and zigzag patterns were used. Patterns that deposit material in a concentric manner, following the contour of the object, tend to result in circular shapes, which may not be suitable when there are corners, for example.
- Extra wall: Initially, an extra wall was present in the zigzag pattern tests. However, since the object was small and rectangular, it caused the shape to become circular due to the filling pattern used. In the final tests, the extra wall was removed, but this caused the filling to directly "connect" to the outer layer of the object. Depending on the filling and the geometry of the object, this can lead to deformation (as was the case with the zigzag filling without the extra wall).

The printability test was performed using a line test. For that, several of lines of 2 mm width, 2 mm height and 15 mm length were printed. The filament lines were photographed and their dimensions were measured using a ImageJ software, the diameter was measured in four different points, using a green square as a reference measure located underneath the filaments, as shown in Figure 2, and they were taken every four squares. Afterwards, the length of each filament was measured. In addition, printability was evaluated by printing squares shapes of 20 x 20mm with 1, 2, and 3 layers, (Figure 3).

### 3. RESULTS

The printability test by filament line pattern was successfully performed using the Cu\_CMC\_ii paste, the results can be seen on Figure 1.

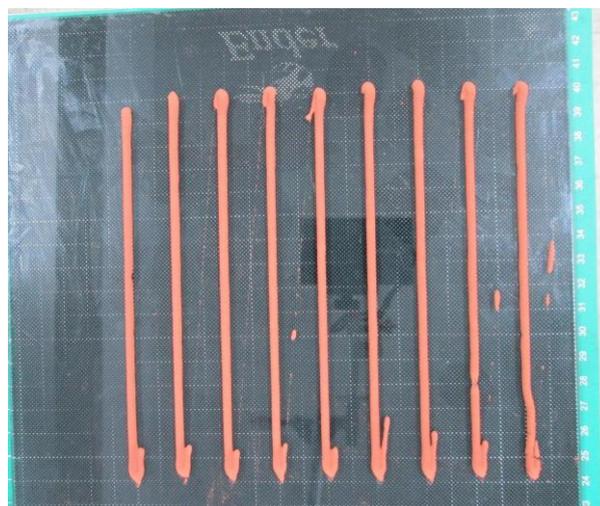


Figure 2. Line test for Cu\_CMC\_ii paste.

Table 2. Line test for Cu\_CMC\_ii Paste.

	Length (mm)	Area (mm <sup>2</sup> )	Diameter (mm)
Filament 1	14.695	1.433	0.390065
		1.300	0.353862
		1.151	0.313304
		1.130	0.307588
Filament 2	15.133	1.613	0.426353
		1.493	0.394634
		1.456	0.384854
		1.442	0.381154
Filament 3	15.189	1.710	0.450326
		1.321	0.347883
		1.369	0.360524
		1.722	0.453486
Filament 4	15.372	1.494	0.388759
		1.201	0.312516
		1.308	0.340359
		1.952	0.507937
Filament 5	15.138	1.793	0.473775
		1.730	0.457128
		1.463	0.386577
		1.564	0.413265
Filament 6	15.511	1.925	0.496422
		1.656	0.427052
		1.455	0.375218
		1.460	0.376507
Filament 7	15.606	2.074	0.53159
		1.492	0.382417
		1.281	0.328335
		1.569	0.402153
Filament 8	15.429	1.206	0.312658
		1.260	0.326658
		1.348	0.349472
		1.575	0.408322
Filament 9	15.551	1.496	0.384798
		1.240	0.318951
		1.694	0.435728
		1.745	0.448846

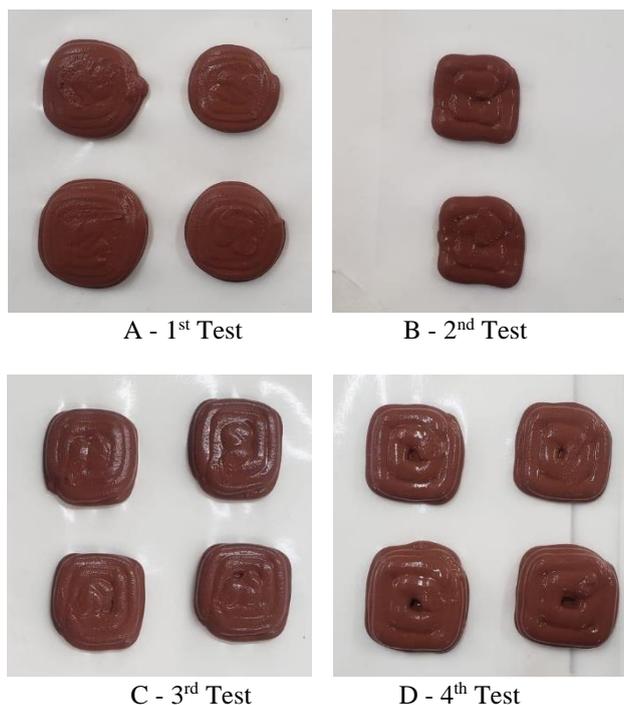
From the data in Table 2, it is possible to notice there is variation in the filament diameter, which can be improved by further adjusting printing parameters. Nevertheless, the results indicated that Cu\_CMC\_ii paste have suitable rheological properties for 3D printing.

It was not possible to print continuous lines using Cu\_OA\_P\_i paste, due to separation between binder and the metal powder during the extrusion process. This phenomenon can be attributed to the compatibility between the binder and the metallic powder that plays a crucial role. In this case, it seems that the combination of PVA and PEG did not provide

sufficient adhesion between the binder and the metallic particles, causing the binder to separate from the metal during the extrusion process. This lack of adhesion can be related to chemical properties and interactions of binder and the metallic powder. The addition of oleic acid improved metal powder dispersion but did not prevent the metal powder/binder separation during printer. The metal powder/binder separation leads to the clog of printer nozzle.

The results of square printing tests Cu\_CMC\_i performed are shown in Figure 3. They show suitable formation of filament, however it is required to improve printing parameter and paste rheology in order to improve dimensional accuracy.

The Cu\_CMC\_iii did not produce suitable filament for square printing tests. Taking into account the ease of extrusion, deposition on the bed, and layer stability, mixtures with lower binder percentages result in a sandy appearance, creating filament discontinuity which hindered their printability.



1<sup>st</sup> Test: Line width = Layer height = 2mm  
2<sup>nd</sup> Test: Line width = 4mm, Layer height = 3mm  
3<sup>rd</sup> Test: Line width = 3mm, Layer height = 2.5mm  
4<sup>th</sup> Test: Line width = 4mm, Layer height = 2.5mm

Figure 3. Photograph of square printed used Cu\_CMC\_i paste.

In the first test, both the line width and layer height were set to 2mm. However, it was observed that increasing the layer height might be beneficial in reducing spreading, which could lead to improved print quality. For the second test, the line width was increased to 4mm, and the layer height was set to 3mm. This configuration resulted in filament deformation during deposition, indicating that the layer height was too large. The excessive layer height likely caused difficulties in maintaining proper filament flow and adherence. Then, in the third test, the line width was adjusted to 3mm, and the layer height was set to 2.5mm. This combination yielded relatively good print quality. The adjustments made struck a better balance between filament flow and layer adhesion, resulting in improved overall printing results. Moreover, in the fourth test, the line width remained at 4 mm, but the layer height was reduced to 2.5mm. This configuration also yielded good print quality.

Overall, the changes made in the line width and layer height parameters throughout the tests allowed for a gradual optimization of the printing process. The adjustments helped in controlling filament flow, layer adhesion, and print quality, ultimately contributing to the improvement of viscosity and the overall performance of the printing system.

#### 4. CONCLUSIONS

Copper pastes were produced by adding copper powder on water polymer solution. By adjusting binder composition and powder loading was possible to achieve suitable printability. Preliminary experiments indicate that is possible to print

copper parts using water-based paste. More studies are currently being conducted in order to improve paste printability and produce 3D Copper parts.

## 5. ACKNOWLEDGEMENTS

We thank the National Council for Scientific and Technological Development (CNPq) for the financial funding.

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