The Effect of PVA Binder System on the Printability of Alumina Paste for Direct Ink Writing

Sh. Mahboubizadeh[1], A. Kazemi [1,*], M. Khodaei[2]

[1]Department of Materials Engineering, SR.C., Islamic Azad University, Tehran, Iran.
[2]Faculty of Materials Science and Engineering, K. N. Toosi University of Technology, Tehran, Iran.
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Abstract

The use of polymeric binders in the fabrication of ceramic parts by extrusion-based 3D printers is considered to be one of the key elements that, in addition to providing a suitable suspension paste for the addition of ceramic particles, directly affects the controllability of their flow behavior and ultimately their printability. To this end, the present research investigated the effect of simultaneously adding different polyvinyl alcohol binders with different debinding temperatures to alumina pastes. Because of the high viscosity of the alumina at high percentages by weight, its printability is difficult for this reason, and the device can be damaged during the printing process. In addition, the density and strength properties of the printed parts suffer from a decrease in printability quality. For this purpose, the effects of hybrid binder systems on the additive manufacturing of alumina components were investigated, evaluating three different compositional ratios (25/75, 50/50, and 75/25) to identify the optimal formulation. The experimental results show that strategic selection of binder proportions significantly improves both the rheological properties critical for extrusion-based printing and the structural integrity of sintered components. Accordingly, it was observed that the sample with the highest PVA ratio with lower debinding temperature showed the best printability, but the strength and density properties of the cured samples of the equal binder combination sample were the highest.

Keywords: Direct Ink Writing, Ceramic Additive Manufacturing, Alumina Paste Rheology, Polyvinyl Alcohol.

1. Introduction

Ceramic parts are economical in two key aspects: first, they can be produced in smaller volumes, and second, they can be produced with fewer defects than those associated with mold manufacturing [1]. One of the most widely used oxide materials in the ceramic industry is alumina, which has good high temperature and corrosion resistance properties. Therefore, there are many applications in manufacturing alumina parts with complex shapes. Therefore, new methods that can lead to the production of parts with complex shapes and simultaneously low defects at the lowest cost are attractive to industrialists and researchers [2-4]. Selective laser sintering (SLS) and selective laser melting (SLM), both of which are powder-based processes, are among the various methods for additive manufacturing of alumina parts. The former is based on the sintering of ceramic powders and the latter on the local melting of ceramic powders [5], [6], as indicated by their names. Of course, these methods are less commonly used to produce alumina parts due to its very high melting point, or if they are used, they require additives and materials such as melting aids that enable melting and sintering at low temperatures. However, other additive manufacturing methods are being developed for this category of ceramics that can produce raw ceramic parts at low temperatures and, after printing the parts, achieve the final ceramic parts by performing subsequent processes such as sintering, using hot pressing, etc.

One of these methods is extrusion-based 3D printing. In this method, printers that include extrusion are used, which in turn are also used in the fused deposition ceramic method (FDC) and the direct ink writing (DIW) or robocasting method. These methods are illustrated in Fig. 1.

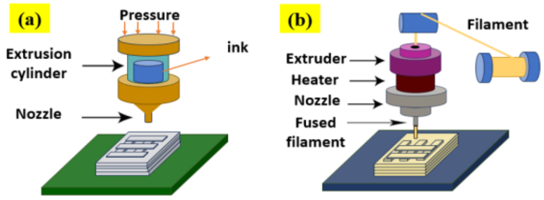

Fig. 1. Schematics of a) DIW and b) FDC extrusion 3D printer[1].

The FDC process, which is a derivative of the (FDM) process, it consists of a ceramic-polymer composite filament in which a high percentage of ceramic material is converted into filament by a polymer binder. When placed in the 3D printer, heat is applied to melt the polymer binder and form a composite paste. This paste is capable of building ceramic parts layer by layer as the printer moves. However, this method cannot always be used because the viscosity of the binder inside the filament can vary greatly due to heat, which can reduce printability. This method is useful for binders made from thermoplastic polymers.

*Corresponding author
Email address: a.kazemi@srbiau.ac.ir

On the other hand, the DIW method has been developed [7, 8], where the polymer binder is first converted into a suspension paste by a solvent and then into a paste with high viscosity control by the addition of ceramic particles and other additives such as dispersants and plasticizers. It also causes no problems with heat-sensitive polymers. The printing process then produces a raw ceramic piece that is subjected to heat treatment, first to remove the solvent from the green body, then to the debinding process, and finally to the sintering process of the patterns. These processes may include hot pressing or other subsequent processing methods[9] .

In the production of ceramic parts such as alumina, the amount of ceramic powder increases, which leads to a decrease in printability and an increase in the viscosity of the paste produced [10], and also causes the behavior of alumina pastes to move toward dilatant, whose viscosity increases sharply with increasing force [11]. Therefore, finding the optimal amount of additives to be used, as well as the appropriate ratio and type of binder, is an essential step [12]. Therefore, in this study, two different types of polyvinyl alcohol binders with different debinding temperatures were used to find the optimal level of printability. This level of printability should be appropriate for the ease of fabrication of the alumina part, as well as for the strength and density of these parts after the first sintering.

2. Materials and Methods

To prepare alumina paste from raw materials, alumina powder with particle size of 15 µm (Yafteh Ceramic-Iran), two types of PVA with different debinding temperatures (industrial grade - China) were used. The TGA-DTA properties of the PVA binders used were reported in a previous study by this group [13]. Also, the optimum amount of additives used in this method was mentioned in another study by this research group and the proposed optimum amount was also used in this study [14]. Fig. 2. shows a schematic of the various steps in the alumina sample manufacturing process. To prepare the paste, we first dissolve the specified proportions of different types of binders in water at a temperature of 70°C for 2 hours on a heating stirrer at a speed of 400 rpm. Then, other additives are added and mixing continues for 15 min on the hot mixer.

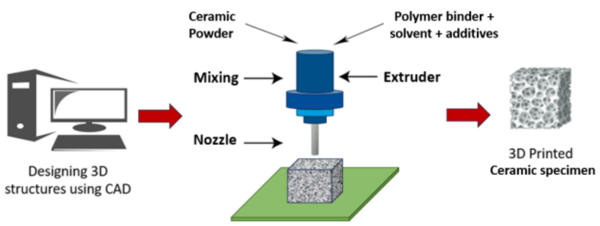

Fig. 2. Schematic of the process of the additive manufacturing of a ceramic part by means of the DIW method.

Alumina powder is then slowly added and mixing is continued mechanically for another 15 min. Then, to study the density and initial strength of the samples, all of them were sintered at a temperature of 1250°C. The alumina paste was produced and then 3D printed by the Abtin 1 (Abtin Teb-Iran) 3D printer. The pieces were 4x2x2 cm in size. In the next step, the rheology of the paste was studied using a rheometer (Anton Paar, MCR300, Astria).

The density of the printed sintered samples was studied using the Archimedes method, and the flexural strength of the sintered samples was studied using three-point bending tests (Sanat Ceram, Iran).

In addition to these tests, a scoring method was used to examine the printability of the pastes, in which the prepared pastes were scored on the basis of the parameters listed in a table previously developed and used by the same research group [13], in which the prepared pastes were given a score from 1 to 10, with a score of 1 being the lowest score and indicating no printability, and a score of 10 indicating the highest printability quality. Finally, in this study, lower debinding temperature PVA is called Type 1 (or PVA_1) and higher debinding temperature PVA is called Type 2 (or PVA_2). The use of different PVA_1/PVA_2 ratios at different debinding temperatures will change the viscosity of the paste and also the printability. Also, in the debinding process, we will see changes in the removal of binder from the printed parts and differences in the creation of binder exit channels, which increases the possibility of defects in the parts during sintering.

3. Results and Discussion

3.1. Study of Printability Properties

First, pastes with different wt% of alumina were prepared at a loading of 70 wt%, then these pastes were printed, and the alumina parts were fabricated, then the ratio of PVA_1/PVA_2 binder to each other was 50/50 and the aim was to study the optimal amount of binder in the paste at 10 wt%, 15 wt% and 20 wt%. Subsequently, with an understanding of the optimal amount of polymer binder required in the manufacture of alumina pastes, the ratio of each binder used was investigated separately and a review of these results is given below. Fig. 2. shows the printability of samples containing 70 wt% alumina at different PVA_1/PVA_2 ratios. It can be seen that as the PVA weight percent increases, the printability of the samples decreases.

This could indicate that as the amount of polymer binder increases, the amount of water absorption required to dissolve the binder and create a polymer solution increase. Since the alumina particles themselves have a significant absorption of water, the amount of water required to form a paste with adequate printability is reduced, and therefore printability is reduced.

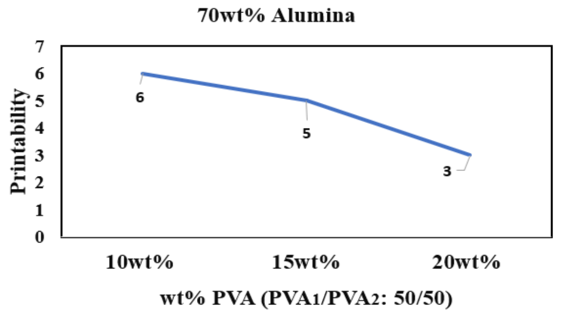

Fig. 3. Investigating the printability of alumina pastes containing 70% w/w alumina with varying amounts of PVA binder.

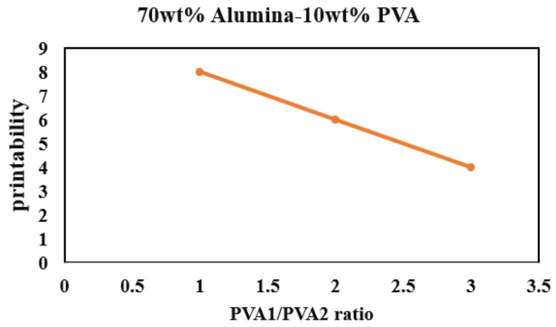

Fig. 4. Printability study of pastes containing 70 wt.% alumina - 10 wt.% PVA with different proportions of the different types of PVA used.

Fig. 3. shows the study of the paste of samples containing 70 wt% of alumina along with 10 wt% of PVA as a binder. In these samples, different ratios of PVA_1/PVA_2 used in the preparation of the samples were studied. It is observed that the higher the ratio of PVA_1, which has a lower evaporation temperature, the higher the printability. This is probably due to the fact that the PVA_1 polymer binder is easier to dissolve in the desired solvent and forms a thinner solution, which contributes significantly to the formation of a paste with better printability.

3.2. Investigating the Viscosity of 3D Printing Pastes

The same point that was made in the previous section in Fig. 4., where the viscosity of the paste samples was examined, is applicable here as well. Fig. 5. shows the viscosity of samples containing 70 wt% alumina, which have different ratios of PVA1 to PVA2. Accordingly, the samples with the highest PVA_1 binder ratio had the lowest viscosity, which improved their printability. Therefore, we can conclude that the more the viscosity of the solution formed by the polymer binder is lowered, the better the viscosity reduction and the possibility of printing at high weight percent of ceramic particles and, in practice, allowing the ceramic particles to absorb water or other solvents to some extent without affecting the viscosity of the paste.

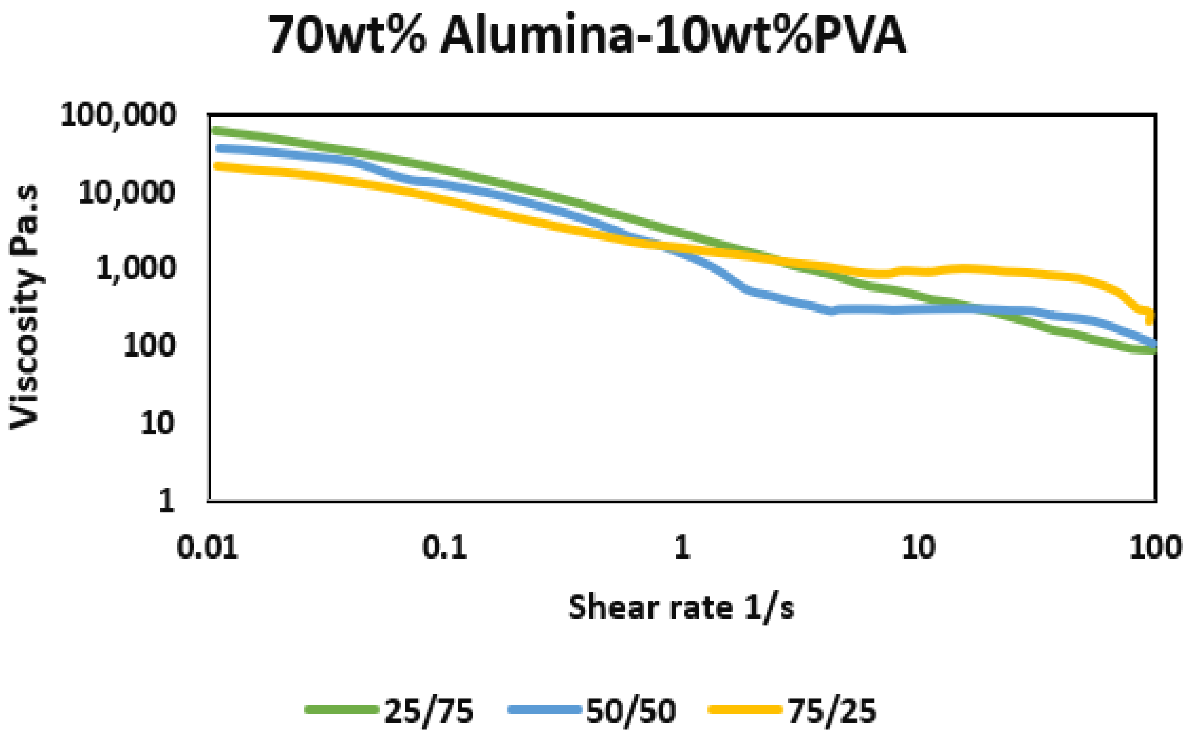

Fig. 5. Viscosity study of pastes containing 70 wt.% alumina - 10 wt.% PVA with different PVA_1/PVA_2 ratios.

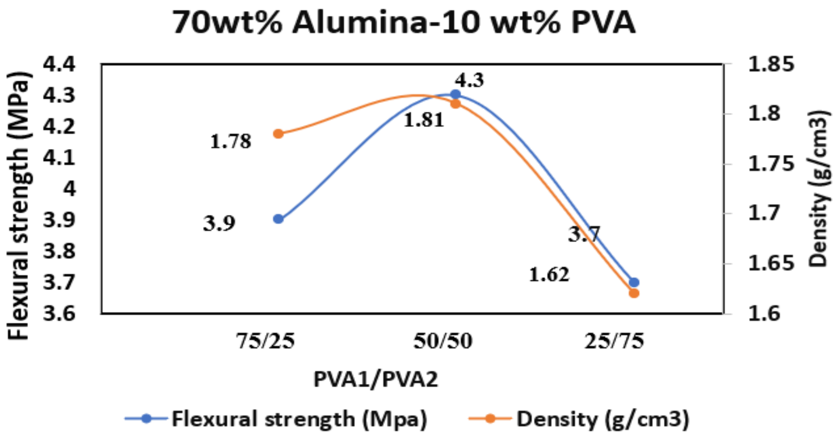

Fig. 6. Investigation of the flexural strength and density of printed samples containing 70 wt% of alumina - 10 wt% of PVA with different proportions of the different types of PVA used, sintered at 1250°C.

3.3. Flexural and Density Testing of Sintered Specimens

It is observed that the density and flexural strength of the specimens containing equal proportions of the PVA binders used had the best values, which could be due to the controlled release of gases resulting from the proper debinding of the alumina specimens under thermal treatment, in such a way that during heating, PVA_1 was first exited from the 3D printed alumina specimens and, as a result of its release, voids were created, which subsequently helped to exit PVA_2 binder from the specimen body. This equilibrium did not exist in other specimens, so that when the PVA_1 ratio is higher, the high volume of gases produced during debinding increases the probability of microcracking in the specimen, resulting in lower final strength and density. On the other hand, at the beginning of the debinding process, the small amount of PVA_2 will decrease the amount of gases released from the sample, thus reducing the amount of holes and porosity created in the sample. As the debinding process continues and the temperature increases, PVA_2, which has a higher volume, is released. As a result, there are fewer pores and exit paths for the gases resulting from the evaporation of PVA_2, and this leads to the formation of defects and cracks caused by baking. Fig. 6. examines the flexural strength and density of alumina samples.

4. Conclusion

The 3D printing of alumina parts demonstrates substantial potential to revolutionize manufacturing in diverse industrial sectors. This is due to the outstanding properties of alumina, such as:
high-temperature corrosion resistance, superior refractoriness, and excellent electrical and thermal insulation properties. These attributes have driven its adoption in demanding applications, ranging from aerospace and metal casting to medical devices and electrical equipment. Additive manufacturing, particularly Ceramic extrusion techniques, such as direct ink writing (DIW), overcome Many limitations of conventional ceramic fabrication, such as mold dependency and defect-prone outcomes. This study highlights the successful fabrication of complex alumina components using DIW with a high-content alumina paste. Careful manipulation of two types of PVA binders was crucial. Specifically, A higher ratio of PVA1 at lower debinding temperatures improved paste flow and printability. However, excessive PVA2 content increased viscosity, hindering the process. Optimal binder ratios facilitated printing, but also produced the densest and strongest sintered parts. This is attributed to controlled gas release and minimized microcracking during debinding.

In summary, precise formulation and control of polymeric binder ratios are essential for optimizing the printability and final quality of 3D-printed alumina parts. Future research should focus on advanced post-processing methods to enhance mechanical performance and pave the way for broader, more robust industrial applications of additively manufactured alumina ceramics.

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References

[1] Lakhdar Y, Tuck C, Binner J, Terry A, Goodridge R. Additive manufacturing of advanced ceramic materials. Prog. Mater. Sci. 2021;1(116):100736.
[2] Yang L, Zeng X, Ditta A, Feng B, Su L, Zhang Y. Preliminary 3D printing of large inclined-shaped alumina ceramic parts by direct ink writing. J. Adv. Ceram. 2020; 9:312-319.
[3] Li H, Liu Y, Liu Y, Zeng Q, Liang J. Thermal treatment of γ-Al_2O_3 for the preparation of stereolithography 3D printing ceramic slurries. Front. Mater. 2019; 19(6):295.

[4] Sun J, Ye D, Zou J, Chen X, Wang Y, Yuan J, Liang H, Qu H, Binner J, Bai J. A review on additive manufacturing of ceramic matrix composites. J. Mater. Sci. Technol. 2023; 1(138):1-6.
[5] Subramanian K, Vail N, Barlow J, Marcus H. Selective laser sintering of alumina with polymer binders. RP Rapid Prototyping J. 1995; 1(2):24-35.
[6] Schwentenwein M, Homa J. Additive manufacturing of dense alumina ceramics. International J. Appl. Ceram. Tech. 2015;12(1):1-7.
[7] Li W, Armani A, Martin A, Kroehler B, Henderson A, Huang T, Watts J, Hilmas G, Leu M. Extrusion-based additive manufacturing of functionally graded ceramics. J. Eur. Ceram. Soc. 2021;41(3):2049-2057.
[8] De Camargo IL, Fortulan CA, Colorado HA. A review on the ceramic additive manufacturing technologies and availability of equipment and materials. Cerâm. 2022; 16(68):329-347.
[9] Diniță A, Neacșa A, Portoacă AI, Tănase M, Ilinca CN, Ramadan IN. Additive manufacturing post-processing treatments, a review with emphasis on mechanical characteristics. Mater. 2023; 26; (13):4610.
[10] Shahzad A, Lazoglu I. Direct ink writing (DIW) of structural and functional ceramics: recent achievements and future challenges. Compos. Part B: Eng. 2021; 15(225):109249.
[11] Cesarano J. A review of robocasting technology. MRS Online Proceedings Library (OPL). 1998; 542:133.
[12] Mahboubizadeh, S, Investigation of the Printability of Highly Loaded Ceramic Pastes by Robocasting Method. The 14th Biennial Congress of Iranian Ceramic Society and the 4th Int. Conf. Ceram. 2024.
[13] Mahbobuizdeh, S, kazemi, A, khodaei, M, The Effect of Various PVA Binder Ratios on 3D Printing Alumina Pastes," 13th International Conference on Materials Engineering and Metallurgy, IMAT2024, karaj, 2024
[14] Mahboubizadeh S, Kazemi A, Khodaei M. Investigating the Effect of Modifying the Binder and Other Additives on the Printability of Ceramic Paste for the Direct Ink Writing (DIW) Technique. Adv. Ceram. Prog. 2024; 10(4):15-24.