

Development of a New Production Process for Thermally Conductive Resin for Additive Manufacturing Using mSLA Process

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Abstract. Injection molding tools are characterized by high costs, due to the use of expensive materials such as aluminum or tool steel, and the lengthy production process involving machining. This greatly limits the economic viability of using metal molds for producing small series, and even more so for rapid prototyping. Additive manufacturing processes, such as masked stereolithography (mSLA), enable the production of molds from polymers providing short production time and good accuracy. However, injection molds manufactured using mSLA using conventional resins suffer from long cooling times and lower strength. This contribution presents a new approach that significantly overcomes these disadvantages by developing and characterizing a novel composite material. To this end, aluminum oxide ceramic particles will be incorporated into a photopolymer resin. Various additives will also be employed to optimize the processability and printability of the newly developed material. This should enhance the thermal and mechanical properties of additively manufactured molds. A series of simple test specimens were produced using mSLA. Sedimentation and printability were analyzed by varying the aluminum oxide mixing ratio. The effect of various additives was also investigated. The composite materials were tested for processability, heat flow and mechanical properties. Scanning electron microscopy (SEM) was used to evaluate the particle size, quantity, distribution and homogeneity of the composite material. To demonstrate the application of the new material in additive tooling, a typical set of tool inserts for injection molding was manufactured.

Introduction

The continuous reduction in development times, the increasing number of variants and the steady rise in product customization have led to a significant increase in the relevance of Additive Manufacturing (AM) for the industry and further strengthened its position as a key technology. It is evident that AM is experiencing an increase in demand, which can be attributed to the growing complexity of components. Conventional manufacturing processes are characterized by restrictions in terms of manufacturability. Conversely, additive manufacturing is distinguished by its design freedom, a capability that no other process can offer, and the potential of this comparatively novel form of manufacturing is considerable [1]. In recent years, this has resulted in a substantial proliferation of printers utilizing a range of technologies [2]. Concurrent with the advancement of processes, there has been an expansion in the range of materials available for almost every application.

Injection molding represents a pivotal industrial production method. A significant share of all polymers is processed in this manner. In the range of 500 to 2000 bar, and at temperatures of 200 to 300°C, liquid plastic can be rapidly shaped into its final form. This process of shaping is accompanied by the hardening of the material as it cools. This facilitates the efficient production of large quantities with low tolerances, a wide variety of shapes and economical use of materials [3]. A significant cost consideration in the context of injection molding is the substantial expense associated with the fabrication of injection molds. The process is known to exert significant demands on materials, with rapid changes in temperature and pressure having a considerable impact on their integrity. The injection molds, which are the core of the process, are both costly and time-consuming to

manufacture, with production times often extending to several months [4]. Consequently, the economic viability of producing small series or prototypes is often limited.

AM processes are becoming increasingly important for reducing the costs and time of mold production. The present process is principally utilized for the validation of prototypes. The aforementioned procedure, also referred to as Additive Tooling, facilitates the examination of both the target material and the target production technology. In addition, it enables the analysis of the anticipated costs and time savings. Existing additively manufactured molds made of plastic exhibit the disadvantage of low thermal conductivity, which renders them unusable since longer cooling times slow down the process and change the materials properties in the molded part [2]. Despite the thermostability of additively manufactured molds made of metals, their manufacturing process is both complex and costly.

The objective of this research is to develop a material that enhances the properties of molds made using additive manufacturing techniques from plastic. For this purpose, a composite material was formulated from resin with aluminum oxide. The processibility, shear flow and mechanical properties of this material were then investigated. In this context, it is imperative to deliberate on the issues associated with such suspensions, particularly with regard to sedimentation, homogeneity, and photo-penetrability. It is well established that these parameters are subject to significant fluctuations, which are primarily attributable to the filler and the degree of filling.

Materials and Methods

Masked stereolithography (mSLA) is a process that involves the solidification of liquid synthetic resins by means of irradiation with Ultra Violet light (UV). The resins are masked during this process using an LCD display [5]. The mSLA process has been demonstrated to be capable of rapidly producing intricate molds with a very high surface quality. In the mSLA process, a chain former and a crosslinker are processed with a photo-initiator and applied in 50 μm or thinner layers, which are then cured by UV light. The material's photo-penetrability imposes limitations on the processing speed, resulting in layers that are thinner than those applied in filament printing and a smoother surface [5]. In comparison with 3D-printers that utilize material extrusion (for example, fused filament fabrication), mSLA printers offer the advantages of high precision and good surface quality at a relatively low cost [6]. In the context of our application, it was necessary to utilize a photosensitive resin that exhibited both adequate mechanical properties and the capacity for photopolymerization. This resin was then subjected to rigorous testing to ascertain its suitability.

In order to investigate the influence of the base matrix resin, two commercially available resin products from two different original equipment manufacturers (OEM) were selected that differ in terms of their mechanical properties (see Table 1) and are suitable for a masked stereolithography printer (mSLA). The tensile tests were performed in accordance with the standard ISO 527-2. The experiment involves the testing of both cured and uncured specimens. The tensile test measurements demonstrate the behavior of a brittle material with resin “3D Jake - Color Mix Resin Basic” [7] and a ductile material with resin “3DM-Tough” [8]. The extent of this phenomenon is quantitatively measured by the elongation at break, as presented in Table 1. This phenomenon must be contemplated within the context of the augmentation in stiffness that is precipitated by the incorporation of particulate matter.

Table 1. Material properties of investigated resins

Resin type (general behavior)	“Brittle” resin		“Ductile” resin	
OEM	3D Jake (Austria)		ADMAT (France)	
Commercial name	Color Mix Resin Basic		3DM-Tough	
Density [g/cm^3]	1.18		1.14	
Curing status	uncured	cured	uncured	cured
Tensile strength at Yield [MPa]	48.8	60.7	45.5	65.6
Elongation at break [%]	0.90	0.62	8.00	0.81

Ceramic particles have been demonstrated to exhibit superior thermal conductivity in comparison to mSLA resin. This combination of properties offers the advantages of both good thermal conductivity and processability using mSLA 3D-printing. The selection of aluminum oxide as a filler material is predicated on its non-hazardous nature, its economic viability, and its high thermal conductivity for an oxide. An investigation was conducted into the viability of various ceramic types of aluminum oxide for specific applications, with a focus on the analysis of grain size, the utilization of scanning electron microscope images (SEM), and the examination of morphology. For the purposes of this study, fifteen different types of commercially available aluminum oxide were selected for analysis. Following the preliminary experiments, the research was narrowed down to three candidates (see Figure 1). The remaining twelve were rejected on the grounds of inadequate miscibility, high sedimentation rates and poor printability.

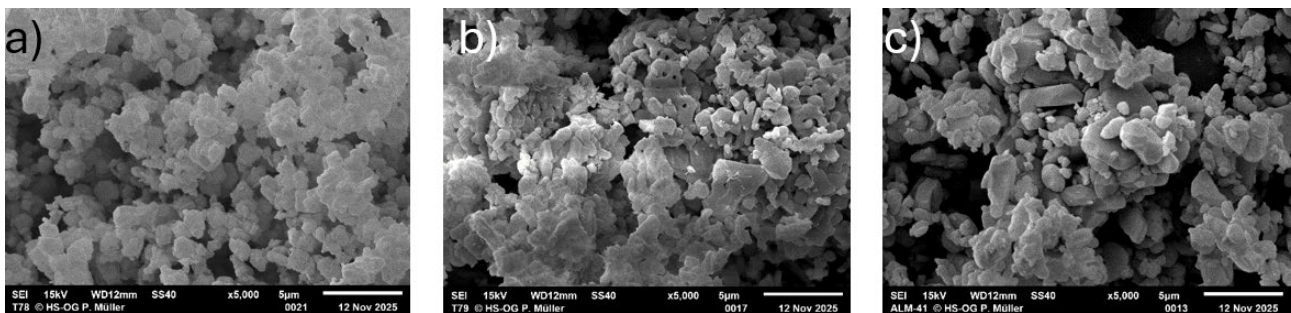


Fig. 1. SEM Pictures of chosen particles of aluminum oxide with a magnification of 5000: a) T78, b) T79 and c) ALM41 powder

The aluminum oxide resin composite is reputed to be distinguished by a high degree of translucency, thermal conductivity [9], sedimentation stability and 3D-Printability. In addition to thermal conductivity, particular attention is paid to the surface quality of filigree injection molds, as these require a surface that fulfils certain criteria. The surfaces were evaluated using a scanning electron microscope. Notwithstanding the introduction of solid particles, it is imperative to ensure the absence of any uneven surface, as this would inevitably lead to an uneven workpiece when utilised as an injection mold.

The ceramic particles are introduced into the liquid resin to be processed as a solid phase using a high-speed planetary centrifugal mixer ("Speedmixer" DAC 330-100 Pro from Flacktek™, USA). The option of coating the particles was initially rejected on economic grounds. Moreover, it has been demonstrated that adequate miscibility of the particles can be attained even in the absence of coating.

Additives were selected with the objective of preventing the formation of air bubbles in the particle-resin mixture during the process of utilization of the centrifugal mixer [10]. It is imperative that all processing steps are carried out in such a manner that a homogeneous distribution of the particles in the subsequent workpiece is guaranteed [11]. It is imperative that the composite after polymerization does not alter the fundamental properties of the resin (e.g. smooth surface, suitability for filigree shapes). In order to obtain a comprehensive overview, specimens were printed with various aluminum oxides, different degrees of filling with the resin and varying layer thicknesses in order to define the limits of the process.

In an initial series of tests, aluminum oxide was mixed with resin without additional additives, which resulted in an inhomogeneous distribution of ceramic particles in the composite. Following this, eight of the aluminum oxides utilized in the experiment failed to attain satisfactory material properties with regard to printability. Consequently, these were excluded from further testing. In a second series of tests, the remaining seven were mixed separately in different concentrations in both resins. The addition of a dispersing additive has been demonstrated to enhance the concentration of aluminum oxide while achieving the desired homogeneity [12]. The used dispersive was Disperbyk 163 TF or Disperbyk 110 from BYK-Chemie GmbH, Germany, or Tego Dispers 655 from Evonik Evonik Operations GmbH, Germany.

Three different mSLA printing devices were utilized in this study: firstly, a standard device, the “Prusa SL1S”; secondly, an advanced device, the “Phrozen Sonic Mini 8K”; and finally, a professional device, the “Formlabs Form 4”. The impetus for these modifications stemmed from the limitations imposed by the system during the developmental process, including elevated fill levels in conjunction with a more viscous resin-ceramic composite, the reproducibility and homogeneity of the specimens, and other factors. The failures that occurred during the developmental process, along with the underlying reasons for each, are illustrated in Figure 2. Consequently, the selection of 3D-Printing devices was based on their distinct features.



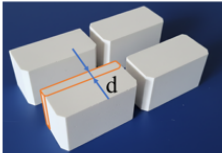

Standard 3D-printing device	Prusa SL1S speed Specifications: Technology: mSLA Volume: 127 x 80 x 150 mm ³ Feature: tilted tank	Failure 	Reason High viscosity leads to resistance at tank tilting.
 <div style="border: 1px solid blue; padding: 2px; display: inline-block;">Possible solution: Adjustable lift and retraction speed and acceleration</div>			
Advanced 3D-printing device	Phrozen Sonic Mini 8K Specifications: Technology: mSLA / DUP Volume: 165 x 72 x 180 mm ³ Features: speed & acceleration settings	Failure 	Reason High viscosity leads to layer thickening at platform lowering.
 <div style="border: 1px solid blue; padding: 2px; display: inline-block;">Possible solution: less mechanical friction and stronger platform drive</div>			
Professional 3D-printing device	Formlabs Form 4 Specifications: Technology: mSLA Volume: 200 x 125 x 210 mm ³ Features: ball screw, strong spindle drive	Failure No failure detected.	

Fig. 2. Selection of different 3D-printing devices

The thermal conductivity of the composite was measured using a measuring instrument “THB advanced” from Linseis GmbH, Germany. The measurement of heat conduction necessitates the utilization of test specimens in the form of thin plates, which should provide complete coverage of both surfaces of the sensor. It is important to note that the sensor is only able to measure tangential heat conduction on the surface. For this reason, both sides of the specimens were required to be measured. Consequently, following the evaluation of numerous dimensional alternatives, the decision was made to utilize two plates of uniform dimensions, measuring 70 x 45 x 5 mm (length x width x height), for the purpose of 3D-printing.

In a second investigation, the focus is directed towards the analysis of thermal conductivity. The measurement of the parameters is conducted using a “THB advanced” device, equipped with a type A sensor. Two sample plates that exactly cover the sensor are utilized for the measurement. It is imperative to note that the measurements are invariably conducted on at least three occasions to ensure the reliability of the results. It is a well-established fact that the thermal conductivity of polymers typically reaches a maximum of 0.2 W/(m*K) [13]. The surface of the material was analyzed using a JSM 6610LV scanning electron microscope from Jeol Ltd, Japan and the element distribution of aluminum in the composite was measured using EDX, element analysis with a X-Max Detector from Oxford Instruments plc, UK in order to ascertain the material's homogeneity.

Results and Discussion

Initially, an examination was conducted into the percentage of aluminum oxide present within the specimens. A series of measurements using an Oxford X-Max EDX Detector were obtained on both the upper and lower sides, with the objective of examining the homogeneity of the distribution of the particles. The results in Figures 3 and 4 demonstrate that the values measured on both sides of the specimens are not identical.

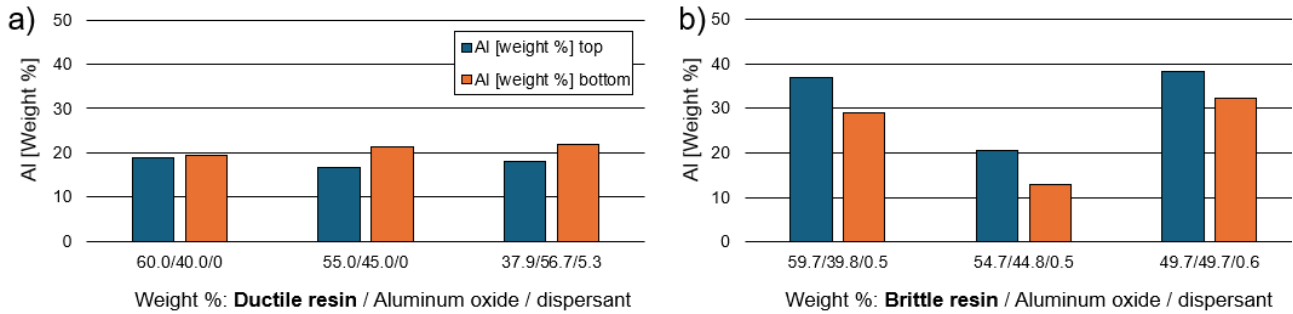


Fig. 3. Aluminum specimens: degree of filling from specimens measured on top and bottom of specimens using a) ductile resin and b) brittle resin. 3D-printed using standard device.

This prompts the question of whether the cause of this phenomenon is attributable to the sedimentation or the printing process. The distribution of aluminum oxide within the resin is a subject of particular interest. For the purposes of this study, the specimens were measured along the edge, and the values thus determined are to be considered qualitatively rather than quantitatively. Nevertheless, it can be regarded as a reliable indicator of the distribution of aluminum oxide.

The surface images obtained by means of the SEM technique are utilized as indicators, and these images demonstrate the presence of both roughness and irregularities at the edges. Consequently, the measurement was conducted on the lateral surfaces of the specimens exclusively. A selection of examples is shown in Figures 3 and 4. The process was optimized through the execution of a substantial number of tests. The incorporation of a minimal quantity (approximately 0.3% by mass) of a dispersant facilitated the amalgamation of 65% aluminum oxide with the resin, thereby enabling the 3D-printing of the specimens.

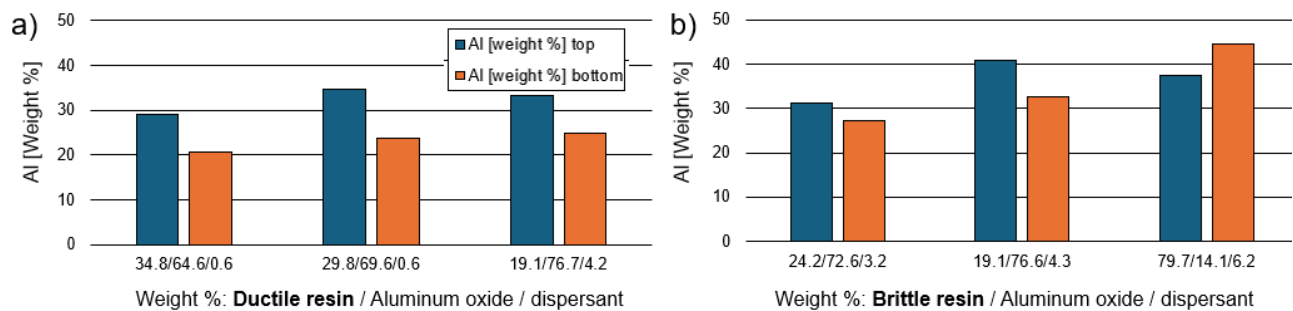


Fig. 4. Aluminum Specimens; degree of filling from specimens measured on top and bottom of specimens using a) ductile resin and b) brittle resin. 3D-Printed using advanced 3D-printing device.

Increasing the amount of aluminum oxide in the ductile resin, utilizing the ceramic filler "ALM-41", results in a paste-like mass. However, the printability of this mass in the mSLA process is no longer guaranteed. The utilization of brittle resin is constrained to a maximum fill level of 50%, at which point the limit of 3D-printability is attained. The incorporation of dispersants has been demonstrated to reduce viscosity and enhance stability against sedimentation. The reduced viscosity of the material allows for the suspension to be printed at a higher fill level. The addition of the dispersant DisperBYK 163 TF, in conjunction with both resins and ALM-41, resulted in the attainment of a fill level of 80 weight %. The SEM examinations reveal that there is an absence of delamination, indicating that the layer structure of the print sample remains intact.

Further defects can be observed in the printed components. The components are being drawn off the build plate by the film, and the layers are sliding and no longer adhering to each other. The problem remained unresolved despite an attempt to increase the exposure time. The emergence of additional issues was observed, manifesting as a tripled thickness in the layer. It was evident that the printer had reached its limits due to the fact that the parameters of lift and retraction could not be altered. The selection was made of the advanced 3D-printing device as described in Figure 2. This apparatus is utilized for the purpose of producing thin layers, with the lifting process being modulated accordingly. In this instance, the layer thickness can be set, as well as the parameters of the lifting process, distance and speed, and the speed of the lowering process. The initial trials have indicated a considerable degree of promise. As demonstrated in Figure 5, the specimens exhibit no optical defects. Furthermore, the results of the EDX analysis and aluminum measurement indicate that the powder is homogeneously distributed in the resin.

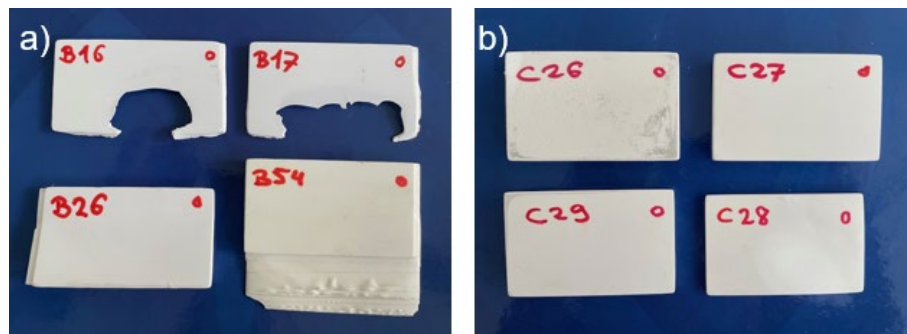


Fig. 5. Specimens with high amount of Aluminum oxide 3D-printed with a) standard 3D-printing device and b) advanced 3D-printing device.

The present investigations, incorporating both alterations, an advanced 3D-printing device, and the addition of a dispersive, demonstrate that with the novel printing processes, a filling level of 65% by mass could be achieved with the Resin 3DM and a filling level of 85% by mass with the brittle resin with the aluminum oxide ALM-41. It was also determined that the specimens were not only printable, but also suitable for utilization. As demonstrated in Figure 6, a reproducible value of approximately 1.6 W/m²*K was achieved at a filling level of 80% by mass.

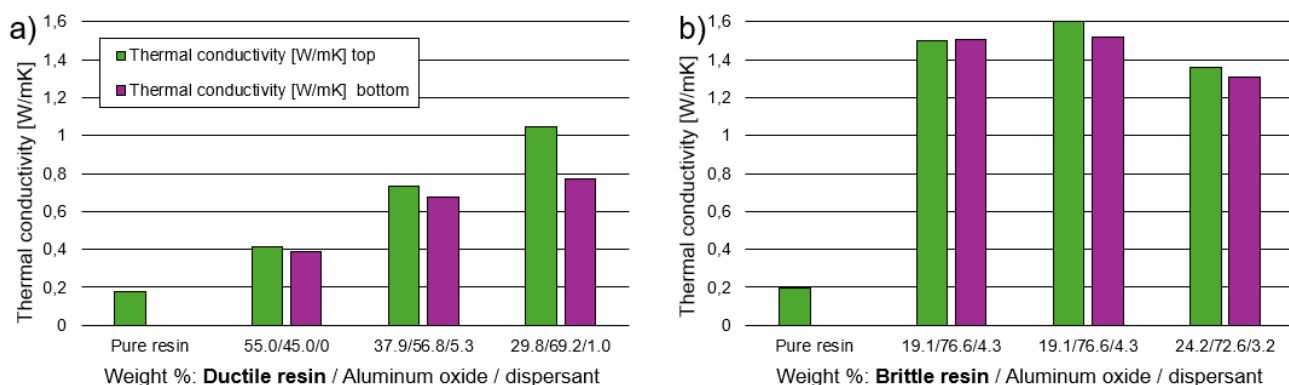


Fig. 6. Thermal conductivity of specimens measured on top and bottom surface and comparison with pure resin.

A program of research was conducted in order to identify potential additives, the results of which identified three candidates. These were examined in detail. The most significant properties identified were, in particular, good dispersibility, a reduction in the viscosity of the mixture and an increase in the possible degree of filling. The attainment of a printable resin mixture with 80% weight filling was accomplished through the utilization of one of the three additives. The behavior of particles is influenced by the quantity of additives employed. The investigation focused on additive quantities ranging from 0.1% to 10%, with optimal levels between 0.4% and 5% being identified for certain

resins. It is becoming increasingly challenging to work accurately and reproducibly with the advanced 3D-printing device due to the high fill level and homogeneity.

In order to achieve greater freedom in parameter optimization, for example a stronger platter feed, a professional 3D-Printing device was used. To demonstrate an application-oriented example, a set of tool inserts was 3D-printed as a demonstrator (see Figure 7). This tool is used for injection molding two tensile test specimens. The tool consists of a plate with two cavities for the specimens (tool plate). Additionally, a simple counter plate without a cavity was molded to enable the tool to close. Both halves of the tool also contain the necessary holes for assembly and the sprue. EDX measurements were performed in low vacuum mode so that the specimens did not have to be gold-sputtered, as is usually necessary. Our EDX measurement proved the aluminum in the sample to be homogeneous. The sample was 3D-printed with a mixture of aluminum oxide “T79” and brittle resin, which showed the best result in terms of thermal conductivity.

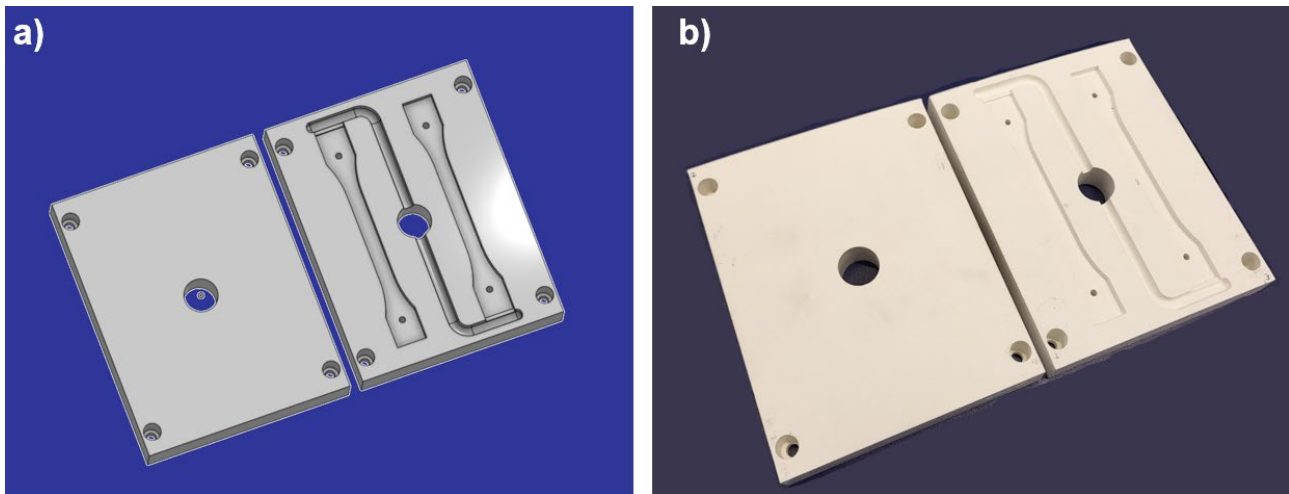


Fig. 7. Tool inserts for injection molding: a) CAD model of counter plate (left) and tool plate (right) and b) additively manufactured tool set from the developed composite material using mSLA.

Following the 3D-printing of the tool inserts the dimensions of which were 178 mm × 137 mm × 20 mm (length x width x height), the distribution of the aluminum oxide powder in the resin was measured on two sides of each of the two plates. As demonstrated in Figure 8, the material exhibits excellent homogeneity. While the initial 3D-printed specimens exhibited a significant discrepancy in aluminum concentration between the two sides, the discrepancy is now near to the margin of error. This can be considered acceptable.

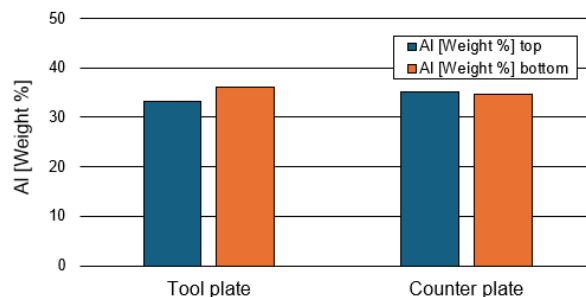


Fig. 8. Aluminum specimens: degree of filling from specimens measured on top and bottom tool plate and counter plate of the tool inserts.

The surface plays a pivotal role, as it is a crucial parameter for the components that are subjected to subsequent injection molding. The enhancement of the layers exhibited in Figure 9 is attributable not only to the different 3D-printing devices, but also to the optimization of the parameters employed in the production of the mixture of resin, aluminum oxide and dispersants.

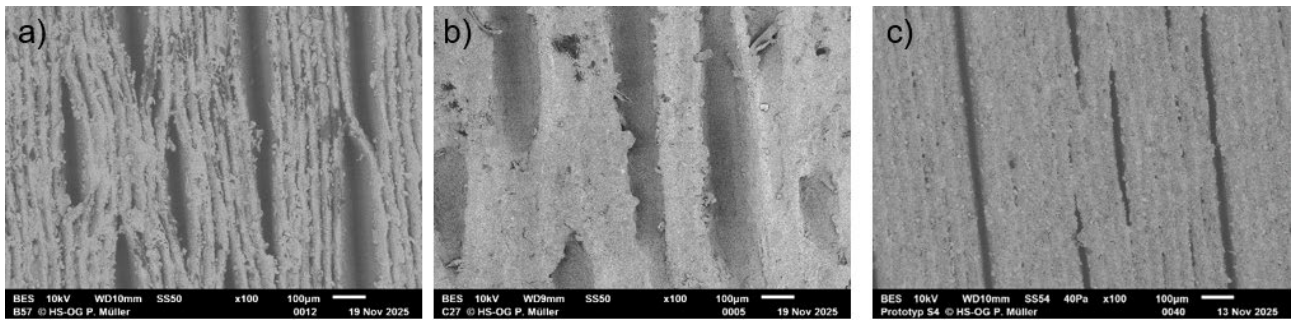


Fig. 9. SEM image of the edge of sample form a) standard 3D-printing device (Weight %: resin / Aluminum oxide / dispersant: 37.9/56.8/5.3), b) advanced 3D-printing device (Weight %: resin / Aluminum oxide / dispersant: 24.2/72.6/3.2) and c) surface of the tool insert using professional 3D-printing device.

Conclusion

This research successfully developed a novel composite material for additive manufacturing of injection molding tools, addressing the limitations of conventional resins in Masked Stereolithography (mSLA) processes. The primary objective was to enhance the thermal and mechanical properties of molds, leading to reduced cooling times and improved part quality in injection molding. The study achieved this by incorporating aluminum oxide ceramic particles into a photopolymer resin, alongside the strategic use of various dispersants to optimize processability and printability for additive tooling.

The investigation involved a comprehensive analysis of different aluminum oxide types, ultimately narrowing down the selection to three candidates based on miscibility, sedimentation, and printability. The study meticulously examined the influence of resin type, filler loading, and additive selection on the final composite properties. Detailed analyses using Scanning Electron Microscopy (SEM) and EDX measurements were employed to evaluate particle size, distribution, and homogeneity within the composite material.

The research demonstrated that the addition of dispersants significantly improved the homogeneity and printability of the composite, allowing for higher filler loadings up to 85% and thus, higher thermal conductivity. Similarly, the homogeneity of the aluminum concentration was significantly improved during the course of the investigations. The use of advanced and professional 3D-printing devices was crucial in achieving the desired results. The developed composite material exhibited a thermal conductivity of approximately 1.6 W/m²K at an 80% weight fill level, which is significantly higher than the thermal conductivity of the pure resin.

Finally, to demonstrate the practical application of the developed material, tool inserts for injection molding were successfully manufactured. The resulting tools exhibited excellent homogeneity in the distribution of aluminum oxide, confirmed by EDX measurements. The surface quality of the additively manufactured tool inserts was also optimized. This application-oriented example highlights the potential of the new composite in the development of more efficient and cost-effective tooling solutions for injection molding, particularly for rapid prototyping and small-series production. The findings of this research provide a valuable foundation for further exploration and optimization of composite materials for additive manufacturing in tooling applications.

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