

Printability and functional performance of DIW-fabricated LSR/TiO₂ composite ink

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Abstract. Direct Ink Writing (DIW) has become an effective additive manufacturing method to print complex structures of elastomers with high-viscosity printable inks. As part of this research, LSR/TiO₂ composite inks were developed and tested to determine their printability and functional performance in DIW processing. The preparations of 5 ink compositions with 1-5 wt% TiO₂ nanoparticles were first performed with liquid silicone rubber (LSR), catalyst, and glycerol as a rheological modifier. A pre-trial experiment was carried out to determine the extrusion characteristics and dimensional stability of the developed inks. Among the tested compositions, the one with 5 wt% TiO₂ was found to be the most stable in forming filaments and for the purpose of giving excellent geometry retention upon deposition. Thus, this ink was optimized and chosen to perform another characterization of the material and printing analyses. The rheological measurements showed that the higher the content of TiO₂, the more the rheology was increased and extrusion was achievable. The X-ray diffraction analysis revealed the existence of rutile-phase TiO₂ in the silicone matrix without any change of structure. Thermogravimetric analysis demonstrated the existence of good thermal stability of the composite to about 350°C, and scanning electron microscopy depicted the relatively uniform distribution of nanoparticles in the elastomer matrix. Moreover, DIW printing experiments were able to print different geometries such as straight filaments, rectilinear tracks, multilayer sheets, and solid discs with controlled processing environments. The findings indicate that the developed LSR/TiO₂ composite ink has the right rheological, structural, and thermal qualities to be confidently DIW-fabricated silicone-based functional structures.

Introduction

Additive manufacturing has immensely increased the ability of making complicated polymer designs with managed geometry and practical performance. DIW has received significant attention among other popularity techniques in additive manufacturing due to its capability to extrude very viscous materials and at the same time ensure dimensional stability as deposition proceeds. Materials made of silicone especially the LSR are extensively researched as DIW materials because of their high elasticity, thermal stability, chemical resistance, and electrical insulation. Such properties render LSR an attractive material in flexible electronics, dielectric and soft functional systems. It has however been shown that effective DIW processing of silicone materials necessitates the close implementation of ink rheology, extrusion characteristics, and filler dispersion to secure statistically stable printing and structural fidelity consistency. TiO₂ is often used as functional fillers in silicone matrices since it is capable of altering the dielectric and electrical insulation properties of polymer composites. Other past researchers have also shown that polarization process and dielectric responsiveness can be boosted in silicone-based materials by incorporation of TiO₂ particles.



According to Francis and Jain [1], the addition of functional fillers into 3D printed polymer substrates may enhance significantly dielectric permittivity as well as material functionality. Ali et al. [2] examined TiO₂ doped polymer nanocomposites and were also able to show the enhanced electrical qualities due to the compact arrangement of filler in the polymer matrix. Razzaghi-Kashani et al. [3] demonstrated that the alignment of particles in silicone rubber-TiO₂ composites is a great influence on the dielectric performance and mechanism of polarization. Qenawy et al. [4] performed a study on dielectric strength of SiR/TiO₂ composites assessed through neural network analysis that confirmed the role of filler content on insulation. Tugui et al. [5] have shown that all-silicone 3D printing can be used to fabricate complex geometry elastic dielectric structures. Yang et al. [6] came up with silicone elastomer composite with TiO₂-based nanoparticles in order to maximize dielectric and energy harvesting. Kalaš et al. [7] investigated electronic polymers 3D printing dielectric and thermal behavior, indicating some performance limits of the materials. Madidi et al. [8] examined TiO₂/silicone rubber micro- and nanocomposites, and concluded that the dielectric properties were enhanced as a result of increased interfacial polarization. Das et al. [9] stressed the significance of polymer rheology in additive manufacturing using extrusion technology and its impact on the quality of the printed structures. M'Barki et al. [10] developed the importance of proper rheological behavior in order to ensure extrusion and structural integrity stability in direct ink writing systems.

Nevertheless, there are some limitations in the existing literature despite these developments. Several of the studies put an emphasize on dielectric characterization of silicone-based composites, others put an emphasis on rheological aspects of DIW printing in isolation. A little literature has been done on the effect of the combined rheological behavior, extrusion stability, and the functions performance of LSR/TiO₂ composite inks that have been prepared to be used in DIW fabrication. Besides this, systematic experimental research to correlate ink formulation, printing behavior and dielectric response of the printed structures are inadequately reported. This disconnect limits the successful optimization of silicone based composite inks to the high-end additive manufacturing.

The current study thus examines printability of LSR/TiO₂ composite ink synthesized using DIW and its functional performance. The study will determine the rheological properties of the ink created and also will examine the extrusion behaviour of the ink upon DIW printing and will evaluate the structural and thermal manufacture of the printed composites. The originality of the work is that the direct correlation between the rheological suitability and DIW processing structural stability was employed. This combined research gives a better insight into the processes of involving materials and processes and it helps to create functional silicone-based inks to apply to the advanced additive manufacturing technologies.

Materials and Methods

The composite inks were developed in LSR and reinforced with TiO₂ nanoparticles to assess the reinforcing properties regarding the printability and functional behavior within DIW. The LSR-2 series base elastomer (LSR-220) and curing catalyst (LSR-2 Series, CAF-2) were provided by Jay Enterprises Specialty Chemicals (India). Padmanathi Distributors supplied heading filler, which was rutile-phase TiO₂ nanoparticles with the average particle size of about 100 nm. Glycerol, which was purchased at RK World Infocom Pvt. Ltd., was added as a rheological modifier to control the viscosity and help in the dispersion of particles in the silicone matrix. According to earlier research, it has been demonstrated that the choice of DIW process parameters and material formulations has a significant impact on the stability of printing and structural fidelity of silicone-based composites [11].

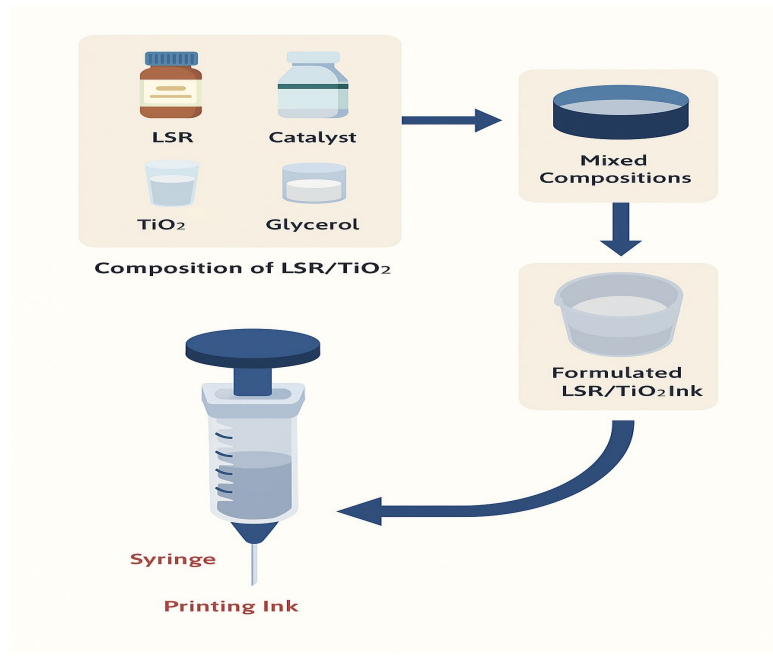


Fig. 1 Ink Formulation Process for LSR/TiO₂ Composite Inks.

The process of ink formulation is shown in Fig. 1, in which LSR, TiO₂ nanoparticles, catalyst, and glycerol were added, one after another, to the reaction to produce a homogenous printable ink. The preparation of the inks was made in terms of percentage of weight as shown in the equation below (E1): The ratios of LSR, catalyst, glycerol and TiO₂ contents were increased gradually. Table 1 summarizes the detailed compositional distribution and the concentration of LSR was between 97 wt% to 85 wt% and TiO₂, Catalyst and Glycerol was used 1 wt% to 5 wt%. This controlled change in filler content can be used to study the effect of TiO₂ loading on rheology and print qualities. Like compositional approaches are reported to be able to optimize silicone composite materials in additive manufacturing systems [12].

$$wt\% = \frac{\text{Component Mass}}{\text{Total mass}} \times 100 \quad (1)$$

Where:

1. Component Mass refers to the amount of LSR, TiO₂, Catalyst, or Glycerol.
2. Total Mass = *LSR + Tio2 + Catalyst + Glycerol*

where the total mass is the sum of LSR, TiO₂, catalyst, and glycerol. Based on this formulation strategy, five different ink compositions were prepared with TiO₂ concentrations ranging from 1-5 wt%, as summarized in Table.

Table 1. LSR/TiO₂ Ink Compositions.

Comp No.	LSR (wt%)	TiO ₂ (wt%)	Catalyst (wt%)	Glycerol (wt%)
1	97	1	1	1
2	94	2	2	2
3	91	3	3	3
4	88	4	4	4
5	85	5	5	5

The preparation of ink required correct weighing of the individual parts using a digital balance, and mixing them using a magnetic mixer. The rotational speed was regulated within the range of 300 to 2000 rpm to ensure uniform dispersion of the nanoparticle and avoid agglomeration. The mixture was then put under vacuum, to remove all the bubbles of air that may otherwise disrupt extrusion stability. Extrusion-based additive manufacturing requires proper rheological regulation since the viscosity and shear behavior have direct effect on filament formation and dimensional stability in DIW printing [13,15]. The rheological properties of the prepared inks were determined using a rotational viscometer (Labman LMVD-200) at 19.1 °C with spindle L4 rotating at 10 rpm. The thermal stability of the nanoparticles was determined by thermogravimetric analysis (TGA4000, PerkinElmer) at temperatures of 30 °C to 800 °C under the nitrogen environment. X-ray diffraction was used to perform phase analysis (Bruker D8 Advance), whereas microstructural analysis of printed structures was done using field-emission scanning electron microscopy (JEOL JSM-7610F Plus with EDS). These characterization techniques are usually used to determine structural and functional characteristics of DIW-fabricated silicone composites [16].

Results and Discussion

A pre-printing experiment was initially carried out to determine the printability of the five developed LSR/TiO₂ composite inks as in Table 1. The DIW system was used to extrude each formulation under the same conditions in order to study filament formation and dimensional stability. In this pilot study, those inks with lower TiO₂ content (Sample 1-4) showed relatively lower viscosity and shape retention after deposition. These inks demonstrated significant spreading and loss of structural fidelity with layer stacking. In Contrast, the behavior of Sample 5 (LSR 85wt%, TiO₂ 5wt% catalyst 5wt%, and glycerol 5wt%) was the most stable in extrusion with continuous filament formation and its higher dimensional accuracy. The increased concentration of TiO₂ raised the internal resistance to flow and the viscoelastic recovery of the composite ink necessary to keep the geometric stability during DIW printing. Religious correlations between extrusion stability and rheological properties have also been cited in silicone-based inks used in the additive manufacturing process [17,18]. Resting on these observations, Sample 5 was chosen to conduct a detailed characterization of the materials and 3D printing experiments.

The rheological properties of the formulated inks are given in Fig. 2A. It could be seen that the viscosity was growing steadily with the TiO₂ content to about 41879 mPa.s in Sample 5. This growth is explained by more intensive interactions between particles and polymers and the existence of a more interwoven filler network in silicone matrix. These viscosity values are favourable to DIW since the extruded filament will retain its geometry after deposition and at the same time enable flow through the printing nozzle with ease. The x-ray diffraction was used to analyze the structural properties of the composite as presented in Fig. 2B. Diffraction pattern of the printed film that was produced with developed ink exhibits typical peaks that represent rutile-phase TiO₂. These peaks indicate that the crystalline organization of the TiO₂ nanoparticles has not been destroyed in the course of mixing and processing. Meanwhile, the halo on the broad background signifies the amorphous character of the silicone elastomer matrix which means that inorganic particles have been successfully dispersed into the polymer system.

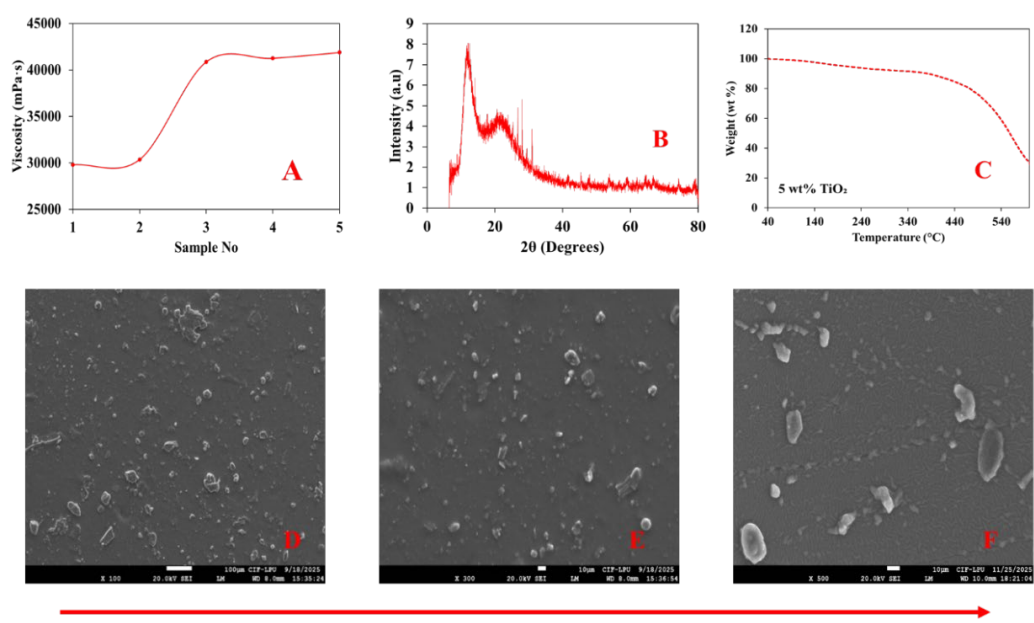


Fig. 2 Viscosity measured, XRD pattern, TGA curve, and SEM micrographs of the LSR/TiO₂ composite ink.

Thermal stability of the composite has been measured by using thermogravimetric analysis which is shown in Fig. 2C. The TGA curve shows a minimum weight loss at a temperature of about 350 °C and this shows the good thermal stability of the LSR-based composite. The significant degradation phase that is evident at approximately 400 °C to 550 °C is the degradation of silicone polymer backbone. The inclusion of TiO₂ nanoparticles prevents enhanced thermal resistance since the nanoparticles serve as a thermally stable inorganic phase in the composite structure [19]. Results of microstructural analysis via scanning electron microscopy are provided in Fig. 2D-F in which films made with developed composite ink (ink sample-5) demonstrate a comparatively homogenous distribution of TiO₂ particles inside the silicone framework. The minor particle agglomeration is observed at elevated magnifications, but the dispersibility over time shows that there are a strong mixing and a favourable interfacial fit among the filler and polymer phases.

S.No.	Temperature (°C)			Print Speed (mm/min)			Printed Geometry
	T1	T2	T3	240 mm/min	390 mm/min	540 mm/min	
1.	40	60	80				Printed straight line
2.	40	60	80				Rectilinear Tracks
3.	40	60	80				Multilayer solid sheet formation

							
4.	40	60	80				Multi-layer Solid Disc
				Constant extrusion multiplier (1.00)			

Fig. 3 Part fabrication of LSR/TiO₂ (5 wt% TiO₂) composite ink showing representative DIW-printed geometries produced at substrate temperatures of 40-80 °C and print speeds of 240-540 mm/min under a constant extrusion multiplier (1.00).

The DIW printing performance of developed composite ink is illustrated in Fig. 3, where several representative geometries were successfully fabricated, including printed straight lines, rectilinear tracks, multilayer solid sheets, and multilayer solid discs. The printing experiments were conducted at substrate temperatures ranging from 40-80 °C and printing speeds between 240-540 mm/min under a constant extrusion multiplier of 1.00. The results show that stable filament deposition and continuous layer formation were achieved across the investigated processing window. Moderate printing speeds provided improved filament uniformity, while elevated substrate temperatures facilitated rapid curing and better layer adhesion. These results confirm that the optimized rheological behavior of the developed ink supports reliable extrusion and structural stability during DIW fabrication. Comparable relationships between rheological properties, printing parameters, and structural fidelity have been reported in previous DIW studies [20]. The experimental results demonstrate that the optimized LSR/TiO₂ composite ink (Sample 5) exhibits suitable rheological, structural, and thermal characteristics required for stable DIW-based additive manufacturing.

Conclusion

The research study examined the development, characterization, and DIW printability of LSR/TiO₂ composite inks in extrusion-based additive manufacturing. Five contrasting ink compositions were first prepared by changing TiO₂, Catalyst and Glycerol concentration (1 to 5 wt%). The pilot printing study indicated that the composition with 5 wt% TiO₂ (Sample 5) would have the best extrusion properties and better dimensional stability during deposition than the other compositions. Their enhanced printing performance was ascribed to increased viscosity as well as more viscoelastic recovery of the composite ink that is necessary to sustain the structural integrity during DIW processing. A detailed material characterization of the streamlined ink formulation was then done. The rheological character of stable ink formation was verified through the measurement of viscosity, which ensured that the high filler concentration contained rheological properties to produce stable filaments. The analysis conducted by XRD confirmed that TiO₂ nanoparticles in rutile phase were present without structural changes when mixed.

The thermogravimetric study showed that the composite had good thermal stability as high as 350 °C, whereas SEM analysis showed that the suspension remains reasonably homogeneous throughout the silicone phase. The DIW printing experiments were able to achieve a diverse range

of geometries (straight lines, rectilinear tracks, and multi-layered sheets as well as solid discs) with the constancy of extrusion and good layering formation leading to consistent processing conditions. In the final discussion, the findings validate that the optimized LSR/TiO₂ composite ink has the right rheology, structure, and thermal properties needed to fabricate silicone-based functional structures by using DIW. The findings can be used to develop printable elastomer composites for advanced additive manufacturing in the field of electronic applications.

Author Contributions

The authors equally contributed to the conception, experimental design, and data analysis and prepared the final version of the paper, all authors have approved the final version of the paper.

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Conflict of interest

The authors declare that they have no conflict of Interest regarding the publication of this article.

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Data Availability Statement

Data and materials would be available on reasonable request.

References

- [1] V. Francis and P.K. Jain, 3D printed polymer dielectric substrates with enhanced permittivity by nanoclay inclusion, *Virtual Phys. Prototyp.* 12 (2017) 203–210. <https://doi.org/10.1080/17452759.2017.1312466>
- [2] A.A.B.A. Ali, H. Ahmad, H. Yap and H.A. Ismail, Investigation of electrical properties of TiO₂ nanocomposite-based polymer, *J. Phys.: Conf. Ser.* 2120 (2021) 012031. <https://doi.org/10.1088/1742-6596/2120/1/012031>
- [3] M. Razzaghi-Kashani, S. Javadi and N. Gharavi, Dielectric properties of silicone rubber–titanium dioxide composites prepared by dielectrophoretic assembly of filler particles, *Smart Mater. Struct.* 19 (2010) 035019. <https://doi.org/10.1088/0964-1726/19/3/035019>
- [4] S.A. Qenawy, L.S. Nasrat, H.M. Ismail and J.N. Asaad, Evaluation of dielectric strength of SiR/TiO₂ composites using feed-forward neural network, *IET Nanodielectr.* 3 (2020) 74–80.
- [5] C. Tugui, M. Cazacu, D.M. Manoli, A. Stefan and M. Duduta, All-silicone 3D printing technology: Toward highly elastic dielectric elastomers and complex structures, *ACS Appl. Polym. Mater.* 5 (2023) 7936–7946.
- [6] T. Yang, C. Wang, L. Liu and L. Zhang, Silicone elastomer dielectric composites by introducing novel O-MMT@TiO₂ nanoparticles for energy harvesting application, *Compos. Part A Appl. Sci. Manuf.* 185 (2024) 108351. <https://doi.org/10.1016/j.compositesa.2024.108351>
- [7] C.C. Uydur, Assessment of dielectric strength for 3D printed solid materials in terms of insulation coordination, *Appl. Sci.* 14 (2024) 11860. <https://doi.org/10.3390/app142411860>
- [8] F. Akin and O. Arikan, Effect of thermal aging on solid insulating materials under different voltage levels and frequencies, *Eng. Fail. Anal.* 148 (2023) 107222.

- [9] D. Kalaš, K. Šíma, P. Kadlec, R. Polanský, R. Soukup, J. Řeboun and A. Hamáček, FFF 3D printing in electronic applications: Dielectric and thermal properties of selected polymers, *Polymers* 13 (2021) 3702. <https://doi.org/10.3390/polym13213702>
- [10] F. Jia, C. Liu, B. Yang, A. Lee, L. Wu and H. Ning, Preparation of graphene/silicone rubber nanocomposite dielectric foams, *Polymers* 14 (2022) 3273. <https://doi.org/10.3390/polym14163273>
- [11] J.K. Mishra and V. Francis, Optimization of direct ink writing process parameters for liquid silicone rubber/TiO₂ composite ink, *J. Polym. Compos.* 13 (2025) 240–259. <https://doi.org/10.37591/JOPC.v13i06.233033>
- [12] F. Madidi, G. Momen and M. Farzaneh, Dielectric properties of TiO₂/silicone rubber micro- and nanocomposites, *Adv. Mater. Sci. Eng.* (2018) 4682076.
- [13] X. Sui, W. Zhou, L. Dong, Z. Wang, X. Liu, A. Zhou, J. Cai and Q. Chen, Fiber-reinforced silicone rubber composites with enhanced dielectric and thermal properties, *Adv. Polym. Technol.* 37 (2018) 1507–1516.
- [14] N. Wen, L. Zhang, D. Jiang, Z. Wu, B. Li, C. Sun and Z. Guo, Emerging flexible sensors based on nanomaterials: Recent status and applications, *J. Mater. Chem. A* 8 (2020) 25499–25527. <https://doi.org/10.1039/d0ta09556g>
- [15] A. M'Barki, L. Bocquet and A. Stevenson, Linking rheology and printability for dense and strong ceramics by direct ink writing, *Sci. Rep.* 7 (2017) 6017. <https://doi.org/10.1038/s41598-017-06115-0>
- [16] A. Das, E.L. Gilmer, S. Biria and M.J. Bortner, Importance of polymer rheology on material extrusion additive manufacturing: Correlating process physics to print properties, *ACS Appl. Polym. Mater.* 3 (2021) 1218–1249.
- [17] Y. Shao, R. Han, X. Quan and K. Niu, Study on ink flow of silicone rubber for direct ink writing, *J. Appl. Polym. Sci.* 138 (2021) 50819. <https://doi.org/10.1002/app.50819>
- [18] C. Mo, R. Yin and J.R. Raney, Direct ink writing of tough, stretchable silicone composites, *Soft Matter* 18 (2022) 7341–7347. <https://doi.org/10.1039/D2SM0023D>
- [19] M.A.S.R. Saadi et al., Direct ink writing: A 3D printing technology for diverse materials, *Adv. Mater.* 34 (2022) 2108855. <https://doi.org/10.1002/adma.202108855>
- [20] S. Tagliaferri, A. Panagiotopoulos and C. Mattevi, Direct ink writing of energy materials, *Mater. Adv.* 2 (2021) 540–563.