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Preparation and characterization of starch-based binders for binder jetting

Hongtao Jiang, [ID] * Xinhao Yang and Hao Wang

In recent years, binder jetting technology has made significant advances across industries, expanding the range of material options to meet diverse needs. Commonly used binders may leave residues during the sintering process, affecting surface quality and performance, and some may contain harmful substances. Therefore, there is a high demand for binders that are environmentally friendly and easy to remove. This study proposes to use sodium alginate and polyvinylpyrrolidone as additives to prepare starch-based inks that are both environmentally friendly and safe. The effects of additive composition, starch content, dispersant content, and dispersant ratio on the viscosity and stability of starch-based inks were studied. Through performance testing, the particle size, surface tension, rheological properties, and printability of inks with different components were demonstrated. The optimal ink formulation consists of 1 wt% starch and 0.3 wt% additives (30 wt% sodium alginate and 70 wt% PVP). The viscosity reaches 23 mPa s and the stability is excellent. The surface tension of the ink is 69.5 mN m^{-1}, which is slightly higher than the surface tension requirements for the printhead. This article provides a new process route for binder jetting technology and lays the foundation for its application in green and environmental protection.

Introduction

Additive manufacturing (AM) is a rapidly developing manufacturing technology that constructs objects by fabricating materials layer by layer, as opposed to traditional subtractive methods.[1] It offers advantages such as higher flexibility, shorter production cycles, and lower production costs, thus driving the rapid development of various industries. According to the ASTM standard, the major 3D printing technologies include binder jetting,[2,3] powder bed fusion,[4] material jetting, vat photopolymerization,[5–11] material extrusion,[12–17] sheet lamination, and directed energy deposition.[18] Among these, binder jetting stands out for its fast forming speed, ease of operation, absence of supports, wide material sources, and easy control of component and microstructure, making it more suitable for manufacturing large-sized parts.

The selection of binders is crucial for binder jetting, as it directly affects the final shrinkage and density after sintering, and determines whether satisfactory strength of the green parts can be achieved. Binder jetting technology has been successfully used to print sand molds and complex-shaped metal components. However, issues such as high porosity and shrinkage still exist, leading to inaccurate dimensions and formation of creep, which adversely affect mechanical properties such as compressive strength, flexural strength, and modulus.[19] Current research both domestically and

internationally mainly focuses on optimizing binder jetting technology using different fillers to enhance the strength and performance of molded parts. Gonzalez *et al.* from the University of Texas at El Paso and Sun Changning *et al.* from Xi'an Jiaotong University proposed that small particles,[20,21] as fillers, occupy the voids between powder particles to increase the density of molded parts. Researchers from Ohio University,[22] Hanyang University in South Korea,[23] and East China Jiaotong University respectively added nano-alumina particles,[24] copper nanoparticles, and nano-zirconia to binders, resulting in printed parts with higher sintering density and strength. Although nanoparticle suspensions as binders have many advantages, nozzle clogging remains a major limiting factor. The suspensions used usually contain insoluble micro- or nanoparticles, which easily clog the nozzles. Researchers from Virginia Tech and the team led by Ye Chunsheng from Huazhong University of Science and Technology applied metal organic compound decomposition solution and inorganic colloids as binders to improve the sintering density of molded parts.[25,26] Therefore, binder performance is crucial to ensuring high-quality binder jetting printing results.

Furthermore, with increasing attention to environmental protection, green and low-carbon development is an inevitable trend. However, commonly used binders on the market not only leave residues during sintering, affecting the surface quality and performance of the products, but also may contain harmful substances, affecting the environment and the health of workers.[27] Therefore, environmentally friendly binders that are easy to be removed have become an urgent need in the current

School of Materials Science and Engineering, Shaanxi University of Science & Technology, Xi'an, 710021, China. E-mail: htjiang_333@163.com

market. Bio-based ink is biodegradable and non-toxic, which can reduce the environmental impact during the production process. It has advantages in terms of environmental protection and safety compared to traditional inks.[28]

A starch-based ink preparation method for use in binder jetting technology is proposed in this paper, with systematic experimental research and optimization of starch-based ink being conducted. Sodium alginate and polyvinylpyrrolidone, which are food-grade compounds friendly to both humans and the environment, were selected as dispersants. The effects of additive composition, starch content, dispersant content, and dispersant ratio on the viscosity and stability of the starch-based ink were investigated. Through performance testing, the particle size, surface tension, rheological properties, and printability of the ink with different compositions were demonstrated. This study aims to provide a new process route for binder jetting technology, laying a foundation for its application in green and environmentally friendly aspects.

Experiment details

Experimental materials

In the ink preparation, cornstarch (food grade, Shanghai Yishen Health Food Co., Ltd., China) functions as the solute, deionized water as the solvent, and stabilizers include sodium alginate (chemically pure, Sinopharm Chemical Reagent Co., Ltd., China), polyvinylpyrrolidone (PVP) (chemically pure, Tianjin Kemiou Chemical Reagent Co., Ltd., China), gelatin (Analytically pure, Wuxi Yatai United Chemical Co., Ltd., China), agar powder (biological reagents, Beijing Aoboxing Biotechnology Co., Ltd., China), Tween 80 (chemically pure, Sinopharm Chemical Reagent Co., Ltd., China), and polyvinyl alcohol (PVA) (chemically pure, Tianjin Kemiou Chemical Reagent Co., Ltd., China).

Preparation of starch-based ink

As shown in Fig. 1, starch was added into deionized water and stir. The ratio of starch to deionized water was (0.5–3 wt%) to (97–99.5 wt%) to form a starch solution. Sodium alginate and polyvinylpyrrolidone were mixed at a ratio of (10–30 wt%) to (70–90 wt%) or (70–90 wt%) to (10–30 wt%) to obtain mixed dispersants. The mixed dispersants were added into the starch solution. The ratio of the mixed dispersant to the starch

solution was (0.1–0.5 wt%) to (99.5–99.9 wt%). The mixture was stirred on a magnetic stirrer at 70–75 °C for 1–2 hours until the dispersants were completely dissolved. At last, the final starch-based ink was prepared after the mixture was standed.

To identify suitable additive types, a comparative analysis of different additives on ink performance was conducted. Initially, the additive content was set at 0.2 wt%, and ink performance was tested with varying starch contents of 0.5 wt%, 1.0 wt%, 1.5 wt%, 2.5 wt%, and 3.0 wt%. The appropriate starch content was then selected. Next, the additive content range was adjusted between 0.1 wt% and 0.5 wt% to determine the optimal additive content. Based on these findings, further studies on additive combinations were conducted by varying the proportions of sodium alginate and PVP at ratios of 9 : 1, 8 : 2, 7 : 3, 3 : 7, 2 : 8, and 1 : 9. Ultimately, the optimal formulation for the starch-based ink was determined.

Testing and characterization

The ink particle size was analyzed quantitatively using a laser image particle size and shape analyzer (Bettersize3000plus, Dandong Baite Technology Co., Ltd., China). The rheological performance of the ink was evaluated using a rotational rheometer (DHR-1, Thermo Scientific, Germany). The surface tension properties of the ink were assessed using a surface tension meter (QBZY series fully automatic surface tension meter, Shanghai Fangrui Instrument Co., Ltd., China). The dispersion stability of inks were analyzed quantitatively by using Turbiscan (Turbiscan LAB, Formulaction Inc., France).

The interaction between the binder and the powder bed affects the accuracy, strength, and surface quality of the samples, while the influence of the binder on the powder bed is influenced by inertial forces, surface tension, and viscous forces.[29] Therefore, the flow of the binder and its interaction with the powder bed are influenced by the Ohnesorge number (O_h). Studies have shown that,[30] in order to obtain stable droplets and good printing applicability, the value of O_h should be in the range of 0.1 to 1.

$$O_h = \frac{\eta}{\sqrt{\rho D \gamma}} \tag{1}$$

where ρ is the density of the droplets, kg m^{-3}; D is the diameter of the droplets, m; γ is the surface tension, N m^{-1}; η is the dynamic viscosity of the droplets, N s m^{-2}.[30–32]
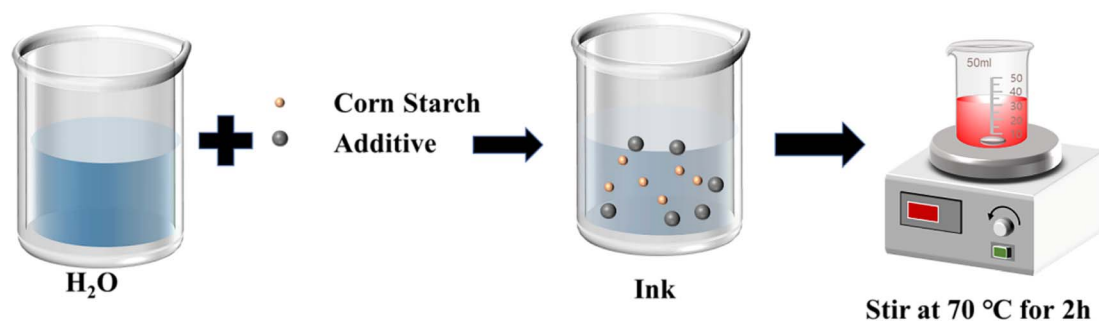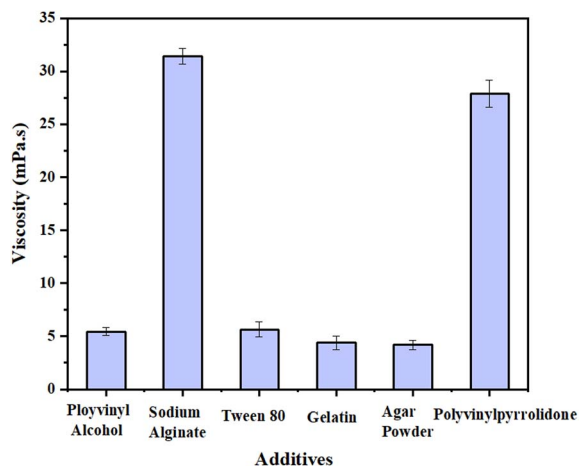

Fig. 1 Experimental process diagram.

Fig. 2 The viscosity of ink with different component additives.

Results and discussion

Additive composition of ink

To prevent layering and clogging during printing, it is essential for good dispersion stability of the ink to be maintained over a certain period. With a reference solid content of 2 wt% starch and 0.2 wt% additive, the impacts of various additives on ink dispersion stability were investigated. The dispersion performance of different additives in the ink was evaluated. The additive that most effectively enhances ink dispersion stability was ultimately identified through a comparison of their effects.

Fig. 2 illustrates the comparison of viscosity among starch solutions with different additive components. It is evident from the figure that when sodium alginate is added to cornstarch, the viscosity is measured to be approximately 31.5 mPa s, and it is found to decrease to around 27 mPa s when polyvinylpyrrolidone is added. The overall viscosity is observed to be relatively high. Conversely, when additives such as PVA, Tween 80, gelatin, and agar powder are used, the viscosity is measured to be approximately 5 mPa s. This difference is attributed to the larger molecular weight of sodium alginate and polyvinylpyrrolidone, which forms a denser network structure, consequently increasing the viscosity of the solution. In contrast, additives like PVA, Tween 80, gelatin, and agar powder, which have smaller molecular weights, are unable to establish a dense network structure.

Fig. 3(a) shows the relationship between the sedimentation ratio of ink with different additive components and time. Upon adding sodium alginate to the ink, it maintains good stability owing to the entanglement of larger molecules. Precipitation initiates after 15 min, yet stabilizes for 90 min with a final sedimentation ratio of 80%. When PVA is introduced, slow sedimentation within 90 min, stabilizing thereafter with a final sedimentation ratio of 37%. Polyvinylpyrrolidone addition results in rapid sedimentation, reaching relative stability at 30 min and full stability at 60 min, with a final sedimentation ratio of 23%. Despite its initial rapid sedimentation, polyvinylpyrrolidone quickly stabilizes, yielding a higher final sedimentation ratio compared to gelatin, agar powder, and Tween 80. In contrast, when gelatin, agar powder, and Tween 80 are used as additives, ink sedimentation begins immediately, reaching stability at 60 min, with a final sedimentation ratio of 17%, indicating poor stability.

The ink necessitates low viscosity and excellent stability. Through a comparison of viscosity and sedimentation ratio across various additives, it is determined that the ink exhibits superior performance when additives such as PVA, sodium alginate, and polyvinylpyrrolidone are employed.

Despite heating and stirring for 2 hours after adding PVA to cornstarch for ink preparation, significant flocculation persisted in the ink. Fig. 4 illustrates the infrared spectra of cornstarch, PVA, and their mixture. In these spectra, cornstarch shows stretching vibration peaks of starch hydroxyl groups (O–H) at 3482 cm^{-1}, C–H stretching vibration peaks at 2933 cm^{-1}, peaks at 1652 cm^{-1} associated with in-plane bending vibrations of C–H, and a peak at 1003 cm^{-1} related to C–O–C bonds in the polysaccharide chain, possibly indicating characteristic vibrations of α-glucan.[33] PVA exhibits hydroxyl (–OH) vibrations at 3439 cm^{-1}, C–H stretching vibration absorption at 2946 cm^{-1}, and asymmetric and symmetric carboxyl group stretching vibration peaks at 1573 cm^{-1}.[34]

When cornstarch is mixed with PVA to prepare ink, the absorption peak at 3215 cm^{-1} in the infrared spectra
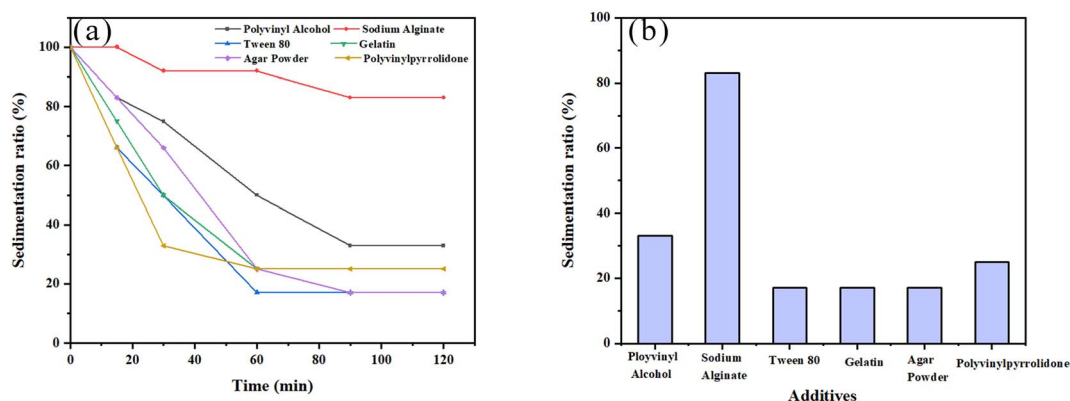

Fig. 3 Ink with different component additives (a) the relationship between sedimentation ratio and sedimentation time (b) sedimentation ratio after 120 min.
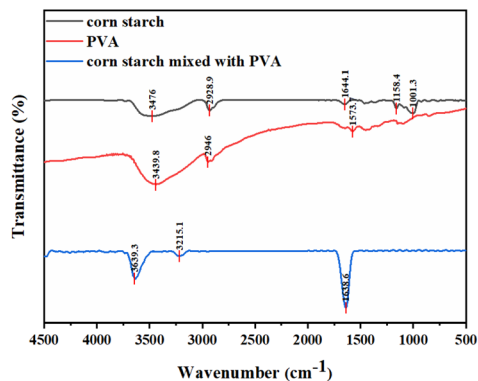
Fig. 4 The infrared spectrum of corn starch, PVA, and their mixture.

corresponds to the stretching and bending vibrations of C–H bonds. Compared to pure cornstarch and PVA, this peak shifts to a higher wavenumber. Additionally, strong peaks appear at 3634 cm^{-1} and 1636 cm^{-1}, corresponding to the stretching and bending vibrations of –OH groups in cornstarch and PVA molecules, respectively. The absorption peak at 3634 cm^{-1} shows a blue shift, indicating disruption of hydrogen bonds within and between PVA molecules, and the formation of new hydrogen bonds between PVA and cornstarch.[35,36] Influenced by these hydrogen bonds, PVA molecules may aggregate within the ink, leading to flocculation.

Due to causing nozzle clogging during printing, the ink containing PVA as an additive is unsuitable for printing. Consequently, sodium alginate and polyvinylpyrrolidone (PVP) were selected as additives for the ink instead.

Starch content of ink

The concentrations of corn starch (0.5, 1.0, 1.5, 2.5, and 3.0 wt%) were employed, and the viscosity and stability of the ink were observed with different levels of corn starch supplemented with sodium alginate and polyvinylpyrrolidone.

Fig. 5(a) illustrates the relation between the viscosity of ink with 0.2 wt% sodium alginate and varying corn starch content. The viscosity of ink is observed to rise with the increase of sodium alginate content. When the sodium alginate content reaches 1.5 wt%, the viscosity of ink is highest, reaching 33 mPa s. With the increase in sodium alginate content, the viscosity of ink progressively decreases, reaching a minimum of 26.5 mPa s at the sodium alginate content of 3 wt%. The viscosity of ink of 0.2 wt% polyvinylpyrrolidone with varying starch content was shown in Fig. 5(b). Initially, as the corn starch increases, the viscosity decreases, then increases and finally decreases again. The maximum viscosity of 27 mPa s occurs at 2 wt% corn starch, while the minimum viscosity of 7 mPa s is observed at 3 wt% corn starch. Corn starch, as the base of the ink, undergoes changes in viscosity within a specific concentration ranges, but these fluctuations do not always indicate a significant rise. Viscosity can be influenced by various factors, such as concentration, temperature, and shear rate. A higher concentration can increase viscosity due to the presence of more binder molecules, which interact more and raise viscosity. However, this relationship may saturate within a certain concentration range, where further increases in concentration may no longer significantly affect viscosity.

Fig. 6(a) shows the sedimentation profiles of ink containing sodium alginate with corn starch concentrations. As the concentration of corn starch increases, the stability of the ink demonstrates an upward trend. With a corn starch concentration of 0.5 wt%, the ink exhibits poor stability, settling to 66% sedimentation after 90 min. Conversely, at a corn starch concentration of 3.0 wt%, the ink demonstrates good stability, reaching a stable state at 15 min, continuing to settle at 60 min, and achieving 83% sedimentation completion at 90 min. This trend can be attributed to the higher concentration of starch molecules within the binder as the corn starch concentration rises. These molecules contribute to the formation of a dense colloidal network structure in the liquid, which enhances the viscosity and adhesion of the binder, consequently improving its stability.

Fig. 6(b) shows the sedimentation profiles of ink containing polyvinylpyrrolidone (PVP) with different corn starch concentrations. In comparison to sodium alginate, polyvinylpyrrolidone (PVP) demonstrates inferior stability. The stability of the ink improves as the concentration of starch
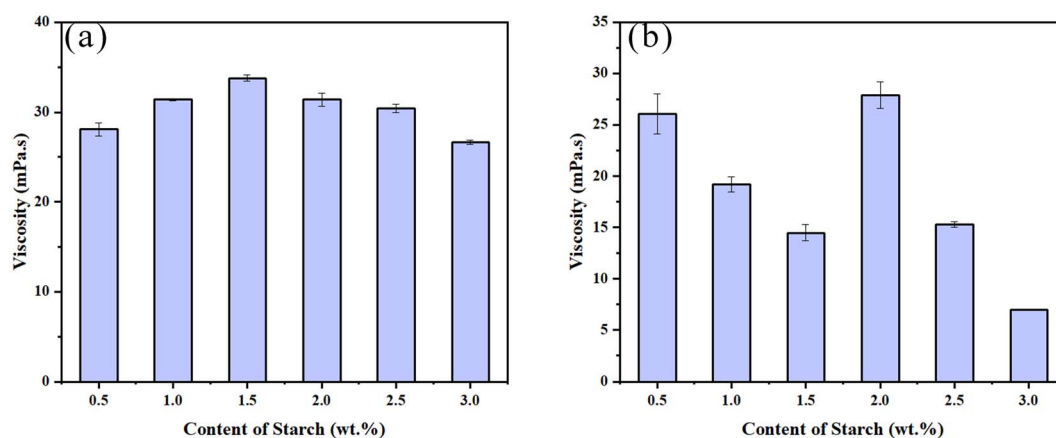

Fig. 5 The viscosity of different additives with varying starch content (a) sodium alginate (b) polyvinylpyrrolidone.
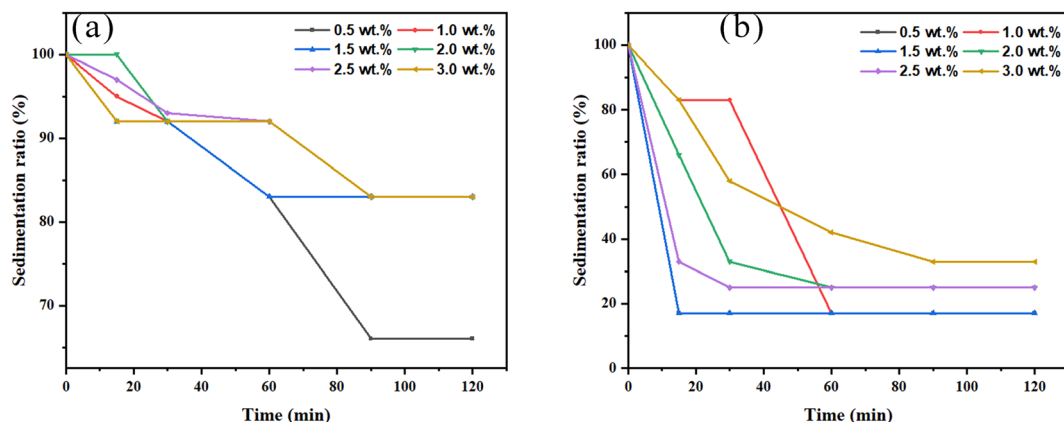
Fig. 6 The sedimentation records of different ink formulations with varying starch content (a) adding sodium alginate (b) adding polyvinylpyrrolidone.

increases, with most inks settling to a stable state between 15 and 30 min across various starch concentrations. Specifically, at a starch concentration of 1.0 wt%, the ink maintains good stability from 0 to 30 min, experiences rapid settling between 30 and 60 min, and eventually reaches a stable state.

After comparing the viscosity and sedimentation profiles of ink with varying starch concentrations following the addition of sodium alginate and polyvinylpyrrolidone (PVP), it is evident that ink with 1 wt% and 2 wt% starch content demonstrates superior performance. As depicted in Fig. 7, the manually bonded ink sample with 1 wt% starch content displays a clearer boundary and retains its shape more effectively. Therefore, 1 wt% starch was chosen for further experimentation.

Additive content of ink

To ensure that the ink possesses the desired viscosity and stability, it is essential to ascertain the suitable additive content after establishing the starch content and type of additive.
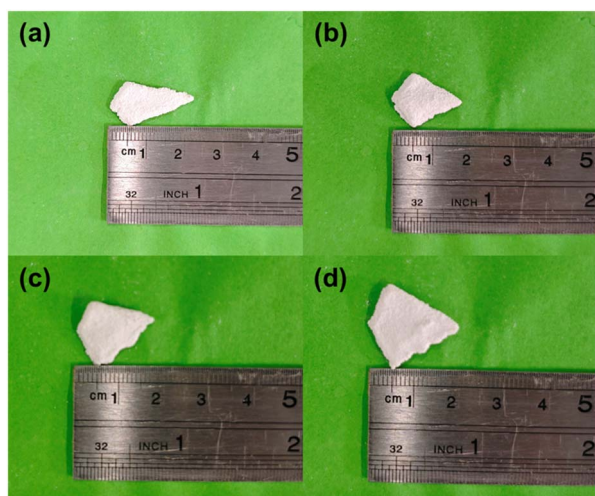

Fig. 7 Different starch content ink bonding samples (a) 1 wt% starch with 0.2 wt% sodium alginate (b) 2 wt% starch with 0.2 wt% sodium alginate (c) 1 wt% starch with 0.2 wt% polyvinylpyrrolidone (d) 2 wt% starch with 0.2 wt% polyvinylpyrrolidone.

Maintaining the starch content at 1 wt%, various additive contents ranging from 0.1 to 0.5 wt% are employed. The ink's viscosity and stability are then assessed to determine the optimal additive content.

Fig. 8(a) depicts the viscosity of starch ink after the addition of sodium alginate. The viscosity of the ink increases with the rise in sodium alginate content. From 0.1 wt% to 0.3 wt% sodium alginate content, the viscosity experiences a gradual increase. Beyond 0.3 wt% sodium alginate content, the viscosity of the ink escalates rapidly. In Fig. 8(b), the viscosity of the corn starch-based ink initially rises and then decreases with increasing PVP content. The ink viscosity peaks at 19 mPa s when the PVP content is 0.2 wt%. Sodium alginate possesses viscosity and gelling properties, contributing to an overall increase in ink viscosity.[37] Consequently, the viscosity of the ink rises with increasing sodium alginate content. However, when the viscosity of sodium alginate is low, its impact on ink viscosity is minimal. Conversely, PVP enhances ink viscosity to some extent. Given starch's inherent stability and viscosity-regulating capabilities, the effect of PVP is relatively minor under these conditions.

Fig. 9(a) illustrates the sedimentation patterns of ink with varying concentrations of sodium alginate. As the sodium alginate content increases, the ink's stability gradually enhances. At 0.1 wt% sodium alginate content, the ink settles to 83% at 30 min and continues to sedimentation at 60 min, reaching a minimum of 66%. With 0.2 wt% sodium alginate content, the ink settles more slowly, achieving a minimum sedimentation of 83% after 120 min. When the sodium alginate content is 0.3 wt%, sedimentation initiates at 15 min, reaching a minimum after 90 min. The ink displays optimal stability at 0.5 wt% sodium alginate content, with sedimentation commencing only after 60 min. In Fig. 9(b), the sedimentation records of ink with various concentrations of polyvinylpyrrolidone (PVP) are presented. In contrast to ink with sodium alginate, ink stability is inferior with PVP. Furthermore, the stability of starch-based ink diminishes with increasing PVP content. The ink with 0.2 wt% PVP exhibits the highest stability, with temporary stability at 15 min, followed by rapid sedimentation at 30 min, reaching a minimum at 60 min.
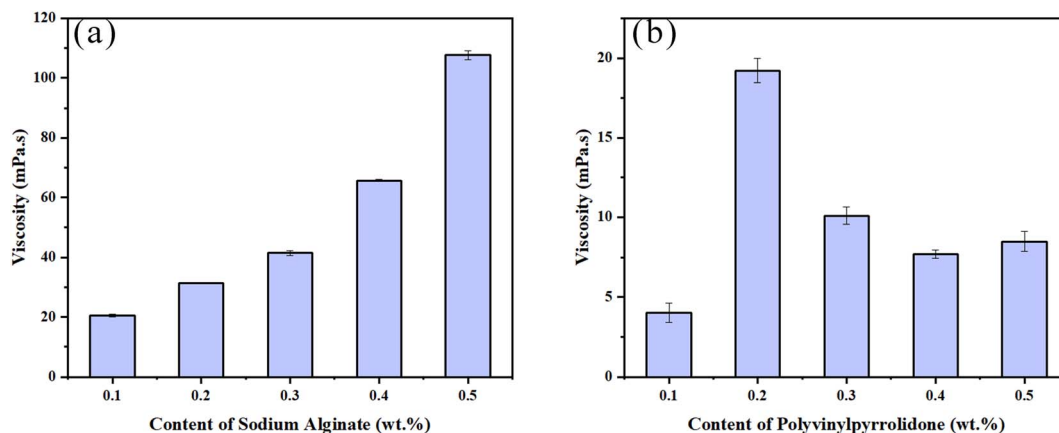
Fig. 8 Starch ink viscosity with varying additive concentrations. (a) adding sodium alginate (b) adding polyvinylpyrrolidone.

Conversely, the ink with 0.4 wt% PVP demonstrates the lowest stability, with sedimentation reaching a minimum at 15 min.

When the sodium alginate content is low, it does not provide sufficient viscosity to maintain particle dispersion, resulting in poor stability and rapid sedimentation. As the sodium alginate concentration rises to 0.5 wt%, ink stability notably improves, indicating that at this concentration, sodium alginate provides adequate viscosity. Conversely, the stability of the ink diminishes with increasing PVP content. The ink with 0.2 wt% PVP exhibits the highest stability, whereas the ink with 0.4 wt% PVP with the lowest stability. This is attributed to the fact that lower concentrations of PVP aid ink dispersion to some extent, while higher concentrations of PVP may induce ink instability.

In terms of stability, ink stability enhances with higher sodium alginate content, but decreases with increased polyvinylpyrrolidone (PVP) content. Concerning viscosity, ink viscosity gradually rises when sodium alginate content is below 0.3 wt%, but sharply increases beyond 0.3 wt%. Hence, both viscosity and stability of the ink are optimal when additive content is at 0.3 wt%.

Additive ratio of ink

By examining the influence of different additive concentrations on ink performance, the optimal concentration of additives was identified to be 0.3 wt%. However, the addition of sodium alginate and polyvinyl pyrrolidone (PVP) led to varied improvements in ink viscosity and stability. Hence, a subsequent experiment was conducted to explore the impact of incorporating sodium alginate and PVP in different proportions
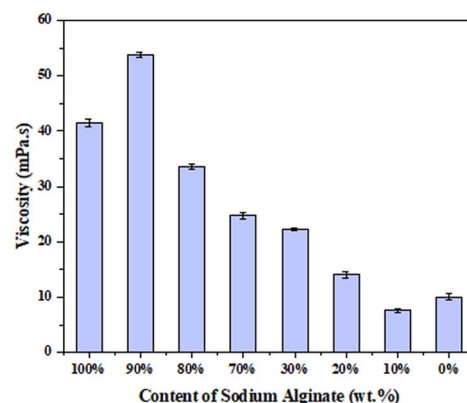

Fig. 10 Ink viscosity with varying sodium alginate content in the additives.
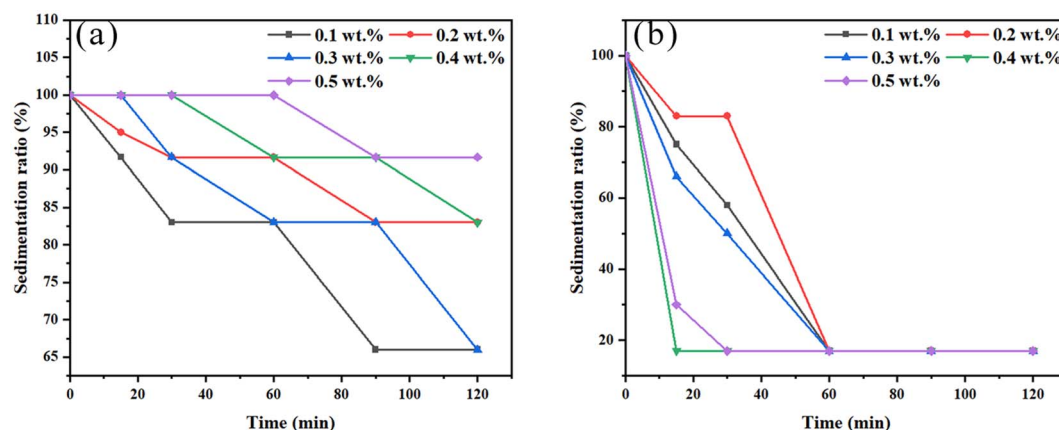

Fig. 9 Different ink settling records with varying additive concentrations (a) adding sodium alginate. (b) adding polyvinylpyrrolidone.
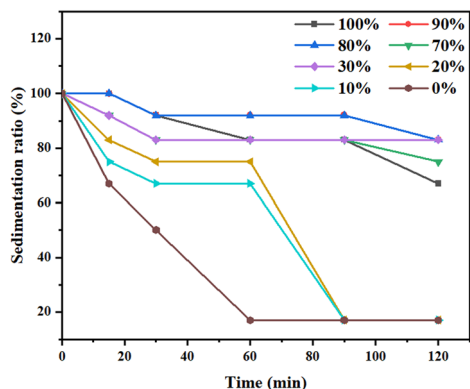
Fig. 11   Ink settling records with varying sodium alginate content in the additives.

Fig. 12   Particle size distribution of inks with different sodium alginate content.

on ink performance. Fig. 10 depicts the effect of varying sodium alginate proportions in the additives on ink viscosity. As the proportion of sodium alginate decreased, the ink viscosity generally declined. A transient increase in viscosity was observed when the sodium alginate proportion decreased from 100 wt% to 90 wt% or from 10% wt% to 0 wt%. However, the overall ink viscosity decreased with diminishing sodium alginate concentration. This trend may be attributed to the polysaccharide nature of sodium alginate, which tends to gel. With increasing concentration, sodium alginate may have formed a gel network, elevating viscosity. Yet, upon reaching a certain threshold, it might have formed a relatively loose gel network, leading to a sudden viscosity decrease. Notably, when the sodium alginate proportion ranged from 30 wt% to 70 wt%, ink viscosity remained relatively stable, fluctuating between 20 and 30 mPa s.

Fig. 11 depicts the impact of varying sodium alginate proportions in the additives on ink stability. It is evident that higher proportions of sodium alginate in the ink result in better stability. Even at a sodium alginate proportion of 30 wt%, the ink maintains good stability. However, when the sodium alginate proportion decreases to 20 wt%, rapid sedimentation of the ink is observed after 60 min. Moreover, at a sodium alginate proportion of 0 wt%, the ink experiences steady and gradual sedimentation from the outset, completing sedimentation by 60 min.

Sodium alginate and polyvinylpyrrolidone interact synergistically, forming a specific structure at particular ratios that enhances ink stability. The solubility and compatibility of these additives within the ink change with varying ratios. At lower sodium alginate levels, the ink maintains low viscosity while retaining good stability, meeting operational requirements. Conversely, when the sodium alginate proportion in the additive is 20 wt%, the ink exhibits low viscosity but poor stability. However, at a 30 wt% sodium alginate proportion, the ink demonstrates both low viscosity and enhanced stability. Beyond a sodium alginate proportion of 70 wt%, ink viscosity increases. The dispersibility of sodium alginate and polyvinylpyrrolidone significantly influences ink stability. Optimal dispersion within the 20 wt% to 50 wt% sodium alginate proportion range
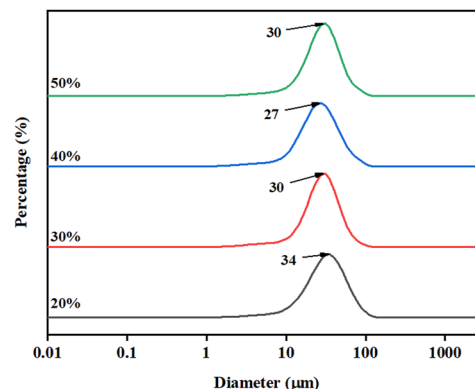
mitigates particle sedimentation. Moreover, inks within this range exhibit favorable viscosity and rheological attributes, further aiding in sedimentation prevention. Hence, inks with sodium alginate proportions ranging from 20 wt% to 50 wt% in the additive are selected for performance evaluation.

Particle size of the prepared starch-based ink

The binder jetting technology imposes requirements on the ink particle size, as too large particles may cause nozzle clogging, while too small particles may not effectively bind the powder. Fig. 12 illustrates the distribution of ink particle sizes after varying the sodium alginate content in the additive. It can be observed from the figure that when the sodium alginate content in the additive is 40 wt%, the main particle size of the ink is 27 μm, whereas when the sodium alginate content is 20 wt%, the ink particle size is larger, mainly at 34 μm.

The variation in sodium alginate content in the additive has little effect on the ink particle size distribution. This is because the mixture of sodium alginate and polyvinylpyrrolidone has good dispersibility, effectively preventing particle aggregation and precipitation in the ink. Therefore, even with changes in content, the additive can still maintain the stability of the ink, with minimal impact on the particle size distribution.

The minimum nozzle size of the GS12 model in the Xaar2002 print head is 34 μm, and that of the GS40 model is 47 μm. The average particle size distribution of starch-based ink is 30 μm, so the ink can be adapted to the print heads available on the market.

Rheological property of the prepared ink

The influence of different sodium alginate contents in the additive on the rheological properties of the ink was investigated. Fig. 13 illustrates the relationship between ink viscosity, shear stress, and shear rate with varying the sodium alginate content in the additive. Panels (a), (b), (c), and (d) represent sodium alginate contents of 20 wt%, 30 wt%, 40 wt%, and 50 wt%, respectively. With an increase in sodium alginate content, the ink viscosity initially increases and then decreases as the shear rate increases. This phenomenon occurs because the values of sodium alginate and polyvinylpyrrolidone reach

a threshold. Further increasing the sodium alginate content results in a decrease in ink viscosity. Additionally, as the shear rate increases from 0.1 s^{-1} to 100 s^{-1}, the ink viscosity exhibits varying degrees of reduction, indicating shear thinning, which is characteristic of non-Newtonian fluids.

Observing the curve of shear stress *versus* shear rate, it can be observed that at low shear rates, shear stress increases rapidly with increasing shear rate. However, as the shear rate reaches a certain value, the increase in shear stress begins to slow down. This trend aligns with the behavior of shear stress in non-Newtonian fluids, where shear stress changes with shear rate.

Surface tension of the prepared ink

The surface tension of the ink affects the accuracy and speed of jetting, as well as the printing quality and precision of the sample after jetting onto the powder surface. Therefore, it is essential to control the surface tension of the ink properly. Fig. 14 illustrates the effect of varying sodium alginate content in the additive on the surface tension of the ink. As depicted, the surface tension of the ink shows a rapid decline followed by a gradual stabilization over time, ultimately stabilizing within the range of 68.5–69.5 mN m^{-1}. The variation in sodium alginate content has minimal impact on the surface tension of the ink. This is because the primary function of sodium alginate and polyvinylpyrrolidone is to enhance the stability and viscosity of the ink, without significantly affecting the surface

tension. Therefore, adjusting the ratio of sodium alginate to polyvinylpyrrolidone content does not lead to a noticeable change in the surface tension of the ink. In general, the surface tension requirement for ink in binder jetting technology falls between 30 and 65 mN m^{-1}.[38] The surface tension of the starch-based ink is slightly higher than the performance requirements of the print-head in binder jetting technology. Further optimization of the formulation is needed to reduce the surface tension of the starch-based ink.

Stability of the prepared ink

To ensure the uniformity and consistency of the ink during the printing process and to prevent aggregation or precipitation, the ink should exhibit good dispersibility. Additionally, the ink should possess sufficient stability to maintain its stability during storage and usage, thereby avoiding precipitation and contributing to further enhancing the printing quality of the ink. Fig. 15 illustrates the effect of varying sodium alginate content on stability. As observed in the graph, with an increase in sodium alginate content, the stability of the ink within 1 hour shows an upward trend. When the sodium alginate content is 20 wt%, the stability test of the ink reaches 6 after 1 hour, indicating poor stability. However, when the sodium alginate content is increased to 30 wt%, the stability test of the ink reaches 3, and further increasing the sodium alginate content to 40 wt% results in a stability test value of 2.5. It is evident that as
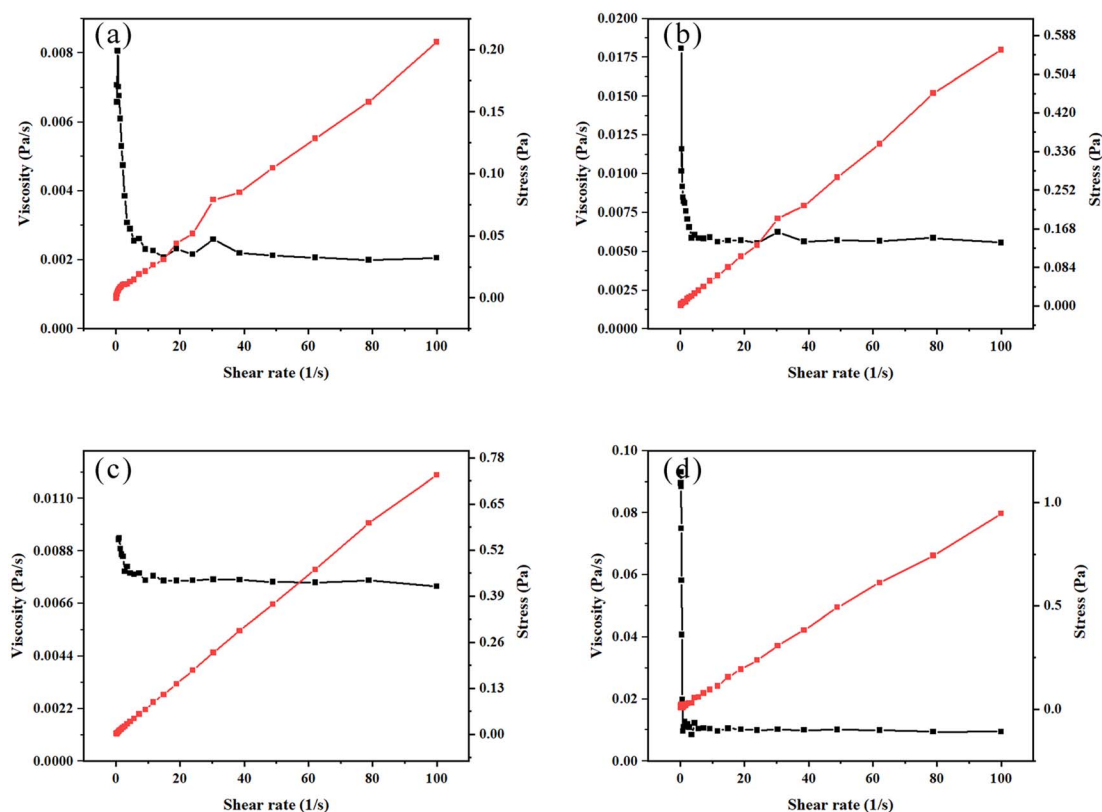

Fig. 13 The relationship between ink viscosity, shear stress, and shear rate as a function of sodium alginate content in the additive (a) 20 wt% sodium alginate content ratio (b) 30 wt% sodium alginate content ratio (c) 40 wt% sodium alginate content ratio (d) 50 wt% sodium alginate content ratio.
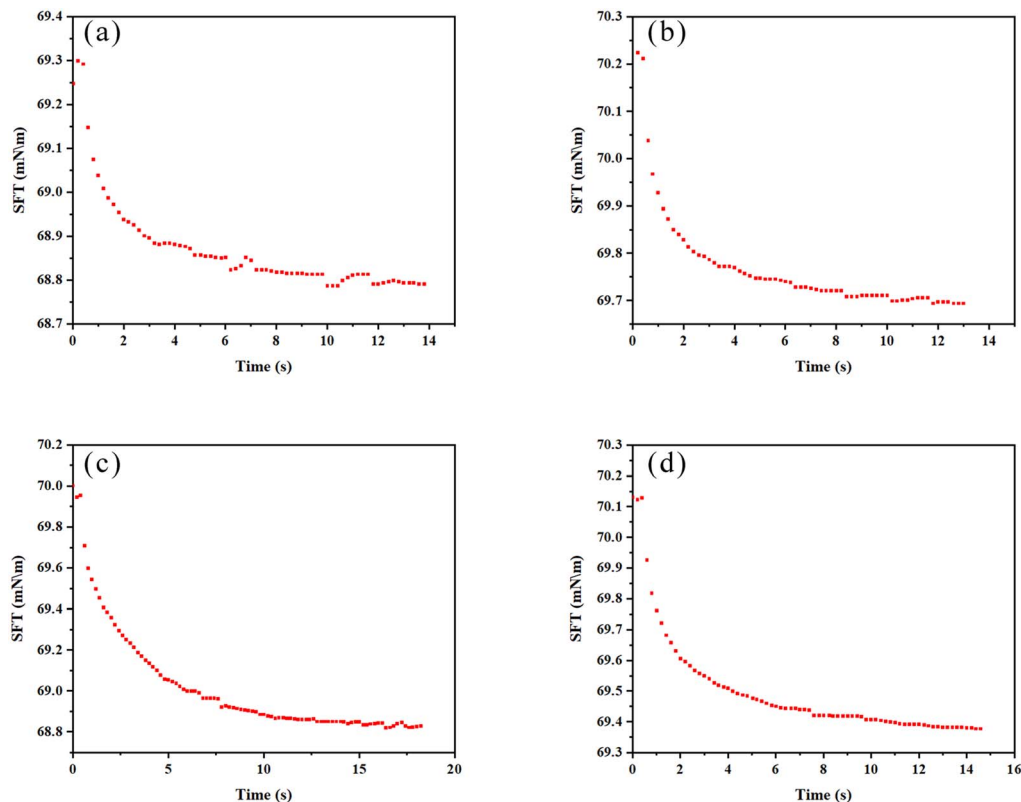
Fig. 14 The surface tension of ink as a function of varying sodium alginate content in the additive (a) 20 wt% sodium alginate content ratio (b) 30 wt% sodium alginate content ratio (c) 40 wt% sodium alginate content ratio (d) 50 wt% sodium alginate content ratio.

the proportion of sodium alginate in the additive increases, the ink exhibits higher stability. This is because sodium alginate can form a gel-like structure, which helps prevent particle precipitation and dispersion in the ink, thereby thickening and stabilizing it. Sodium alginate has a more significant role in enhancing the stability of the ink compared to poly-vinylpyrrolidone. Therefore, selecting sodium alginate content at 30 wt% and 40 wt% in the additive ensures that the ink exhibits excellent performance.

Printability of the prepared ink

Fromm and colleagues initially investigated the mechanism of droplet formation and defined the parameter $Z = 1/O_h$ to describe the printability of the binder.[39] Reis *et al.* further studied the printable Z-value range ($1 < Z < 10$) and calculated that when $Z < 1$,[40] the binder viscosity is too high, leading to
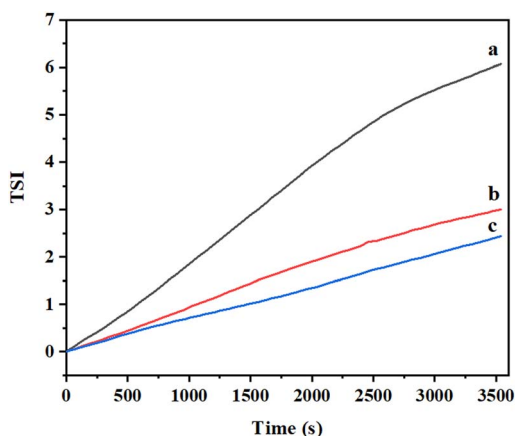

Fig. 15 The stability of ink as a function of varying sodium alginate content in the additive (a) 20 wt% sodium alginate content ratio (b) 30 wt% sodium alginate content ratio (c) 40 wt% sodium alginate content ratio.
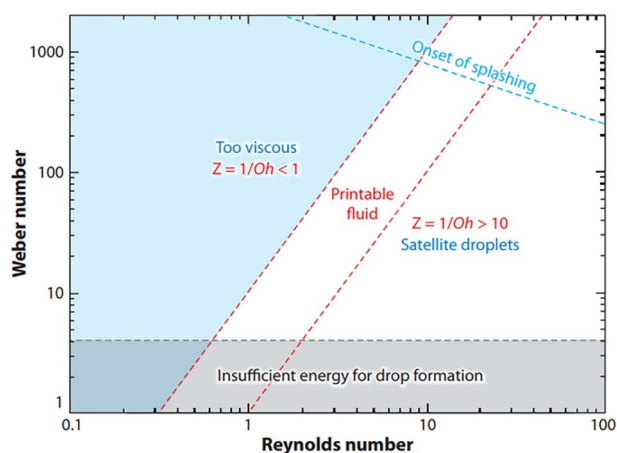

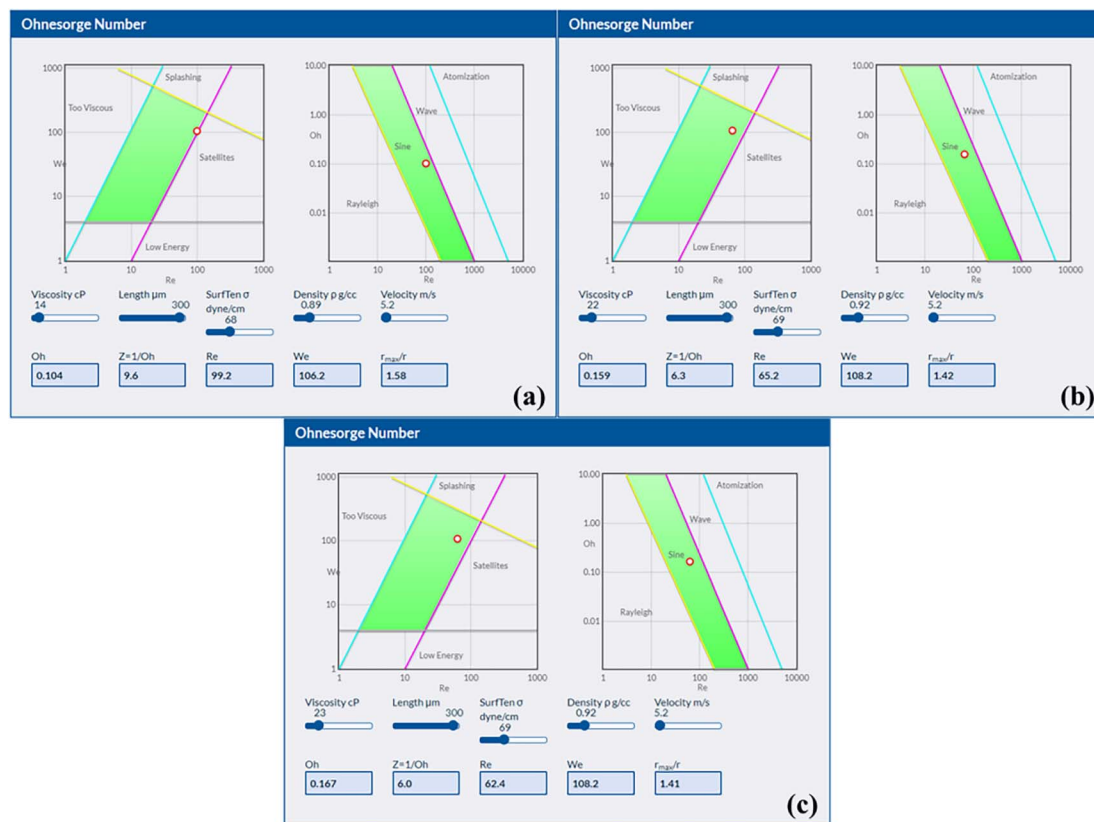Fig. 16 The allows stable printing range.[41]

Fig. 17 The printability of ink after adding different contents of sodium alginate (a) 20 wt% sodium alginate content ratio (b) 30 wt% sodium alginate content ratio (c) 40 wt% sodium alginate content ratio.

nozzle clogging, while when $Z > 10$, it tends to generate a large number of dispersed droplets, resulting in poor viscosity.[41] Fig. 16 illustrates the range where stable printing is permitted.

Fig. 17 shows the printability of ink after adding different contents of sodium alginate, it can be observed that when the sodium alginate content in the additive is 20 wt%, the printability of the ink is located at the edge of the printable region. However, when the sodium alginate content is 30 wt% and 40 wt%, the printability of the ink is within the printable region. This indicates that the printability of inks with sodium alginate content of 30 wt% and 40 wt% is superior to that of inks with 20 wt% content. However, the viscosity of the ink with 30 wt% sodium alginate content is lower than that of the ink with 40 wt% sodium alginate content, and it exhibits better stability. Therefore, the optimal choice is to have 30 wt% sodium alginate content and 70 wt% polyvinylpyrrolidone content in the additive.

Conclusion

This study explores the optimization of starch-based inks for binder jetting technology, focusing on enhancing ink viscosity, stability, printability, through controlled starch content and additive composition. The ink formulated with sodium alginate and polyvinylpyrrolidone exhibits superior viscosity and stability compared to that formulated with PVA, Tween 80, gelatin, and agar powder additives. Therefore, sodium alginate

and PVP were evaluated as additives to improve ink dispersion stability. The optimal ink formulation consists of 1 wt% starch and 0.3 wt% additives (30 wt% sodium alginate and 70 wt% PVP). This formulation exhibited favorable viscosity (23 mPa s) and stability, effectively preventing nozzle clogging and maintaining dispersion uniformity during printing. The surface tension of the ink is 69.5 mN m^{-1}, which is slightly higher than the surface tension requirements for the printhead. The ink demonstrated excellent printing performance and forming stable printed structures. This article provides crucial experimental evidence for the application of starch-based inks in binder jetting technology and highlights their potential as environmentally friendly binder materials. The formulation of starch-based ink can be further optimized in future research to enhance its adhesive properties and mechanical performance. By introducing other functional additives, the strength, durability, and applicability of the ink can be improved to meet the demands of more complex industrial applications.

Abbreviations

AM	Additive manufacturing
PVP	polyvinylpyrrolidone
PVA	polyvinyl alcohol
O_h	Ohnesorge number

Data availability

The data that support the findings of this study are available from the corresponding author, Xinhao Yang, upon reasonable request. All relevant data are included in the manuscript and its supplementary information files. Additional data related to the experimental procedures and results can be obtained by contacting 745623255@qq.com.

Conflicts of interest

There are no conflicts to declare.

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References

1 T. D. Ngo, A. Kashani, G. Imbalzano, K. T. Q. Nguyen and D. Hui, *Composites, Part B*, 2018, **143**, 172–196.

2 H. P. Zhao, C. S. Ye, S. H. Xiong, Z. T. Fan and L. Z. Zhao, *Addit. Manuf.*, 2020, **32**, 101025.

3 H. P. Zhao, C. S. Ye, Z. T. Fan and C. M. Wang, *J. Eur. Ceram. Soc.*, 2017, **37**(15), 5119–5125.

4 E. H. Kim, H. H. Choi and Y. G. Jung, *J. Manuf. Process.*, 2020, **53**, 43–47.

5 B. Ozkan, F. Sameni, F. Bianchi, H. Zareadeh, S. Karmel, D. S. Engstrom and E. Sabet, *J. Eur. Ceram. Soc.*, 2022, **42**(2), 658–671.

6 C. J. Bae, D. Kim and J. W. Halloran, *J. Eur. Ceram. Soc.*, 2019, **39**(2–3), 618–623.

7 H. Li, Y. S. Liu, Y. S. Liu, Q. F. Zeng and J. J. Liang, *J. Eur. Ceram. Soc.*, 2021, **41**(4), 2938–2947.

8 H. Li, K. H. Hu, Y. S. Liu, Z. G. Lu and J. J. Liang, *Scr. Mater.*, 2021, **194**, 113665.

9 H. Li, Y. S. Liu, P. Colombo, W. B. Li, Y. S. Liu, K. H. Hu and Z. G. Lu, *Ceram. Int.*, 2021, **47**(19), 27668–27676.

10 H. Li, Y. S. Liu, Y. S. Liu, Q. F. Zeng, K. H. Hu, Z. G. Lu, J. J. Liang and J. G. Li, *Ceram. Int.*, 2021, **47**(4), 4884–4894.

11 H. Li, Y. S. Liu, W. B. Li, Y. S. Liu and Q. F. Zeng, *Mater. Chem. Phys.*, 2021, **263**, 124443.

12 S. Y. Tang, L. Yang, X. W. Liu, G. J. Li, W. M. Jiang and Z. T. Fan, *J. Eur. Ceram. Soc.*, 2020, **40**(15), 5758–5766.

13 S. Y. Tang, L. Yang, G. J. Li, X. W. Liu and Z. T. Fan, *Addit. Manuf.*, 2019, **28**, 546–553.

14 S. Y. Tang, L. Yang, G. J. Li, X. W. Liu and Z. T. Fan, *Adv. Appl. Ceram.*, 2019, **118**(3), 145–152.

15 S. Y. Tang, Z. T. Fan, H. P. Zhao, L. Yang, F. C. Liu and X. W. Liu, *Int. J. Adv. Manuf. Technol.*, 2018, **96**, 3809–3819.

16 L. Yang, S. Y. Tang, G. J. Li, F. C. Liu, X. W. Liu, W. M. Jiang and Z. T. Fan, *Ceram. Int.*, 2019, **45**(6), 7681–7689.

17 L. Yang, S. Y. Tang, G. J. Li, L. Qian, J. K. Mei, W. M. Jiang and Z. T. Fan, *Ceram. Int.*, 2019, **45**(17), 21843–21850.

18 A. E. Alexander, N. Wake, L. Chepelev, P. Brantner, J. Ryan and K. C. Wang, *J. 3D Print. Med.*, 2021, **7**, 1–6.

19 K. L. Zhao, Z. H. Su, Z. J. Ye, W. X. Cao, J. Z. Pang, X. L. Wang, Z. C. Wang, X. C. Xu and J. Q. Zhu, *J. Mater. Res. Technol.*, 2023, **27**, 5449–5469.

20 J. A. Gonzalez, J. Mireles, Y. Lin and R. B. Wicker, *Ceram. Int.*, 2016, **42**(9), 10559–10564.

21 C. N. Sun, X. Y. Tian, L. Wang, Y. X. Liu, C. M. Wirth, J. Gunster, D. C. Li and Z. M. Jin, *Ceram. Int.*, 2017, **43**(1), 578–584.

22 P. Kunchala and K. Kappagantula, *Mater. Des.*, 2018, **155**, 443–450.

23 Y. H. Son, M. K. Kang and C. S. Lee, *Mater. Chem. Phys.*, 2019, **223**, 779–783.

24 H. P. Zhao, A. J. Wang, G. H. Li, Q. Hu, C. S. Ye, M. X. Shen, Y. L. Xiao, S. P. Liu and D. H. Ji, *Ceram. Int.*, 2022, **48**(22), 33580–33587.

25 Y. Bai and C. B. Williams, *Mater. Des.*, 2018, **147**, 146–156.

26 S. J. Huang, C. S. Ye, H. P. Zhao and Z. T. Fan, *Addit. Manuf.*, 2019, **29**, 100802.

27 T. T. Li, J. H. Zuo, C. Y. Tang and Y. X. Hu, *China Adhes.*, 2020, **12**, 13.

28 S. S. Siwal, K. Mishra, A. K. Saini, W. F. Alsanie, A. Kovalcik and V. K. Thakur, *J. Polym. Environ.*, 2022, **30**, 4501–4516.

29 X. Y. Lv, F. Ye, L. F. Cheng, S. W. Fan and Y. S. Liu, *Ceram. Int.*, 2019, **45**(10), 12609–12624.

30 S. Barui, S. Mandal and B. Basu, *Curr. Opin. Biomed. Eng.*, 2017, **2**, 116–123.

31 J. O. Marston, S. T. Thoroddsen, W. K. Ng and R. B. H. Tan, *Powder Technol.*, 2010, **203**(2), 223–236.

32 T. Colton and N. B. Crane, *Addit. Manuf.*, 2021, **37**, 101711.

33 W. Song, *Study on Domestic Maize Amylose Glass Fiber Infiltrating Agent*, Southwest University of Science and Technology, 2024.

34 C. H. Wang, Q. Zuo, L. J. Wang, B. X. Long, K. M. Salleh, N. I. S. Anuar and S. Zakaira, *Mater. Chem. Phys.*, 2021, **271**, 124969.

35 P. Zhou, Y. Y. Luo, Z. Lv, X. W. Sun, Y. Q. Tian and X. X. Zhang, *Int. J. Biol. Macromol.*, 2021, **183**, 1903–1910.

36 R. Tanwar, V. Gupta, P. Kumar, A. Kumar, S. Singh and K. K. Gaikwad, *Int. J. Biol. Macromol.*, 2021, **185**, 451–461.

37 H. P. Zhao, *Study on the Key Technology of Rapid Forming Casting Molds and Cores by Micro-jetting and Bonding*, Huazhong University of Science and Technology, 2015.

38 Q. M. Zhong, *Study of Ready-To-Use 3D Printed Sodium Alginate Blended Gels*, Wuhan Polytechnic University, 2023.

39 J. E. Fromm, *IBM J. Res. Dev.*, 1984, **28**(3), 322–333.

40 N. Reis and B. Derby, *MRS Online Proc. Libr.*, 2000, **625**, 117.

41 G. D. Martin, S. D. Hoath and I. M. Hutchings, *J. Phys.: Conf. Ser.*, 2008, **105**(1), 012001.