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Synthesis and Optimization of Fluid Properties of 3D-Printed Modified Chitosan Biopolymer Composite Membranes †

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Abstract: The study investigates the synthesis and optimization of modified chitosan-silver nanoparticles-graphene oxide (CS/AgNP/GO) composite ink's chemical and physical properties using inkjet 3D printing technology with the incorporation of polyvinyl alcohol (PVA) as a plasticizer. The variation in the concentration of PVA co-solvent affected drop ejection from the nozzle orifice. An increase in the PVA mole fraction minimized the entanglement within the CS molecular structure, improved flow rate, and subsequently formed spherical ink droplets on the substrate at 1140.0 Kg/m^3 (density), 0.00748 Pas (viscosity), and 55.6 mN/m (surface tension), indicating that the solvent was responsible for lowering the rheological properties of the composite membranes. The optimized drop velocity was achieved at 1.8 m/s, which also yielded adequate drop formation void of ligament. Therefore, it is very essential to adhere to the printer's ink specifications in order to formulate appropriate generic modified CS ink with an acceptable minimum fluid drop velocity to ensure quality inkjet-printed biopolymer composite membranes for different industrial applications.

Keywords: polymer synthesis; modified chitosan; rheological properties; 3D printing

1. Introduction

In the field of membrane technology, particularly in cases where intricate designs are required, the pursuit of enhancing material synthesis and improving performance has been a prominent focus. The mechanical integrity of membranes fabricated using 3D printing is compromised when subjected to high levels of stress. The drop-on-demand (DOD) piezoelectric inkjet printing process is influenced by many factors, including the driving electrical signal, the formulation of ink qualities such as viscosity, density, surface tension, and the interactions between the printing fluid, air, and substrate [1,2]. In order to ensure the successful synthesis of membranes, it is often necessary to use a meticulously developed and intricate control system. This is due to the fact that inkjet printing is highly susceptible to a multitude of variables, including fluid properties, printer configurations, and ambient conditions. The precise deposition of ink particles onto surfaces within a specified timeframe is a significant challenge in the context of inkjet printing, particularly when there is a high demand for the production of inkjet-printed products.

In the additive manufacturing process, it has become important to focus on optimizing fluid properties like density, volatility, thermal diffusivity, surface tension, and viscosity, as well as the shape and material properties of the substrate. The majority of inks do not consist only of pure liquids. Rather, they are composed of many liquids that possess diverse material properties, including pigments, colloidal particles, latex, cross-linkers, surfactants, and polymers. Effective control of printing settings is crucial when dealing with pigments that have complex compositions.

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This work aimed to identify the optimal physicochemical properties of CS/AgNP/GO ink modified with PVA, for inkjet printing of membrane composites.

2. Materials and Methods

The modified CS composite fluid was produced using the following procedures: Initially, the production of GO was via modified iteration of the Hummer and Offeman process [3]. On the other hand, the synthesis of AgNP involved a modified version of the Tollens' method in which trisodium citrate ($C_6H_8O_7Na$) directly reduced silver nitrate ($AgNO_3$) in the presence of a GO solution [4]. Subsequently, a 1% CS solution was prepared by dissolving 2 g of CS powder in 200 milliliters of distilled water supplemented with 1% acetic acid. The resulting mixture was subjected to continuous stirring for 24 h at ambient temperature. The neutralization of acetic acid (HAc) was achieved by adding 0.5 mL of a 2% (*w*/*v*) sodium hydroxide (NaOH) solution to the reaction mixture. In order to achieve comprehensive degassing, the reaction was subjected to further stirring and then allowed to remain undisturbed for duration of twenty-four hours. The PVA polymer powder was then dissolved in deionized water at a temperature of 40 °C for duration of two hours while maintaining continuous agitation to achieve complete dissolution of the solvent. An aqueous solution of polyvinyl alcohol (PVA) was prepared, having a concentration of 1 wt%.

Three different samples of modified CS composites were prepared according to the following proportions: S1 (CS 85.0% wt., PVA 13.2% wt., AgNP/GO 1.8% wt.); S2 (CS 84.0% wt., PVA 15.2% wt., AgNP/GO 1.8% wt.); and S3 (CS 81.0% wt., PVA 17.2% wt., AgNP/GO 1.8 wt.). In order to ensure that the membranes had an adequate degree of mechanical strength, the weight ratios described earlier were used for the purpose of this experiment [5]. To ensure compatibility with the Z-Corp 310 inkjet printer and to prevent printhead clogging, a solution consisting of 20% deionized water was included in the reaction mixer. An inkjet printer model (Z-corporation 310 USA) which utilizes a HP10 inkjet printhead was used for the fabrication of membrane samples. The fluid parameters used in this work were determined based on the established rheological properties of the ink [6].

3. Results and Discussion

3.1. Influence of Physical Properties on Membrane Printability

The physical parameters of the modified CS composites were estimated using the minimum drop velocity (V_{min}), Reynolds number (*Re*), Weber number (*We*), Ohnesorge number (*Oh*), and Laplace number (*Z*), which are well-established non-dimensional elements as denoted in Equations (1)–(5).

$$\text{Minimum drop velocity } (V_{min}) = \left(\frac{4y}{\rho d}\right) ½ \quad (1)$$

$$\text{Reynolds number } (Re) = \frac{\rho v d}{\eta} \quad (2)$$

$$\text{Weber number } (We) = \frac{\rho d V^2}{\gamma} \quad (3)$$

$$\text{Ohnesorge number } (Oh) = \frac{\sqrt{We}}{Re} \quad (4)$$

$$\text{Inverse Ohnesorge number } (Z) = \frac{1}{Oh} \quad (5)$$

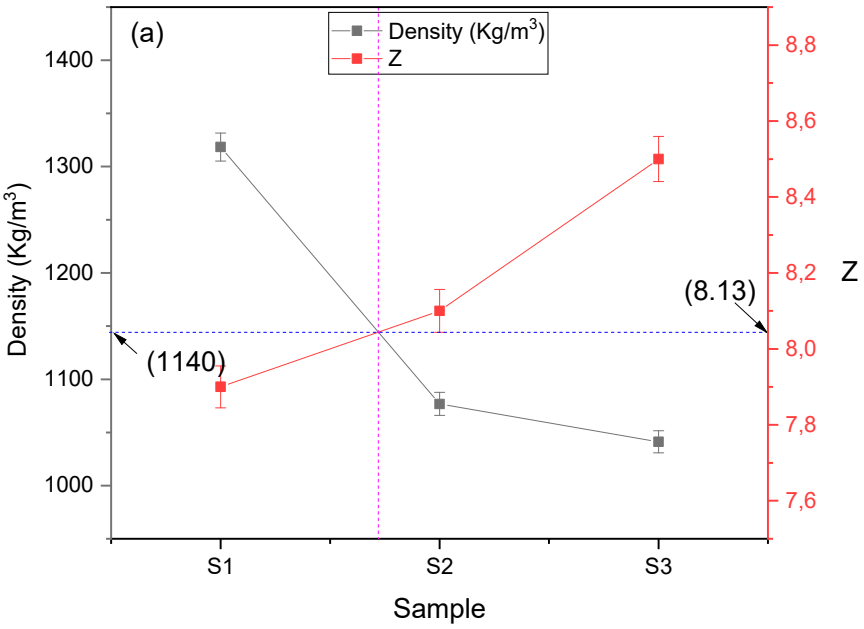
In this context, the variable v represents the velocity at which the droplet falls, d denotes nozzle diameter, η is the dynamic viscosity obtained under conditions of low shear, ρ represents the density of the fluid, and y signifies the surface tension of the fluid samples.

In order to assess the effects of varying PVA concentrations on the printability of the chitosan matrix, the physical properties of the CS/AgNP/GO composite are summarized in Table 1.

Table 1. Physical properties of modified CS generic ink.

Sample	ρ (kg/m³)	γ (mN/m)	η (Pas)	*Re*	*We*	*Oh*	*Z*
S1	1318.41 ± 0.2	57.61 ± 0.4	0.0086 ± 0.05	18.40 ± 0.1	5.49 ± 0.3	0.127 ± 0.05	7.85 ± 0.12
S2	1076.85 ± 0.1	55.73 ± 0.3	0.0074 ± 0.07	17.46 ± 0.2	4.64 ± 0.3	0.123 ± 0.04	8.11 ± 0.09
S3	1041.23 ± 0.3	54.24 ± 0.4	0.0068 ± 0.06	18.37 ± 0.4	4.61 ± 0.2	0.118 ± 0.06	8.50 ± 0.14

Figure 1a shows the changes of density and *Z* values. The membrane fluid density decreased from 1318.41 Kg/m³ to 1041.23 Kg/m³ as result of an increase in PVA concentration and a decrease in the mole percentage of CS. Furthermore, it is observed that increasing the mole ratio of polyvinyl alcohol (PVA) in the modified ink resulted to an elevation in the *Z* value from 7.85 to 8.50. The aforementioned numerical values are within the acceptable printing range for stable inkjet drop output, which is defined as $14 > Z > 4$ [7]. This could suggest that the modified CS ink exhibits superior printability properties.



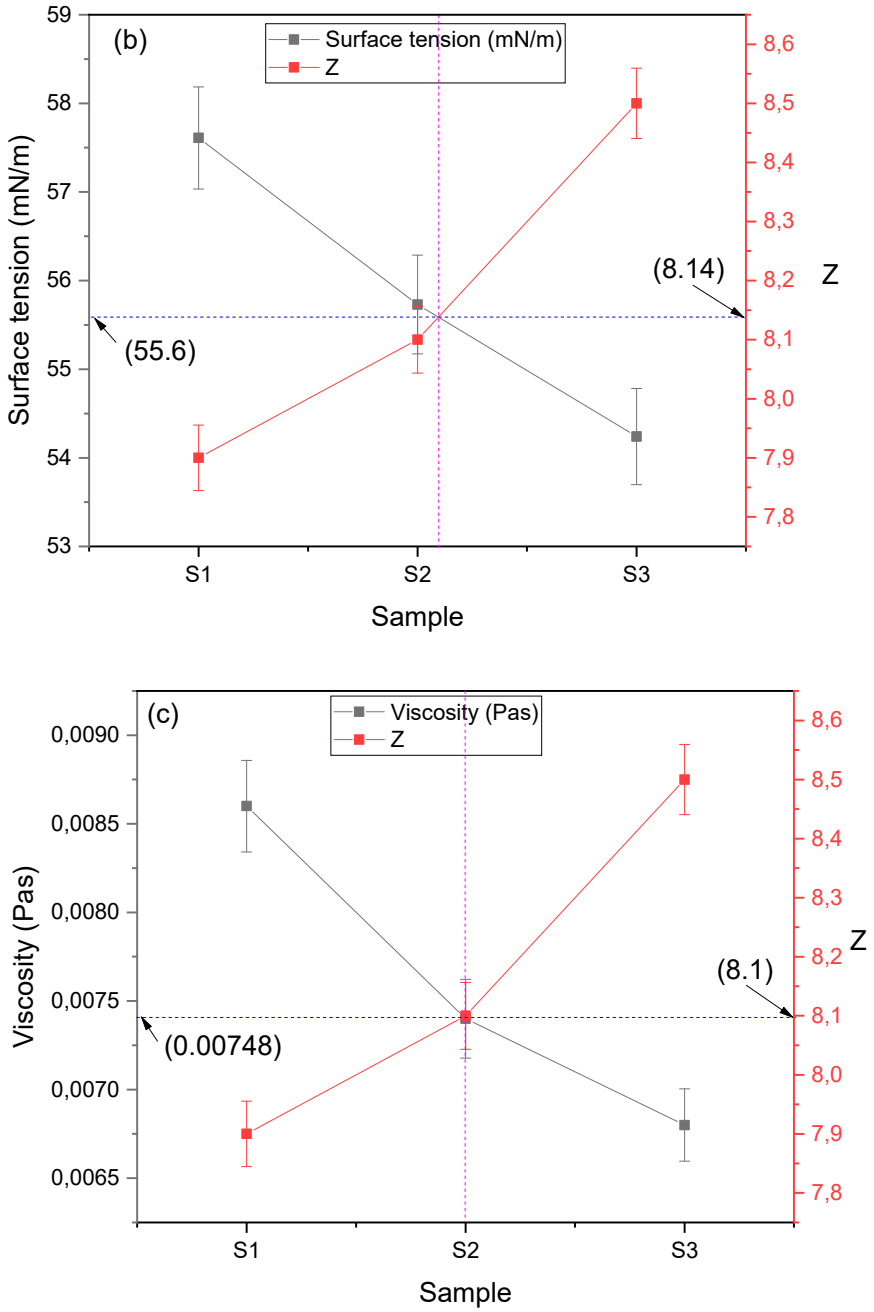


Figure 1. Optimization of modified CS physical properties.

Figure 1b illustrates the correlation between the *Z* value and surface tension of the modified CS fluid. The molecular structure of the original CS may have been disrupted and entangled due to the increased concentration of PVA in the composite ink. This led to an increase in *Z* values and a subsequent decrease in the surface tension of the membrane fluid. The composite exhibits optimal performance at *Z* value of 8.14 and surface tension of 56 mN/m.

Figure 1c shows the relationship between modified CS fluid viscosity and the *Z* printability parameter. The *Z* value also increased with reduction in CS mole fraction and increase in concentration of PVA. The optimal viscosity and *Z* printability values may be achieved when the viscosity is 0.00748 Pas and the *Z* printability value is 8.1 at the point of intersection. This observation implies that sample 2 would provide the most optimal printed composite. Consequently, if the viscosity of the modified CS solution is reduced to 0.0075 Pas, it may result in a decrease in resistance to fluid flow through the nozzle

orifice. However, this reduction in viscosity may also lead to the formation of satellite droplets, which may not be desirable in the context of membrane fabrication.

3.2. Surface structural and Elemental Analysis

The examination of the scanning electron microscopy (SEM) images was conducted in order to determine the impact of the physicochemical properties and drop velocity of the modified CS ink on its surface morphology. Figure 2a depicts the surface structure with a drop velocity of 1.8 m/s, while Figure 2b presents the surface image at a drop velocity of 2.6 m/s. Based on the discernible SEM image characteristics seen at the investigated drop velocities, it can be inferred that the structural appearance of the image generated at a velocity of 1.8 m/s is expected to exhibit a higher degree of surface smoothness compared to that printed at a velocity of 2.6 m/s. The surface structure at a velocity of 2.60 m/s exhibits more irregularity and lack of uniformity in its structural patterns, perhaps indicating erroneous droplet production. Hence, altering the drop velocity from 1.8 m/s may result in increased surface roughness of the membrane.

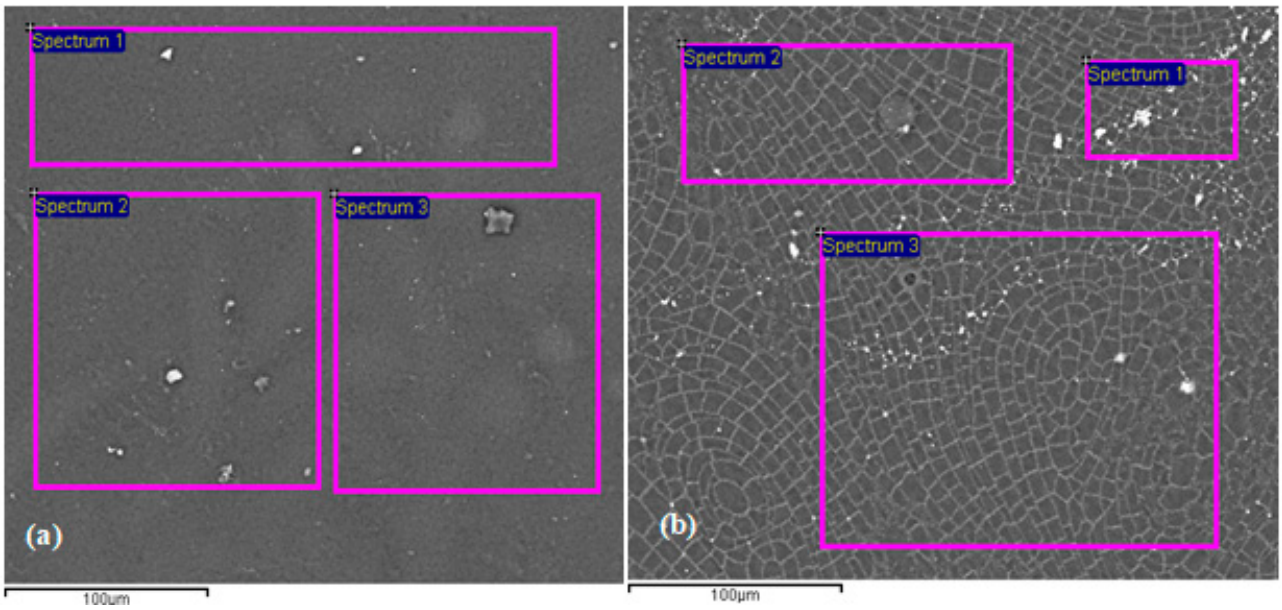


Figure 2. Surface structure analysis.

The elemental analysis of the modified chitosan composite structures is shown in Figure 3. Carbon constitutes major surface elements in both samples, subsequently followed by nitrogen (N) and oxygen (O), while sulfur (S) and silver (Ag) constitute minor elements found in both samples (a) and (b). However, there are traces of calcium ions in sample 'b', which could be due to chemical residue left during membrane preparation, or the presence of contamination on the membrane composite. Furthermore, the percentage weight composition of Ag in each sample is as follows: sample 'a', Spectrum 1 (1.44%), Spectrum 2 (0.27%), and Spectrum 3 (2.36%), respectively. Sample 'b' shows a reduced amount of Ag detected across the membrane surface as shown in Spectrum 1 (1.30%), Spectrum 2 (0.0%), and Spectrum 3 (0.29%). This probably suggests that sample 'a' might exhibit greater adhesive force to protect Ag ions within the modified composite because of its smoother surface structure.

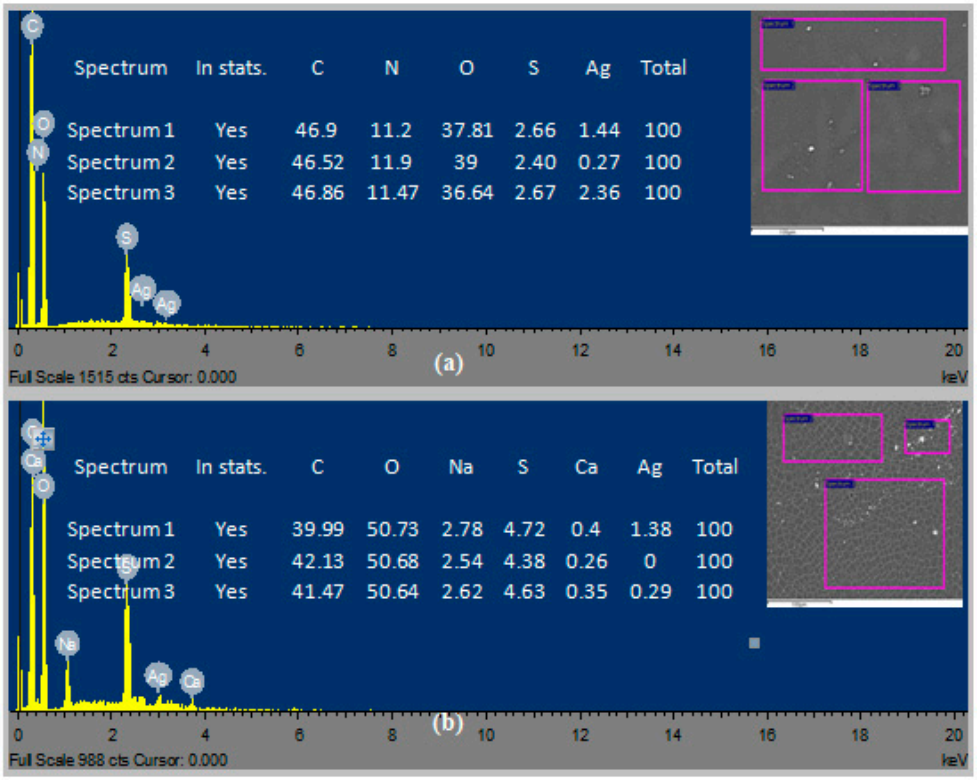


Figure 3. Elemental analysis.

3.3. Proposed Molecular Structures of the Modified CS Composite

The anticipated chemical structure of the enhanced CS composite is illustrated in Figure 4. The CS and graphene oxide (GO) structures could form covalent bonds with the citrate ligands derived from trisodium citrate used in AgNP synthesis. This interaction potentially increases the stability of silver ions (Ag^+) and improves antibacterial properties of the modified CS composite. Furthermore, carbonyl bond (C- O) could be formed between GO and CS molecules to enhance membrane stability. The formation of ionic interactions between Ag^+ ions and oxygen and hydroxide molecules has the potential to increase the antibacterial efficacy of the composite film. Moreover, an increased concentration of polyvinyl alcohol (PVA) will probably induce the formation of more hydrogen bonds between the hydroxyl (OH) and amino (NH_2) groups of chitosan-polyvinyl alcohol molecules. This process would possibly result in the reduction of the primary amino and acetyl groups within the chitosan (CS) chain, thereby facilitating the entrapment of silver particles inside the composite material.

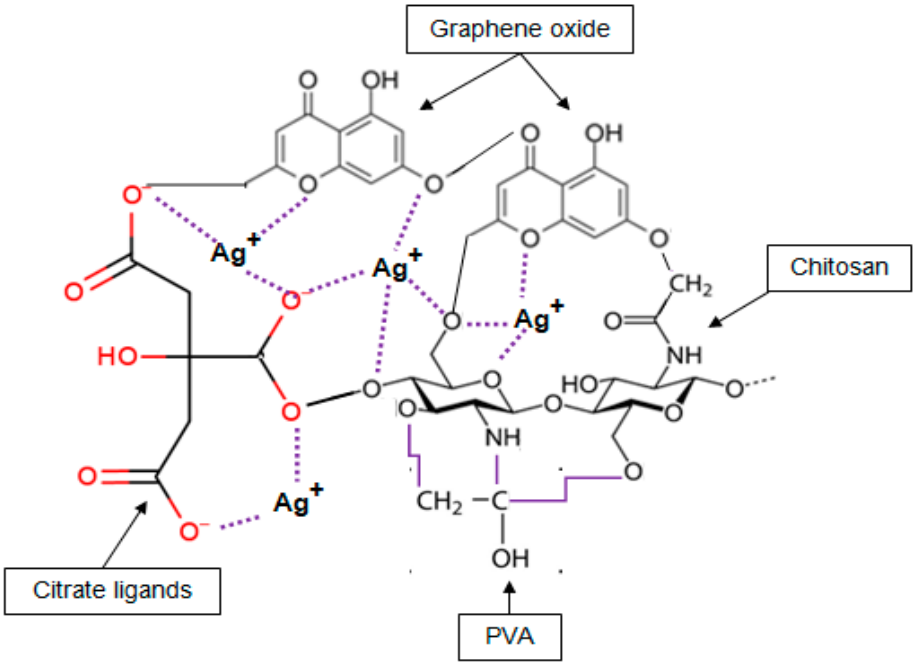


Figure 4. Possible chemical interactions.

4. Conclusions

The optimization of the physicochemical fluid properties of CS/AgNP/GO has been carefully outlined in this study to establish the influence of these characteristics on printability of the membrane composites. The rheological properties described herein were achieved by the appropriate integration of modified chitosan fluid composites, resulting in the creation of maximal droplets. An increase in polyvinyl alcohol (PVA) concentration at a drop velocity of 1.8 m/s resulted in the disruption of the molecular structure of the CS composite, leading to changes in its density, surface tension and viscosity. This alteration in the composite's properties facilitated the improvement of fluid flow. The presence of oxygen and O-H molecules in the composite fluids would increase as the mole fraction of PVA increased, resulting in a reduced need for kinetic energy to expel the ink from the nozzle orifice.

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