Characterization of 3D Printed Chitosan-GO-AgNP Composite for Surface Water Treatment

Anthony C. Ogazi*[1] and Peter O. Osifo[1]

***Abstract*—** This research focused on the characterization of additive manufactured Chitosan-graphene oxide-silver nanoparticles (CS-GO-AgNP) composite membranes for the purpose of surface water treatment. An increase in temperature affected the molecular strength of hydrogen, amides, and epoxy bonds, thereby diminishing the viscosity and shear stress of the modified CS fluids. The XRD diffraction analysis indicated a broad peak at 2θ 20.1°, attributed to enhanced interfacial bond interactions, while the FT-IR analysis verified the existence of a carbonyl group within the polymer matrix. The structural morphology of the CS/AgNP/GO exhibited varying layer thicknesses, with different elemental composition primarily consisting of Carbon (64%), Nitrogen (19.1%), Oxygen (15%), and Silver (1.69%) respectively.

***Keywords*—** 3DP, Modified-chitosan, rheological analysis, surface morphology

I. INTRODUCTION

Three-dimensional printing (3DP) is replacing traditional technologies in various industrial operations and has the capacity to manufacture sophisticated membrane materials. 3DP is a computer-aided design (CAD) additive manufacturing (AM) technique [1-2]. The capacity of 3D printing technology to generate prototypes with intricate shapes and substantial aesthetic appeal has prompted numerous manufacturing companies that previously relied on conventional fabrication methods to implement it [3]. 3DP is employed in a variety of sectors, including the biomedical, marine, educational, and engineering sectors. The applications of additive manufacturing have been previously investigated by researchers. Femmer et al. [4] utilized a digital light processing printer to create sophisticated polydimethylsiloxane (PDMS) membranes for liquid-gas contactors. Ogazi and Osifo [5] employed an inkjet printer to create hybrid modified Chitosan thin film composite membranes. The technology enabled the production of polyamide composites of superior quality in comparison to conventional fabrication methods.

It is imperative to conduct rheological characterization during the formulation of 3D inkjet ink to ensure the effective formation of drops. The ink's reliability is contingent upon the precise alignment of its fluid characteristics with the print-head specifications and its rheological properties. Drop size, drop velocity, satellite formation, droplet morphology upon contact, and the final morphology of polymer inkjet-printed films are all substantially influenced by viscosity and surface tension. The morphology of polymer inkjet-printed films is significantly influenced by the molecular weight, concentration, polymer structure, and solvent used in ink formulation. The formulation of ink must effectively address the wetting and drying behaviors on the substrate, functional performance, and jetting and drop formation. These components are difficult to achieve while maintaining a homogenous layer during the drying process.

Therefore, the rheological flow properties of the modified CS ink and morphology of the 3D-printed membranes are characterized in this study, which employs DMAc as a co-solvent to enhance of the plasticity of the composite structure.

II. METHODS

A. Modified Chitosan ink formulation process

The modified CS ink was formulated using standard procedure. Briefly, one gram of chitosan was dissolved in a 1% acetic acid aqueous solution at room temperature and stirred uniformly for 60 minutes. To neutralize the acetic acid, 0.5 ml of 2 percent (w/v) sodium hydroxide was added to the mixture. The reaction was stirred for an extended period and allowed to rest for 24 hours to facilitate the degassing of air bubbles. Subsequently, 0.5 ml of a 10 w/w% AgNP-GO aqueous solution was incorporated into 80 ml of CS solution and stirred for one hour. At room temperature, the resulting solution was reacted with 120 ml of a 0.5% isopropyl alcohol aqueous solution and stirred for one hour. The pH of the solution was adjusted to 7 using a buffer solution to prevent damage to the printer print head.

B. Fabrication of CS-GO-AgNP

The modified CS polymer was printed by A1630 UV drop-on-demand piezoelectric inkjet print head (Colorsun China) flatbed inkjet printer. The CS nanocomposite membranes were fabricated through the application of different layers of the modified CS ink solution. To ensure proper drop formation with a circular membrane diameter of 70 mm and a thickness of 10 µm, the drop spacing was established at 8 µm. This configuration facilitated adequate drop overlap and mitigated the evaporation of composite fluid samples prior to UV irradiation of the membrane fluid.

III. RESULTS AND DISCUSSION

A. Rheological characteristics of modified CS inks

A rotational rheometer, Physica-MCR 301, Anton Paar, Graz, Austria, was employed to assess the rheological behavior

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(dynamic viscosity and shear stress) of the modified CS fluid at 20 °C and 40 °C under increased shear conditions. Figure 1(a-b) illustrates the changes in dynamic viscosity, shear stress, and the associated shear rates at CS:DMAc ratios of (85:15)% and (81:19)%, with a constant amount of GO/AgNP (0.5 mg). Thus, increasing the shear rate indicates that the viscosity of the modified CS fluid remained relatively constant, suggesting that the ink behaves as a Newtonian fluid, consistent with findings from prior studies [6-7].

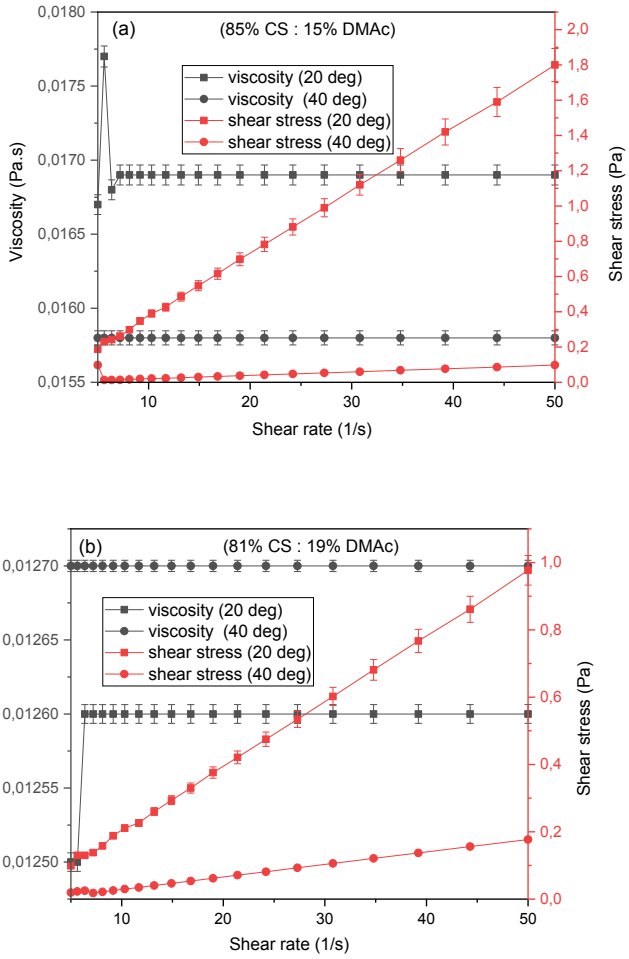


Fig. 1 (a-b): Rheological behavior of the chitosan ink

The viscosity of the prepared ink samples decreased with an increase in DMAc concentration and a decrease in the mole fraction of CS. This indicates that the addition of the co-solvent to the CS matrix reduces both the dynamic viscosity and shear stress of the modified chitosan ink. The shear stress and dynamic viscosity of the fluid composite at 20°C were higher than those at 40°C, which decreased with increasing temperature. This may suggest that an increase in temperature may reduce interfacial molecular strength, thereby impacting the viscosity and shear stress of the modified chitosan fluids.

B. XRD Analysis of modified CS composites

Figure 2 displays the XRD patterns of the modified CS/AgNP/GO composite. The broad peak diffractions happen mostly before the Bragg angle (2°) of 30.0°, which is where the 110 Ag crystal planes are located. The diffraction spectra displayed a large peak at 2θ 20.1°, presumably resulting from intensified hydrogen bond interactions within the CS polymer matrix. Two separate diffraction peaks are detected at 2θ 24.7° and 27.1°, indicating an improved contact between AgNP and the carbonyl groups of CS-GO-DMAc. This interaction could enhance the intermolecular hydrogen bonding among the modified chitosan molecules.

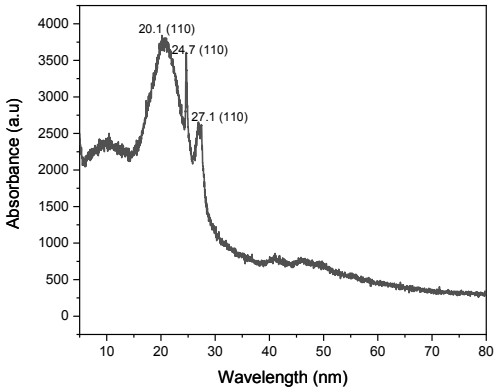


Fig. 2: XRD patterns of the modified CS/AgNP/GO composite

C. FT-IR analysis

The FT-IR spectrum of the modified CS composite illustrated in Figure 3 showed a broad and strong peak for the O-H bond between 3450 and 3240 cm^{-1}, which was used to identify the functional groups in the modified CS printed membrane sample. It's likely that this peak is caused by hydrogen bonds and overlapping areas of O-H in hydroxyl groups, as well as N-H stretching at 2090 cm^{-1} in amino groups. The sample exhibited isolated peaks at 1534, 1383, and 1307 cm^{-1}, indicating the potential presence of nitrogen compounds (N-O), alkanes (C-H), and sulfur oxides (S=O) bonds. The peaks at 899 and 692 cm indicate the asymmetric stretching and C-H bending of aliphatic –C=C- conjugated alkenes. There may be a carbonyl group in the CS-GO/AgNP mixtures because of the band at 1071 cm^{-1}. This band is linked to the stretching of the C=O bond in the primary alcohol.

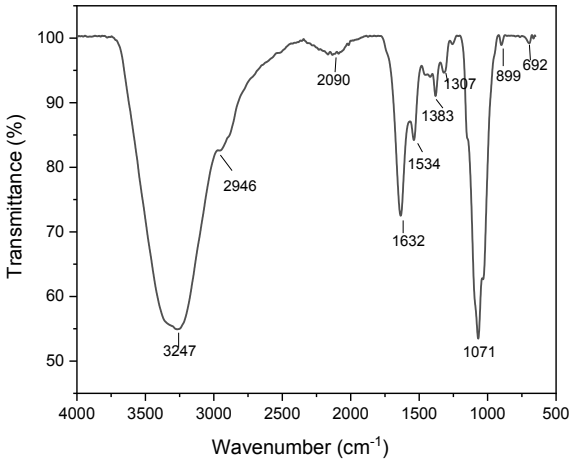


Fig. 3**:** FT-IR spectrum of the modified CS composite

D.Surface morphology and elemental analysis

The surface morphology of the modified CS membrane is shown in Figure 4, which reveals a fairly irregular and sponge-like surface layer thickness, indicating that the film was not formed uniformly. This attribute could suggest various stages of drop generation during the printing process via layer-by-layer interfacial polymerization. According to literature reports, 3D-printed membranes have variable surface roughness and can improve transport performance while reducing fouling and enhancing the functionality of the polymer composite, unlike the conventional membranes, which generally have smooth surface morphologies [9-10]. Furthermore, it is possible that the hydroxyl and amino functional groups from CS-DMAc responsible for primary chemical bonding within the polymer structure could influence the morphology of the polymer, retain a high membrane surface area, and prevent the collapse of the membrane structural network.

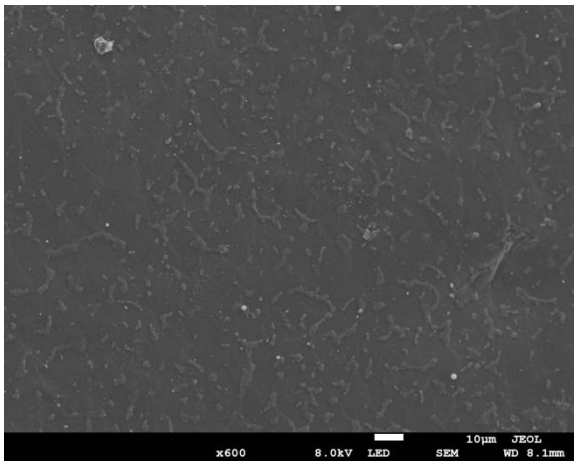


Fig. 4: SEM image of modified CS membrane

The elemental composition of the modified 3D-printed CS was determined using EDS analysis. The principal constituents detected on the membrane's surface include oxygen (15%), nitrogen (19.1%), carbon (64%), and silver (1.69 %). Other trace elements are sulfur (0.2 %) and silicon (0.09 %), respectively. The presence of impurities such as H_2 SO_4 and SiO_2 during ink formulation or post-treatment process could be responsible for the existence of these traced elements.

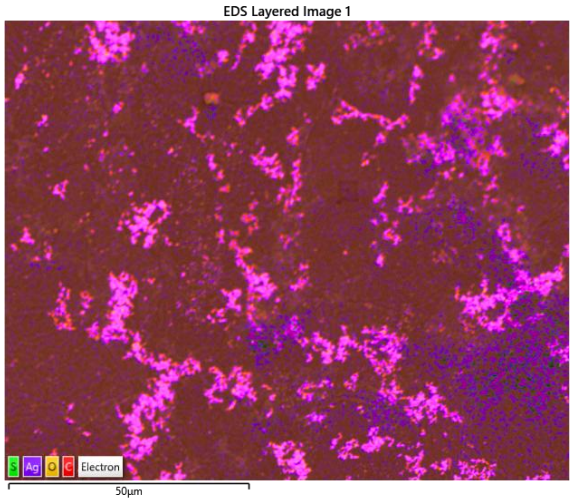
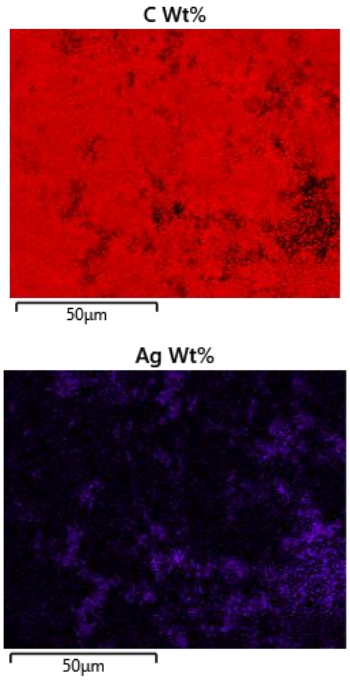


Fig. 5(a): Modified CS surface-layered image structure

The modified CS printed membrane composite's surface-layered image structure is illustrated in Figure 5 (a-b). It illustrates the manner in which the composite membrane's surface is structured with respect to the various strata of elements. In addition, the composite exhibited a variety of elements in the structural layer on the surface, including silver (Ag), carbon (C), oxygen (O), and trace quantities of sulfur (S) identified using different color notations on the membrane surface. Asymmetrical distribution of Ag across the surface of the modified CS membrane is indicated by the dispersed blue colors. As a result, regions with a larger intensity of blue colors would suggest a higher concentration of AgNP with possible superior membrane antimicrobial performance.



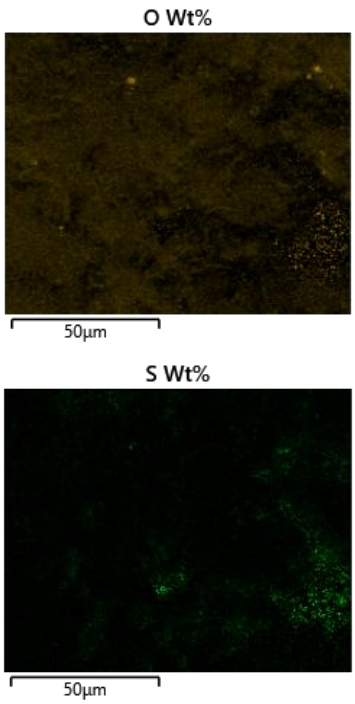


Fig. 5 (b): Modified CS composite elements

IV. CONCLUSION

The rheological and surface characterization of the 3D-printed chitosan-GO-AgNP composite membrane was addressed in this study. The viscosity and shear stress of the modified CS composite decreased with an increase in temperature but improved with an increase in the concentration of GO and DMAc within the polymer matrix due to stronger hydrogen bond attraction. The CS/AgNP/GO composite had different levels of layer thickness, which showed that the polymer film was not formed evenly. This was because of different stages of drop generation during the 3D printing process, which caused interfacial polymerization to happen layer by layer. Carbon, nitrogen, and oxygen were the main elements found on the membrane's surface. Silver was found as a minor element, and sulfur and silicon detected as trace elements because of impurities from the membrane's preparation or post-treatment process. Hence, absolute caution is required to ensure high purity of the printed modified CS membrane.

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