Morphological, structural, mechanical and antibacterial behavior of chitosan/PVA polymeric blends reinforced with silver nanoparticles

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Chitosan (CS) is a biodegradable polymer derived from natural sources. It is a randomly distributed linear polysaccharide. The study examined the characteristics and antibacterial effectiveness of a Chitosan/PVA blend by a ratio of 90:10 sample that is strengthened with silver nanoparticles (Ag NPs) in various amounts (0.5%, 1%, 1.5%, 2%, and 2.5% by weight). The sample is manufactured using the solution casting method. The prepared samples underwent analysis utilizing a differential scanning calorimeter (DSC), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and mechanical testing, specifically a tensile test. The establishment of a blend is indicated by changes in the energy levels and reductions in the intensities of specific FTIR bands. The antimicrobial efficacy of the mixtures generated in varying amounts is assessed using the near-maximum inhibitory concentration approach against Escherichia coli and staphylococci. The scanning electron microscope (SEM) images exhibit a high level of clarity. Silver nanoparticles (Ag NPs) are evenly dispersed throughout the polymer and are integrated. Entirely contained within the polymer. The stress-strain curves of the samples containing a mixture of Ag NPs-reinforced chitosan and PVA demonstrate an increase in hardness. The DSC analysis reveals a marginal reduction in the temperature at which the polymer decomposes. The antibacterial activity is assessed by measuring the inhibition at a concentration of 2.5%. The mixture exhibited greater efficiency against gram-negative bacteria (Escherichia coli (E)) than gram-positive bacteria (S.aureus (s)). The aim of this work to create novel polymeric composites with good mechanical properties that are appropriate for various environmental impacts and are based on chitosan/PVA polymeric blends and silver nanoparticles. It also evaluates the mechanical characteristics and antibacterial behavior of the composites as well as the prospects of employing materials in medical applications.

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1. INTRODUCTION

Chitosan (CS) is a biodegradable polymer derived from natural sources [1]. It is a polysaccharide that is arranged in a straight line and has a random distribution. The structure is derived from cellulose, where the hydroxyl group at position C-2 is substituted with an acetamido group (C2H4NO) [2]. Chitosan is an alkaline deacetylated product. N deacetylation of chitin refers to the process of removing acetyl groups from chitin, which is a poly-amino-saccharide. Chitin is a cationic natural functional biopolymer that consists of a repeating structural unit known as β-(1-4)-2-acetamido-2-deoxy-D-glucopyranose. The user's text is [3]. Chitosan bears a close resemblance to cellulose, consisting of a single glucose monomer [4]. Chitosan exhibits solubility in acidic solutions as a result of the presence of its amino group (-NH2). Also, hydrogen bonding act as a stabilizer for the network in the solid phase and increases its mechanical properties [5]. Chitosan has a wide-ranging of uses, counting fine filtration and wastewater treatment. It is particularly in effect in adsorbing microbial populations and removing metals in solutions that are close to neutral [6]. Moreover, chitosan is active in various biomedical applications due to its inherent source capacity to break down naturally compatibility with living organisms, lack of toxicity, and ability to combat microbial growth. It is used for the prevention of wound infections, delivery of drugs, encapsulation of drugs, dressing of wounds, and as scaffolds for the regeneration of bones and nerves [7]. In addition, chitosan derived from blends is utilized as an antibacterial agent in food packaging [8]. Chitosan possesses several reactive amino side groups, which present opportunities for chemical changes, the creation of a wide range of valuable derivatives, or the production of novel blends through ionic interactions [9]. Polyvinyl alcohol (PVA) is a significant polymer. Polyvinyl alcohol (PVA) exhibits a semi-crystalline structure as a result of the hydrogen bonding present. Polyvinyl alcohol (PVA) is widely used in civil engineering and architectural materials due to its exceptional Young's modulus and cost-effectiveness. However, the breaking strength of PVA is not enough to meet the demands of engineering applications. Therefore, it is crucial to enhance the qualities of PVA, such as increasing its Young's modulus. Additionally, PVA's structure contains many functional groups that can performance as a source of hydrogen bonding, therefore easing the creation of polymer blends. Due to its non-toxic nature, high water solubility, and capacity to form films, it is simply able to connect with doping substances. Silver nanoparticles are highly intriguing since to their distinctive characteristics that including conductivity, stability, catalytic activity, and antibacterial capabilities. Silver and silver-based compounds are applied for their antibacterial properties against a diverse selection of pathogens that including bacteria and fungi [12]. Silver nanoparticles are active in several fields as an antibacterial agent that effectively targeting a broad spectrum of microorganisms including bacteria, fungus, and protozoa. Jung et al. (2018) [13] synthesised papers containing chitosan:starch-silver nanoparticles at different ratios for the purpose of creating antimicrobial packaging. Nanoparticles that are spherical in shape and have an average diameter of 7 nm. The impact of the Cht:St-Ag NPs ratio on both the mechanical characteristics and antibacterial activity is investigated. The 90:10 wt % ratio demonstrated superior mechanical performance and antibacterial activity, making it suitable for use in antimicrobial packaging applications.Kim et al. (2022) [14] pre-pared from Ce(NO3)36H2O, AgNO3, and NH4OH with different molar ratios through a hydro their mal process, and then are completed by carrying out the precursor calcing at 750°C for 2 hinder air atmosphere. Below 1% of Ag concentration in Ag/CeO2nanocomposites, the Ag crystalline structure does not appear. XRD and TEM results show evidence of two different effects (the agglomeration and the barrier effects) governing the process of crystal growth.HR-TEM image and EDX elemental analysis of the Ag/CeO^2 nanocomposite confirmed that isolated Ag nanocrystals are dispersed in the CeO$_2$ matrix. These results are of great significance for the control of microstructure, crystallinity, and applications for the development of nanocomposite materials. Mahmood & Jawad (2019) [15] the impartial of this study is to investigate the influence of weight ratio on the structural properties of the chitosan/PEO polymer. This is attained through the use of XRD and FTIR measurements. Furthermore, the study aimed to determine the

optimal ratio that would result in the maximum mechanical and antibacterial capabilities of the chitosan : PEO mix. The blend is formed using the forming process. The optimal mechanical characteristics are observed at a PEO ratio of 15%. The study exposed that the most effective suppression of bacteria occurred with PEO ratio of 15%. The blend exhibits reduced efficacy against Gram-positive bacteria, specifically Staphylococcus aureus. The sample with the best combination of mechanical properties is enhanced with several concentrations (1, 2, 3, 4, and 5wt %) of silver nanoparticles (Ag NPs) to assess their impact on the structure and antibacterial capabilities.

2. MATERIALS AND METHODS

Chitosan $(C_6H_{11}NO_4)n$ has a medium molecular weight chitosan, 190-310 kDa and Poly vinyl alcohol (PVA) $[C_2H_4O]$ n, average molecular weight of 100kDa. They are purchased from Sigma-Aldrich Company. Chitosan/PVA blend with different PVA weight ratios (10wt%) chitosan (90wt%) the samples are fabricated using the solution casting technique. The specified amount of chitosan is dissolved in 50ml of acetic acid (1% concentration) for each of the samples. This is done in a glass flask at room temperature using a magnetic stirrer. The chitosan is added gradually until it is entirely dissolved. The PVA polymers are dissolved in 2ml of distilled water in a small glass container using a magnetic stirrer at room temperature. The polymers are gradually added drop by drop to the prepared chitosan, while continuously mixing, until the sample material is fully mixed and then reinforced by add silver nanoparticles (Ag NPs) as indicated in Table 1. After calculating each sample's reinforcing ratio separately, based on the specified matrix. The addition is performed incrementally while continuously agitating with magnetic stirrer for a duration of thirty minutes following each addition. Various testing required the usage of Teflon molds in varied shapes.

Table 1 Ratios and components weights of blends samples and its nanocomposites.

Sample	Chitosan wt%	PVA wt %	Ag NPs wt%	Chitosan weight (g)	PVA weight (g)	Ag NPs weight (g)
A0	90	10	0	1.35	0.15	0
A1	89.5	10	0.5	1.3435	0.15	0.0065
A2	89	10	1	1.337	0.15	0.0130
A3	88.5	10	1.5	1.3305	0.15	0.0195
A4	88	10	2	1.324	0.15	0.0260
A5	87.5	10	2.5	1.3175	0.15	0.0325

3. RESULT AND METHODS

FTIR spectroscopy is a tool to identify the variation present in organic and inorganic compounds bands in the sample. Depending on the infrared absorption frequency range 400–4000 cm^{-1}, the specific molecular groups prevailing in a sample, the interaction bands between components of blends and the variation in these bands are determined. Figure 1 shows the comparison between FTIR spectroscopy patterns for chitosan/PVA at a 90:10 blend ratio reinforced with Ag NPs at different ratios. Where the patterns appeared for the PVA aggregates. A wide band appeared at 3440 cm^{-1}. This group appeared compatible with hydroxyl. CH$_2$ vibrating aggregates appeared at 2927 cm^{-1} and 2865 cm^{-1}, respectively. This group corresponding to symmetric and asymmetric expansion. The same characteristic bands are observed in all samples, with some variation. These interactions show that their energy gradually decreased with an increase in the proportion of Ag NPs, and we also note that their intensity increased relatively. The increase by adding the percentage of Ag NPs led to an expansion in the range of 1490 cm^{-1}, which confirms the interaction between the superimposed and the added nanoparticles (Ag NPs). The methylene group arose at 1115 cm^{-1} and expanded to 1160 cm^{-1}.

This group is the appearance of C-O, while at 1455.89 cm^{-1} the appearance of C-H. This is the effect of adding nanoparticles, which led to a decrease in some aggregates and an increase in others. The data showed a decrease in the expansion peaks and expansion, which confirms the addition of nanoparticles, when adding Ag NPs and increasing the percentage of their addition leads to a decrease in intensity. Kalaivani et al 2018 [16], explained in their study that by adding nanoparticles, significant changes occurred, decreasing the intensity and causing a slight shift in the peak.
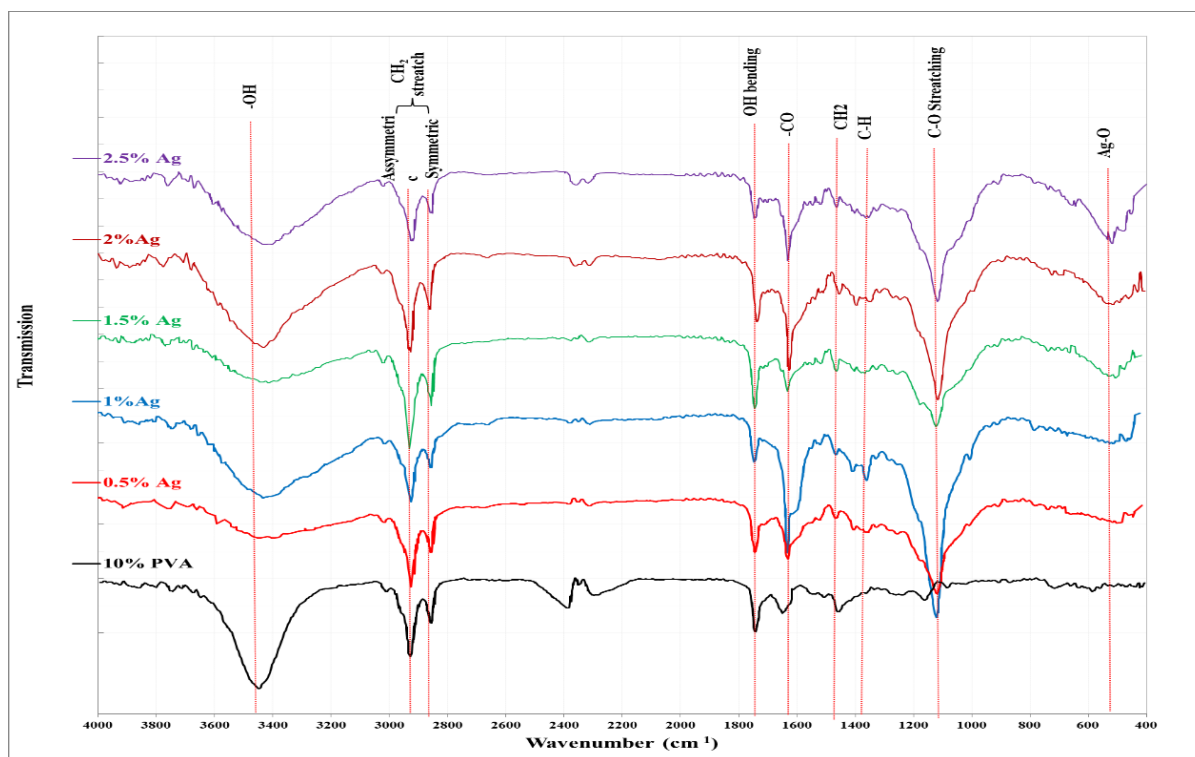

Figure 1 FTIR spectra for Chitosan/PVA at 90:10 blend ratio reinforced with different Ag NPs ratios.

The surface morphology of the chitosan/PVA blend sample reinforced with 1%wt Ag NPs is examined by SEM, as depicted in Figure 2. In the enhanced specimen, the Ag NPs are evenly dispersed at a concentration of 1% within the polymer and fully embedded within its. The chains of the polymer are interconnected by the Ag NPs, resulting in a network of large molecules. As a result, the blend appears more densely packed compared to the polymer blend without reinforcement. The inclusion of these additional bonds inside the polymer network restricts the extension of the chains and diminishes the elasticity of the sample [17].
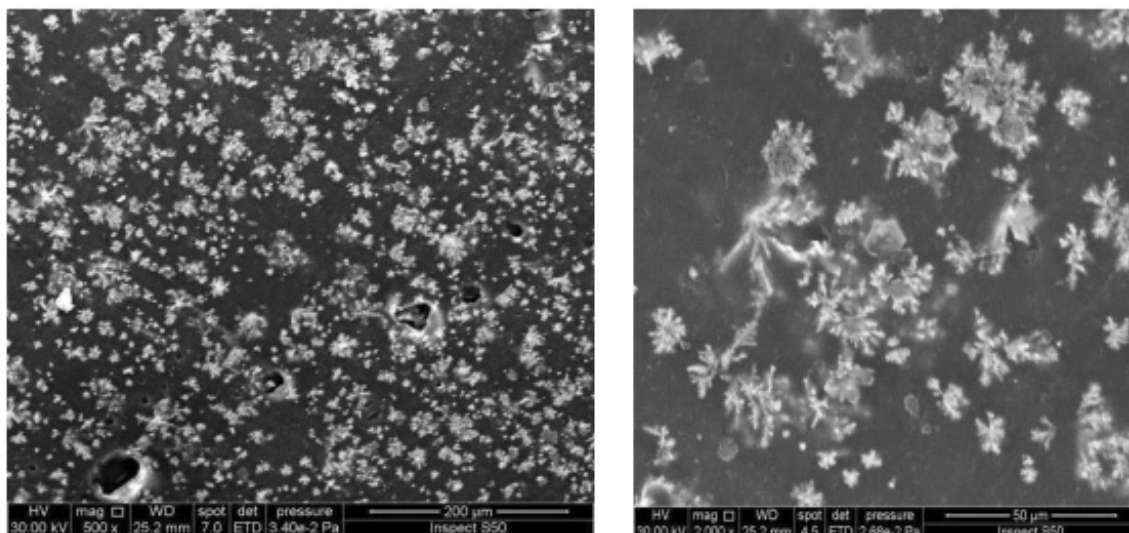
Figure 2 SEM images for Chitosan/PVA (90:10) blend reinforced with 1%wt of Ag NPs.

Figure 3 display the DSC curve of chitosan/PVA blend at 90:10ratio reinforced with different Ag NPs ratios (0.5, 1, 1.5, 2, and 2.5) %. at temperature range from room temperature to 400 °C with heating rate of 10 °C /min. There is a slight decrease in the temperature of the polymer degradation, with an increase in the percentage of addition of silver nanoparticles, while the melting temperature, corresponding to PVA constant chitosan has exhibited thermal stability up to 240 °C upon mixed with Ag NPs in different proportions. Therefore, no thermal decomposition occurred before this temperature and hence the mass change is very slight. After the temperature reaches more than 240 °C, the blend begins to decompose. However, the DSC curve started to rise at the onset point at 245 °C, with a maximum of exothermic peak appearing at 275°C. The decomposition of chitosan is in 2 steps. Approximately 40% of chitosan is lost in the first step, then another 8% is reduced from its mass. The chitosan decomposition this agrees with several previous studies [18]. Also, it is noted from Figure 3 that the thermal decomposition of the mixture increases with increasing proportions of added Ag NPs ratios from 0.5% to 1%, as the added Ag NPs increased the thermal stability of the mixture then its begin to decrease with increasing Ag NPs ratios from 1.5% to 2.5%. Here the Ag NPs particles act as catalysts, which reduces the activation energy, which leads to less of the thermal deterioration.
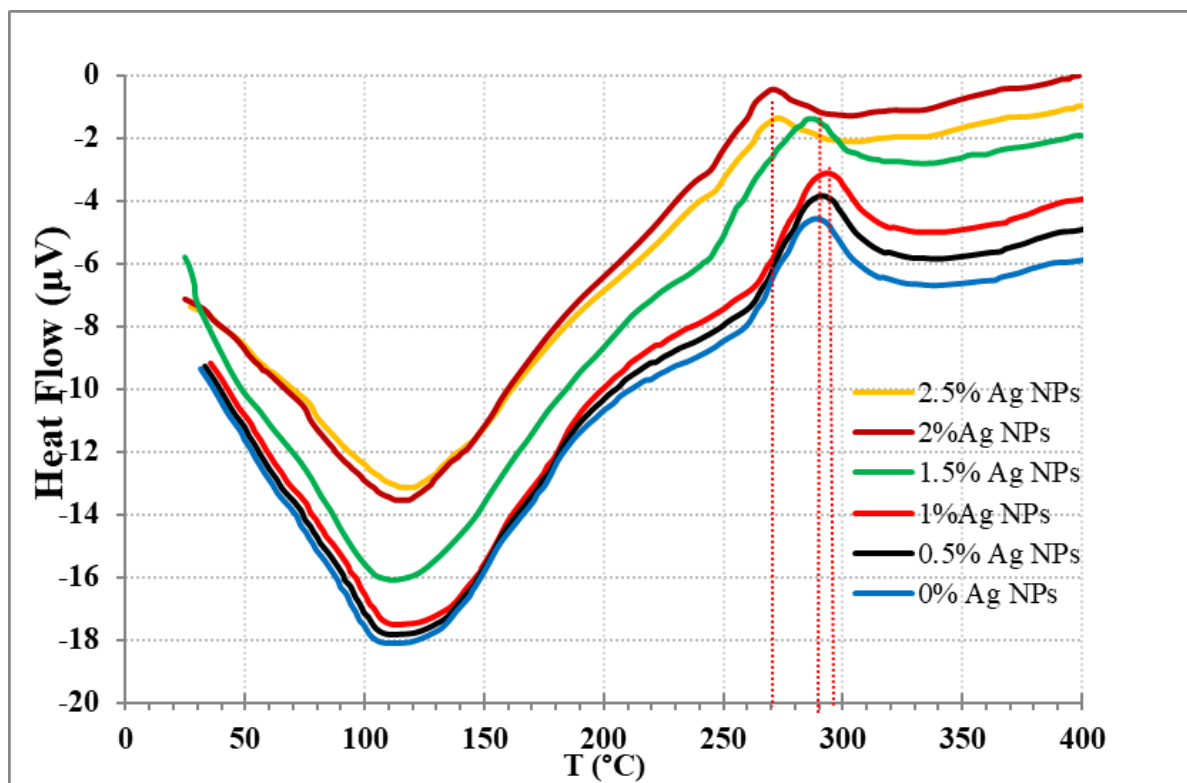
Figure 3 DSC spectra for Chitosan/PVA at 90:10 blend ratio reinforced with different Ag NPs ratios.

The stress-strain curves of Chitosan/PVA blend at 90:10, reinforced with different Ag NPs ratios from 0.5 to 2.5wt% are shown in Figure 4. It is shown that the maximum stress at 1.5% Ag NPs and decrease with more ratio, while the maximum strain before fracture decreases with increasing the Ag NPs ratio. The dispersion of nanoparticles in polymers is a crucial prerequisite for the advancement of polymer-matrix composites [19]. This increment of maximum stress to 1.5% demonstrates the importance of nanoparticle's dispersion while its decrement at more ratio due to agglomeration of Ag NPs.
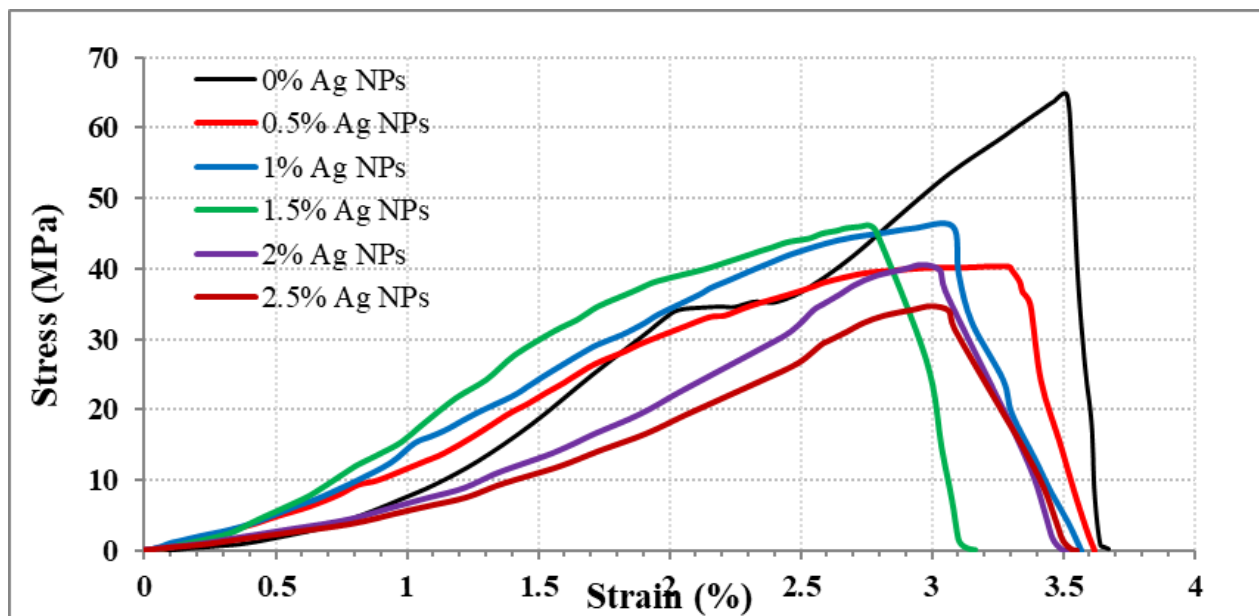
Figure 4 Stress-strain curves for Chitosan/PVA at 90:10 blend reinforced at different Ag NPs ratios.

The variation of Young Modulus and maximum elongation for Chitosan/PVA at 90:10 blend with Ag NPs ratio is shown in Figure 5. In general, both Young Modulus and the maximum elongation decrease with increasing Ag NPs ratio. Table 2 shows the maximum stress, maximum strain, and Young Modules for the Chitosan/PVA blend reinforced at different Ag NPs ratios. The reduce in Young Modulus and the ultimate elongation indicate on reducing the polymer composite stiffness, and elasticity maybe due to low interface between inorganic Ag NPs and polymer matrix [20,21].
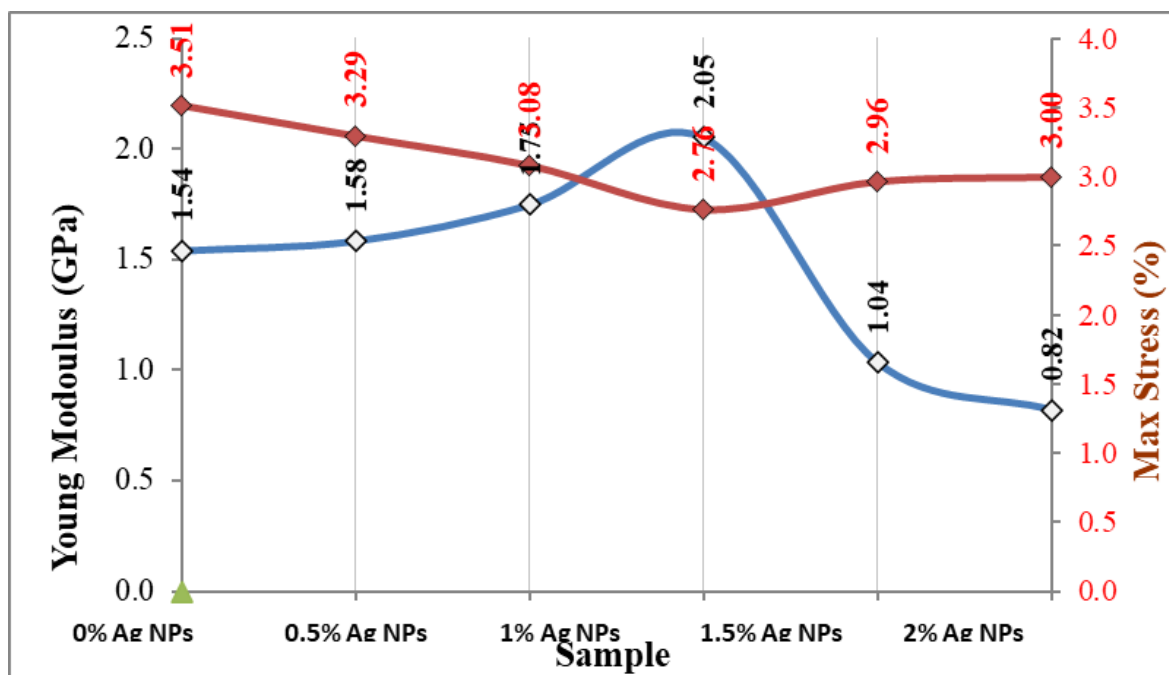

Figure 5 Young Modulus and maximum stress for Chitosan/PVA at 90:10 blend reinforced with different Ag NPs ratios.

Table 2 Tensile parameters for Chitosan/PVA (90:10) blend reinforced at different Ag NPs ratios

Sample	Ag NPs%	Max Stress	Max Strain	Young Modulas (Gpa)
A0	0% Ag NPs	64.60927	3.51	1.54
A1	0.5 % Ag NPs	40.21624	3.29	1.58
A2	1 % Ag NPs	46.061268	3.08	1.75
A3	1.5 % Ag NPs	46.197018	2.76	2.05
A4	2 % Ag NPs	40.54953	2.96	1.04
A5	2.5 % Ag NPs	34.75674	0.00	0.82

The antibacterial efficacy of Chitosan/PVA blend ratio, enhanced with varying ratios of Ag NPs, is assessed against Escherichia coli and Staphylococcus aureus bacteria using the half-maximal inhibitory concentration approach. Figure 6 demonstrates the presence of an inhibitory zone surrounding a small droplet of Chitosan/PVA mix at a ratio of 90:10, which has been enhanced by Ag NPs. This inhibitory zone is observed on the surface of agar following the dispersion of Escherichia coli and subsequent incubation at a temperature of 37°C for a duration of 24 hours. The greatest antibacterial efficacy is seen at a ratio of 2.5% Ag NPs, resulting in an inhibitory halo measuring 16 mm, as indicated in Table 3.The samples exhibited greater efficacy against gram-negative bacteria compared to gram-positive bacteria. It has been shown that the effectiveness of silver nanoparticles in killing Gram-negative bacteria depends on the concentration of the nanoparticles. This effectiveness is strongly linked to the production of dpits T in the bacteria's cell wall. Afterwards, Ag nanoparticles accumulated in the bacterial membrane caused the permeability, resulting in cell death. The test also showed that samples of high Ag NPs concentration have effective against Escherichia coli [15]. While the solutions that did not appear to have an inhibition halo around them, they are considered ineffective solutions against the selected bacteria (Staphylococcus aureus) and are indicated with the symbol n.a - no effectiveness. These results agree with those presented by researchers Sondi and Salopek-Sondi [22-25].

Figure 6 Effectiveness of compounds on bacteria grown in the medium of agar.

Table 3 Determine the minimum inhibitory concentration (MIC) for Escherichia coli (E) and Staphylococcus aureus.

Sample	Concentration Ag NPs (%)	Inhibition halo (mm)	
		Escherichia coli (E) 100%	S.aureus (s) 100%
A1	0.5 % Ag NPs	10	n.a
A2	1 % Ag NPs	12	n.a
A3	1.5 % Ag NPs	10	n.a
A4	2 % Ag NPs	14	n.a
A5	2.5 % Ag NPs	16	n.a

4. CONCLUSIONS

Ag NPs-enhanced Chitosan/PVA blend is prepared in different proportions by simple casting method. Tensile measurement indicated that the rigidity of the samples increased, limiting the elasticity of the sample. The mix samples have antibacterial activity against gram-negative bacteria, making them useful for use in medical applications (such as dressing large open wounds in moving organs) and in food packaging.

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