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Study of structural, mechanical and thermal properties of chitosan/PVA blend by casting method in different proportions

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Chitosan and a combination of Chitosan and PVA with varying PVA weight ratios (5, 10, 15, 20, and 25%) are created using the solution casting technique. The produced samples underwent structural, mechanical, and thermal tests using X-ray diffraction (XRD), Fourier-transformed infrared spectroscopy (FTIR), strain stress test, hardness test, thermal conductivity test, and antibacterial test. The XRD measurements confirm the purity of the Chitosan and PVA powders. Furthermore, the observed alteration in the energy levels of some FTIR bands for polysaccharides, along with a decrease in their intensities, suggests the occurrence of Chitosan: PVA blend synthesis. The highest values for tensile strength, hardness, and thermal conductivity are observed at a PVA ratio of 10%. The antibacterial activity of the chitosan/PVA blends is assessed using the inhibitory concentration technique. The results indicate varying levels of activity among the different samples. The Chitosan/PVA combination at a 15% blend ratio exhibited the greatest suppression of the microorganisms. The mix exhibits lower efficacy against gram-positive bacteria compared to gram-negative bacteria.

Keywords: Chitosan; blend; solution casting; tensile test; hardness test; FTIR test.

1. INTRODUCTION

Chitosan, has a comparable structure to cellulose, is composed of a single glucose monomer [1]. The material is a polysaccharide consisting of copolymers of glucosamine and N-acetyl glucosamine. Chitin can be obtained by partly removing the acetyl groups from the exoskeletons of crabs [2]. The polymer exhibits environmental sustainability [3]. Chitosan is soluble in weak acid when it is in its solid form and its strength increases due to the creation of a network of hydrogen bonds. This results in the formation of favorable mechanical characteristics [4]. Chitosan is used in different applications, such as microbial biosorption and the elimination of metals in wastewater treatment [5]. Chitosan is employed in several biomedical applications because of its antimicrobial properties, compatibility with living organisms, and ability to biodegrade. It is employed in surgical procedures in the field of tissue engineering, which seeks to restore injured organs by employing scaffolds that promote regeneration and closely resemble the original tissue [6]. Furthermore, it is used in drug delivery and safeguarding delicate pharmaceuticals because of its remarkable ability to naturally breakdown, its antibacterial characteristics, and its efficacy against fungal infections [7]. Chitosan is a valuable substance for food packaging since it can be easily renewed and is readily available in nature. Following cellulose, it is the second most prevalent polymer found in nature [8]. The electrostatic contact occurs between the positively charged NH3+ groups of chitosan molecules and the negatively charged membranes of microbial cells. Electrostatic interaction alters the permeability of the cell membrane, leading to internal osmotic imbalances and hindering the growth of microbes. Moreover, the degradation of peptidoglycans in the microorganism's wall leads to the liberation of electrolytes from the intracellular compartment. , ultimately resulting in the death of the cell [9]. Polyvinyl alcohol (PVA) It is a water-soluble and odorless industrial polymer. The process involves polymerizing and partially decomposing vinyl acetate monomer to create the final product. A translucent film with exceptional durability and tear resistance is generated by dissolving it in water and subsequently evaporating the water. The solubility of the polymer is contingent upon the extent of molecular breakdown and its hydrogen bonding capacity [10]. Commercially accessible PVA polymer can be categorized into two types: fully hydrolyzed polyvinyl alcohol (PVA) and partially hydrolyzed polyvinyl alcohol (PVA), based on the level of hydrolysis. The polymer backbone of PVA contains a significant number of acetate groups, which contributes to its chemical stability at normal temperatures. This, combined with its exceptional physical and chemical properties, has resulted in its extensive utilization in various practical applications such as medicine, cosmetics, food, pharmaceutical industries, and packaging. Primarily used in the production of fiber and film products, such as coatings for paper. Polymer mixing is a frequently used method for creating polymeric materials. It aims to offer materials that possess specific features, such as a balance of strength and toughness, at the most affordable price. Furthermore, blending enhanced certain blend characteristics, including homogeneity and flexibility [11].

Extensive study has been conducted on the chitosan mix, exploring its various applications. In their 2014 study, Soo et al. [12] have demonstrated the antibacterial efficacy of an 85/15 (PAN/chitosan, wt%) nanofiber that is generated using electrospinning and tested against several types of bacteria. In their 2015 study, Liu et al. [13] have examined the relationship between the chitosan/PAN mix ratio and the characteristics of yarns. The researchers found that the yarn exhibited optimal qualities when the combined charges of the materials used neared a neutral or zero state. This study examines the influence of various ratios of Chitosan/PVA blend on its structural characteristics. X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) techniques are employed to confirm the synthesis of copolymer blends. To ascertain the ideal ratio for the Chitosan: PVA mixture, which is produced by the drop casting method and demonstrates the utmost mechanical and antibacterial characteristics.

2. EXPERIMENTAL

Chitosan with a moderate molecular weight and Poly Vinyl Alcohol (PVA) with an average molecular weight of 150 (kilodalton) are obtained from Sigma-Aldrich Company. The Chitosan and PVA mixture are prepared using the solution casting technique at different PVA weight ratios (5%, 10%, 15%, 20%, and 25%), as specified in table 1. The chitosan powder is dissolved in 50 ml of acetic acid that had been diluted with water to a concentration of 1% normality. The ratios of chitosan powder used for each of the six samples were 1.5, 1.425, 1.35, 1.275, 1.2, and 1.125 grams. The dissolution procedure occurred in glass containers utilizing a magnetic stirrer at ambient temperature. The chitosan powder is gradually introduced until it achieved complete dissolution, a process that lasted approximately 2 hours. The PVA powder is dissolved in 2 cc of distilled water. Each sample is individually weighed at specified weights (0.075, 0.15, 0.225, 0.3, and 0.375g). The dissolution procedure is conducted utilizing a magnetic stirrer under ambient conditions. Afterwards, the polymers that were created were slowly mixed with the chitosan. Figure 1 illustrates the usage of two distinct mold forms for performing several tests. The samples were left to dry for 48 hours at room temperature before being sent for the corresponding tests. An assortment of methodologies is employed to assess the characteristics of both the pure chitosan and blend samples. The Shimadzu XRD 6000 device is utilized to conduct X-ray diffraction (XRD). A Thermo Scientific Nicolet spectrometer is used to perform Fourier-transform infrared spectroscopy (FTIR). The tensile strength is determined by employing an H10KT model tensile tester, in accordance with the ASTM D638 standard. The hardness is measured using a TH220 type hardness tester, in accordance with the ASTM D2240 standard. The thermal conductivity is determined using the Lee's Disc method, employing a tester manufactured by Griffin & George/England, in accordance with the ASTM D7340 standard. The inhibitory concentration is used to evaluate the antibacterial efficacy of the blend samples against Escherichia coli and Staphylococcus aureus infections.

Table 1 Ratios and components weights of Chitosan blends Samples.

Code	Chitosan wt%	PVA wt %	Chitosan weight (g)	PVA weight (g)
A0	100	0	1.5	0
A1	95	5	1.425	0.075
A2	90	10	1.35	0.15
A3	85	15	1.275	0.225
A4	80	20	1.2	0.3
A5	75	25	1.125	0.375

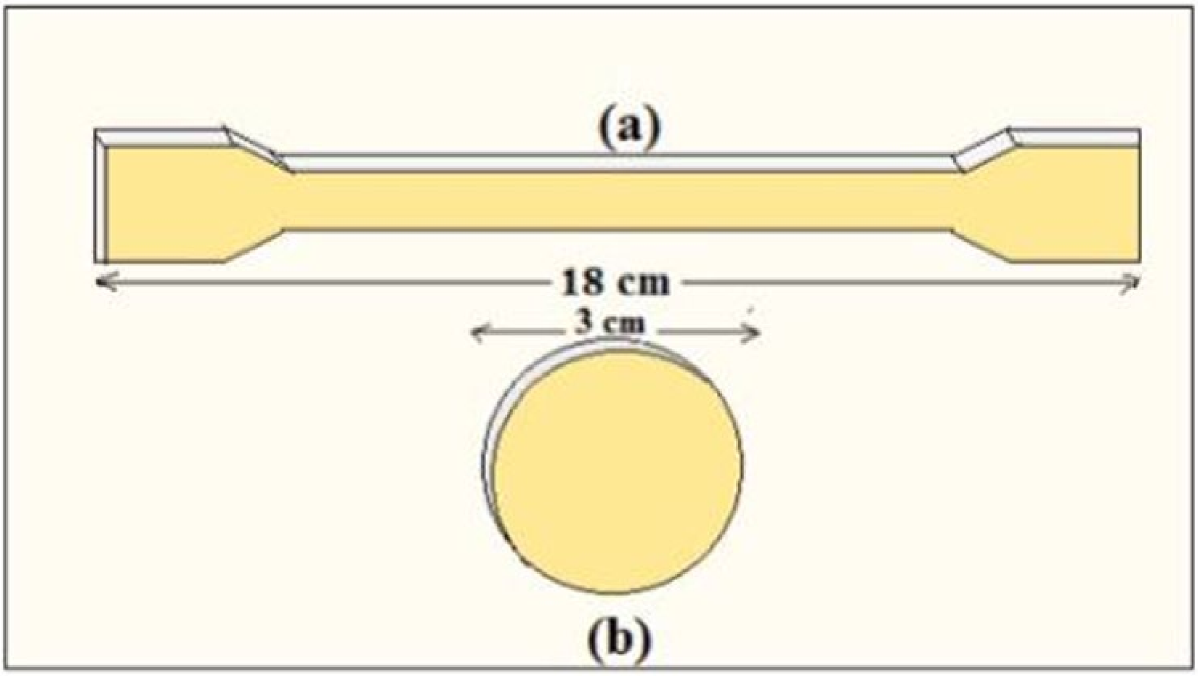

Figure 1 Illustrates the diagrammatic depiction of different mold configurations. (a) is specifically tailored for the purpose of measuring strain stress, whereas (b) serves additional objectives.

3. RESULTS AND DISCUSSIONS

The X-ray diffraction (XRD) pattern of the PVA polymer is depicted in Figure 2. The pattern displays prominent peaks at 2θ = 18.320°, corresponding to the (000) plane, and a smaller peak at 39.420°, corresponding to the (000) plane. The values can also be found in Table 2. The calculation of the inter-plane distance is performed using Bragg's formula [14], which indicates that m λ = 2 dhkl sin θ. Here, λ represents the X-ray wavelength emitted by a Cu target (1.5406 Å), θ denotes the diffraction angle, and m corresponds to the diffraction order.

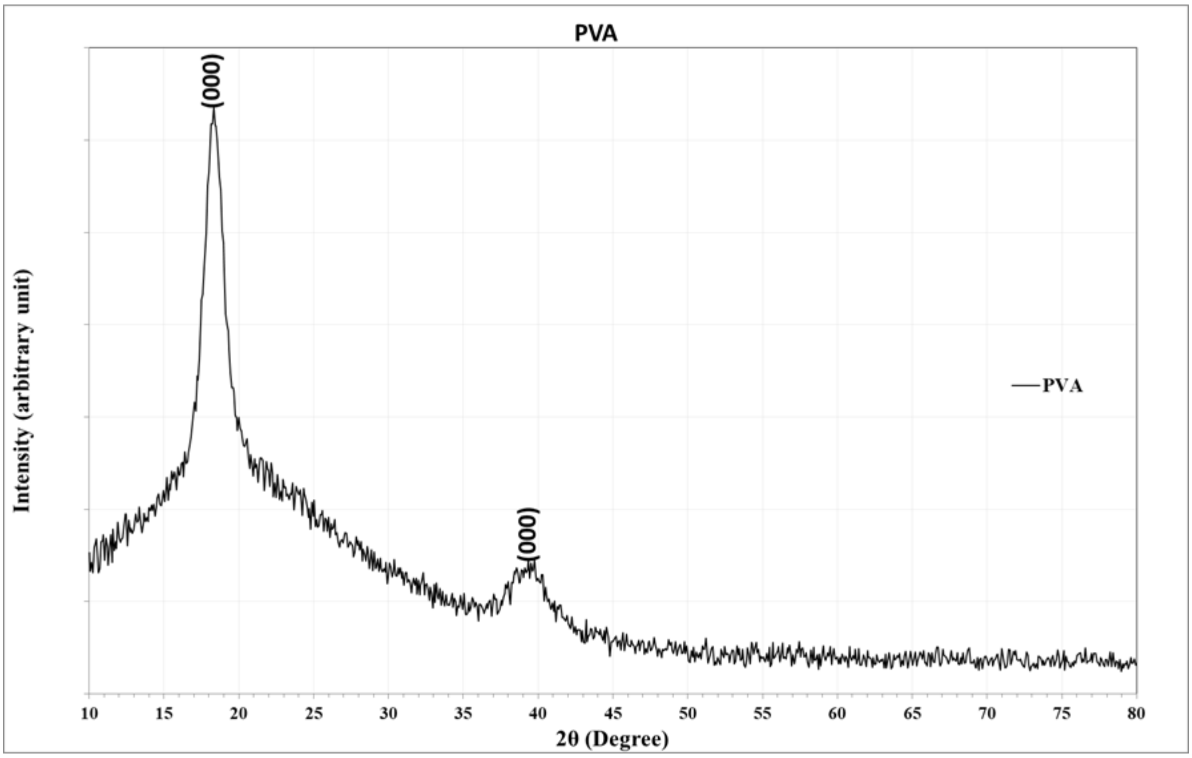

Figure 2 X-ray diffraction (XRD) pattern of polyvinyl alcohol (PVA) powder

Table 2 peak parameters for PVA and Chitosan (Ch) powders.

Sample	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	C.S (nm)	Hkl
PVA	18.320 39.420	1.500 2.875	4.8388 2.2840	5.4 2.9	(000) (000)
Ch	20.100	4.200	4.4141	1.9	(101)

The X-ray diffraction (XRD) patterns depicting the characteristics of chitosan powder may be shown in Figure 3. A peak is observed in the chitosan pattern at an angle of 2θ=20.100°. The distinctive peaks for chitosan are observed on the (101) planes of its orthorhombic structure [15]. A polymorphism caused the emergence of a distinct and wide peak at 20.1. This conclusion is consistent as finding in paper of Hanaa [16].

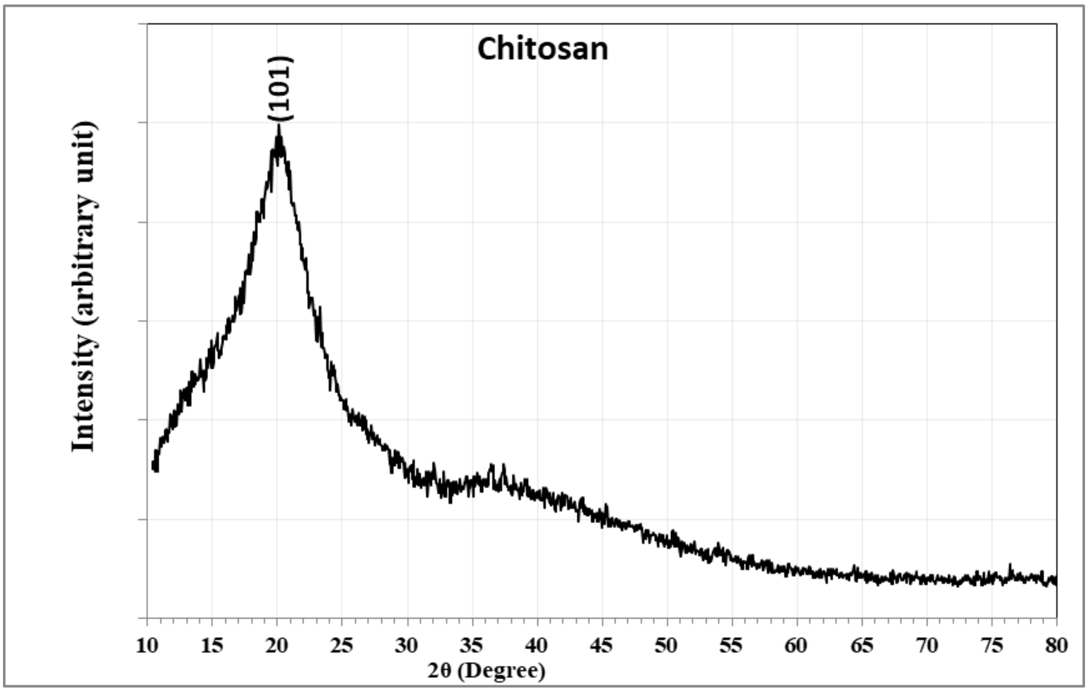

Figure 3 XRD pattern for chitosan powder.

Figure 4 exhibits the FTIR spectrum of chitosan, emphasizing the unique peaks that correspond to the bands of chitosan. The band observed at 3434.64 cm-1 represents the stretching vibration of the hydroxyl group (-OH). The CH2 symmetric stretching peak is detected at a wavenumber of 2891.98 cm−1, whereas the CH2 asymmetric stretching peak is identified at a wavenumber of 2881.76 cm−1. The C-O stretching -CO band is detected at 1085.91 and 1597.23 cm−1, as documented in reference [17]. The bands observed at 1085.91 cm−1 and 591.22 cm−1 correspond to the elongation of the C-O bond and the flexing of the C-H bond in the skeletal vibration [18]. The indicated peaks are characteristic bands that signify the polysaccharide composition of chitosan [19]. The FTIR spectroscopic patterns of chitosan and Chitosan: PVA blends were analyzed and compared. The results showed that there is a shift in the bands corresponding to the asymmetric stretching of the C–O–C bridge in chitosan. Specifically, the shift is from 1085.91 cm−1 to 1183 cm−1. The intensity of this band diminishes due to the decrease in the oxidative glycosidic link between polysaccharides. Moreover, the strength of the symmetric and asymmetric CH2 stretching bonds diminishes as the PVA ratio increases, indicating the creation of the blend.

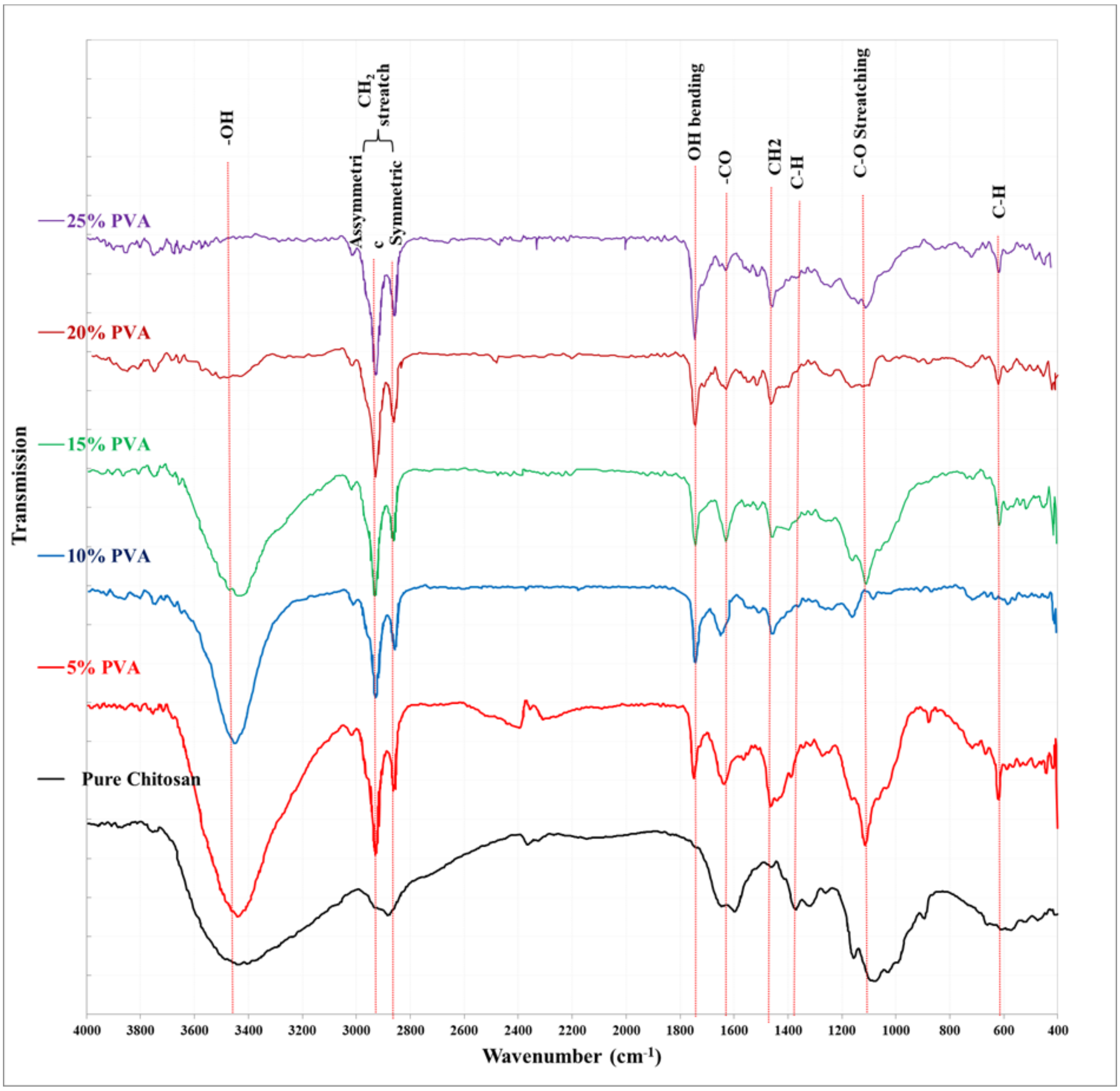

Figure 4 FTIR spectra were obtained for a combination of chitosan and PVA at various ratios.

Stress (σ) is the quantification of the force exerted on a specimen, divided by its cross-sectional area (σ= F/A). Strain (ε) is the quotient of the change in length of the specimen (ε = ΔL/L) divided by its starting length. The Young's modulus (Y) is defined as the ratio of stress to strain in the context of elastic deformation (Y = σ/ε). The phrase quantifies the strength of the bond between atoms [20]. Figure 5 depicts the structures of Chitosan and Chitosan: A PVA mixture is created by combining various weight ratios. The stress-strain curves display two distinct regions: The initial portion of the material demonstrates linear characteristics, referred to as the elastic zone, and concludes upon reaching the elastic limit. The second component relates to the non-linear section, particularly the plastic region, which ends at the fractional point. The Young's Modulus is determined by computing the gradient of the linear portion of the stress-strain curve. The maximum stress of pure chitosan35.963095 closely aligns with the results reported by Mahmood and Jawad [21]. The addition of PVA content in the Chitosan: PVA blend resulted in a 10% rise in maximum stress at the fracture site. However, the maximum stress subsequently dropped as the ratios of PVA content increased. In addition, based on the data in table 3, the 10% ratio shows a maximum elongation of 71.070197 cm before to the decimal point, which corresponds to a maximum strain of 3.51%.

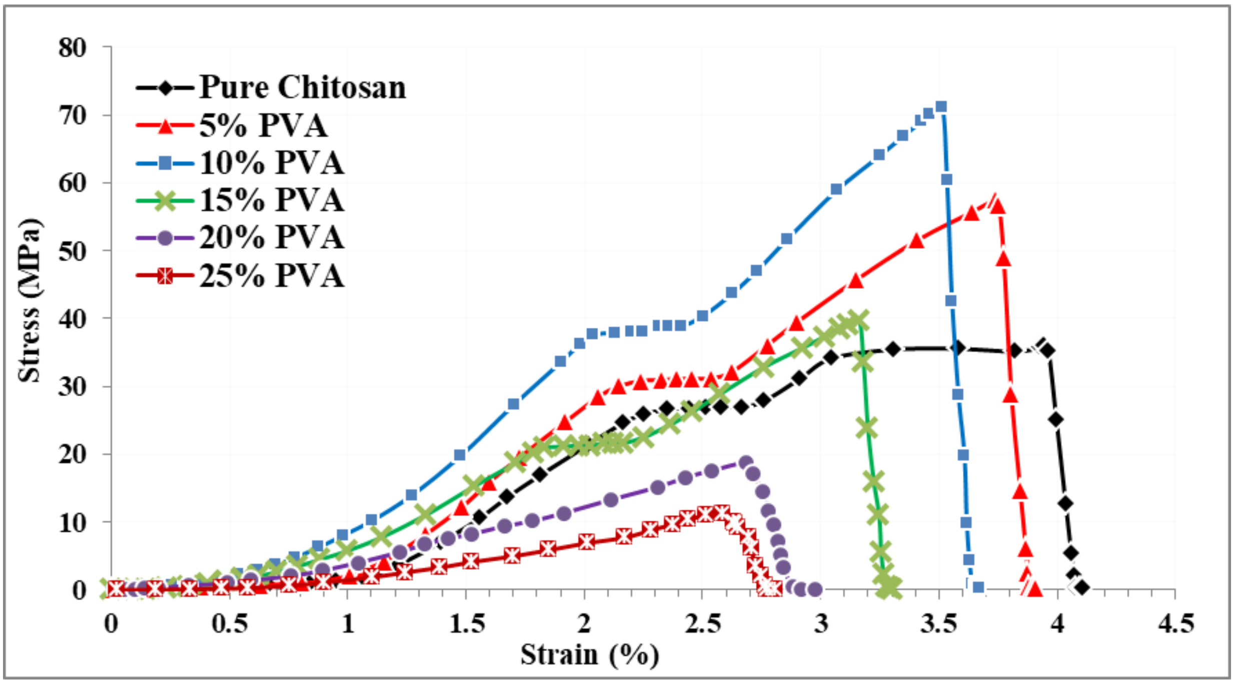

Figure 5 Stress-Strain Carves of chitosan blend at different ratios.

Table 3 Max Stress, Max Strain and Young Modulas (Gpa) of chitosan blends.

Sample No.	PVA %	Max Stress	Max Strain	Young Modulas (Gpa)
A0	0	35.963095	3.93	1.01
A1	5	57.56542	3.74	1.23
A2	10	71.070197	3.51	1.69
A3	15	39.6465975	3.16	1.23
A4	20	18.72333	2.69	0.57
A5	25	11.3552	2.58	0.36

Figure 6 depicts the correlation between the Young Modulus and the PVA ratio in the Chitosan/PVA blend. The Young's Modulus achieves its maximum value of 1.69 GPa when the PVA ratio is 10%. The blend ratio of this mixture exhibited enhanced mechanical properties as a result of molecular interactions between the two polymers, leading to a homogeneous blend. This finding aligns with the research undertaken by Makaremi et al. [22], who observed that the polymer blend has a higher tensile strength in comparison to its individual components. Nevertheless, an elevated polymer concentration results in a reduction in the mechanical properties of the mixture.

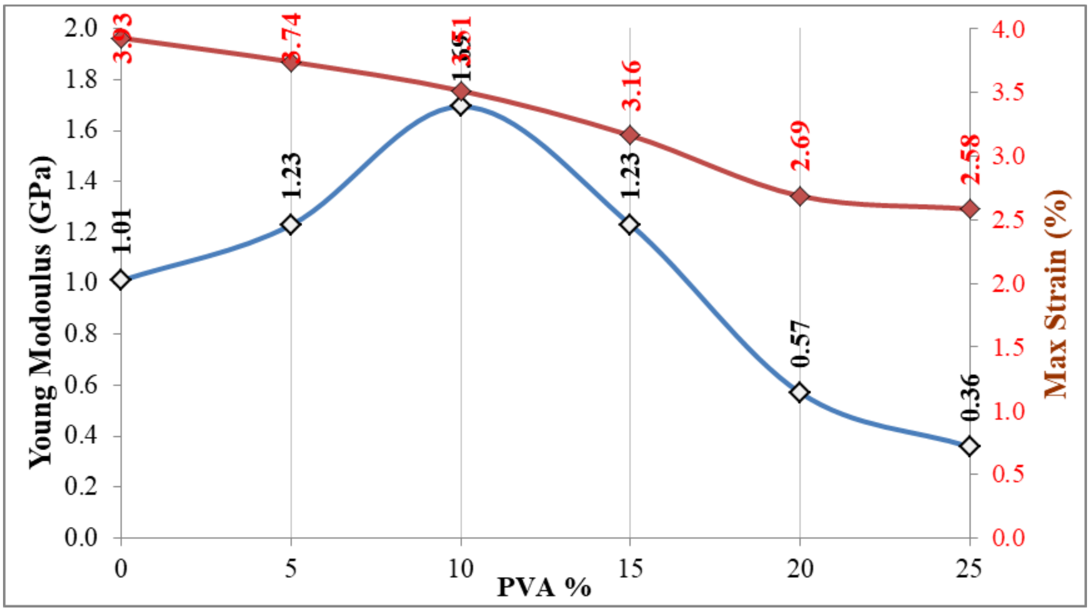

Figure 6 Young's modulus and maximum strain curves are plotted for a chitosan/PVA blend at various ratios.

Figure 7 illustrates the changes in hardness for the Chitosan/PVA blend with varying PVA ratios, as determined by the shore D hardness test. The hardness of the material increases from 72.26 to 76.86 when the PVA ratio is increased to 10%, then lowers to 69.7 as the PVA ratio is increased to 25%. The stiffness of the mix is boosted by increasing the PVA content to its ideal value, as a result of the interfacial contact between the two polymers. The mechanical characteristics of the polymer blend decrease with an increased concentration of PVA. The inadequate interphase adhesive between the two blending components led to interphase division, thereby deteriorating the mechanical properties of the polymer blend [23,24].

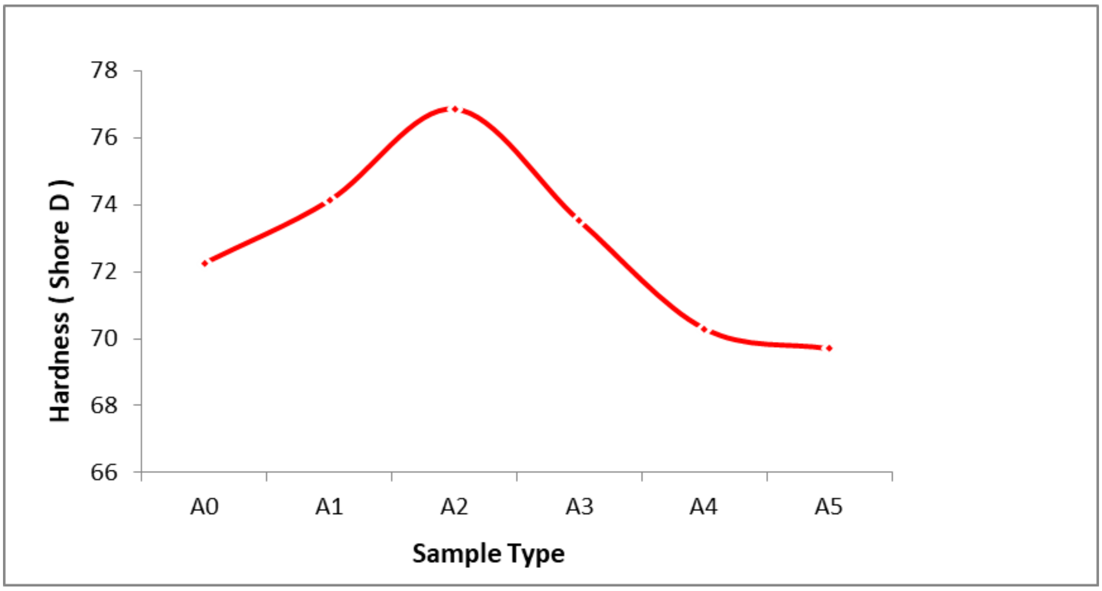

Figure 7 Hardness NO. of chitosan/PVA blend at different ratios.

Polymers have limited heat conductivity due to their low atomic density, weak intermolecular connections or chemical bonding, complex crystal structure, and significant anharmonicity in their molecular vibrations. Phonon transport is the primary process by which heat is transported in the majority of polymers. Phonons enable the transfer of thermal energy through interactions with each other and with subatomic particles. The graph in Figure 8 illustrates the changes in thermal conductivity coefficient for Chitosan/PVA blends as the PVA ratio ranges from 0% to 25%. The relationship between the conductivity and the PVA ratio is evident. As the PVA ratio increases, the conductivity also increases, reaching its greatest value of 0.0073 (W/m.c) at a 10% ratio. However, above a 10% PVA ratio, the conductivity starts to drop. The thermal conductivity is increased at a low ratio as a result of the interaction between the polymer blend. At high PVA ratio, the presence of lattice defects, such as dislocations and voids, in a multi-phase system of polymeric composites leads to scattering of phonons, resulting in a decrease in the thermal conductivity of the mix [25,26].

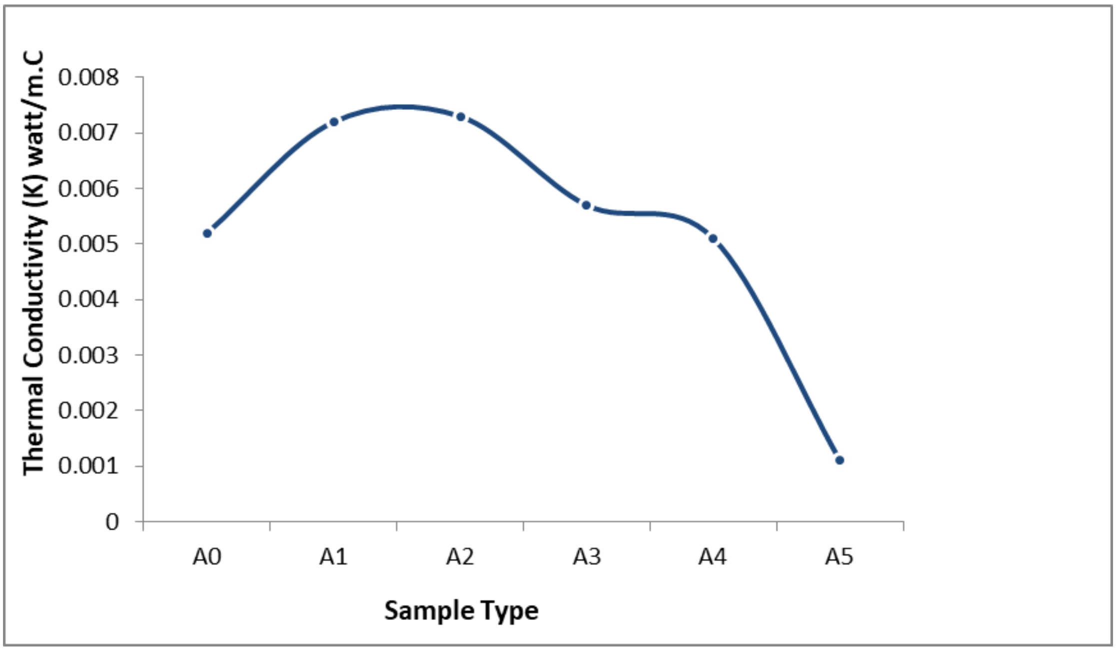

Figure 8 Thermal conductivity (K) of chitosan/PVA blend at different ratios.

The antibacterial effectiveness of Chitosan/PVA blends, produced at different ratios, against Escherichia coli and Staphylococcus aureus bacteria is evaluated using the half-maximal inhibitory concentration method. Figure 9 demonstrates the presence of a zone of inhibition surrounding a small droplet of Chitosan/PVA solution on the agar surface. This event took place following the dissemination of Escherichia coli and its cultivation at a temperature of 37°C for a period of 24 hours. The mixture containing a ratio of 15% demonstrated the most potent antibacterial activity, as indicated in table 4. The research also revealed that samples with a high proportion of PVA exhibit a diminished ability to effectively combat E.coli bacteria. As per the findings of Khesro et al [27], the Chitosan/PVA mixture has antibacterial properties that impede bacterial development. This is accomplished by inducing destabilization of the outer membrane of Gram-negative bacteria. While the solutions that did not have an inhibitory halo were seen, they were found to be ineffective against the specific bacterium being targeted (Staphylococcus aureus) and were labeled as n.a, signifying no effectiveness [28-30].

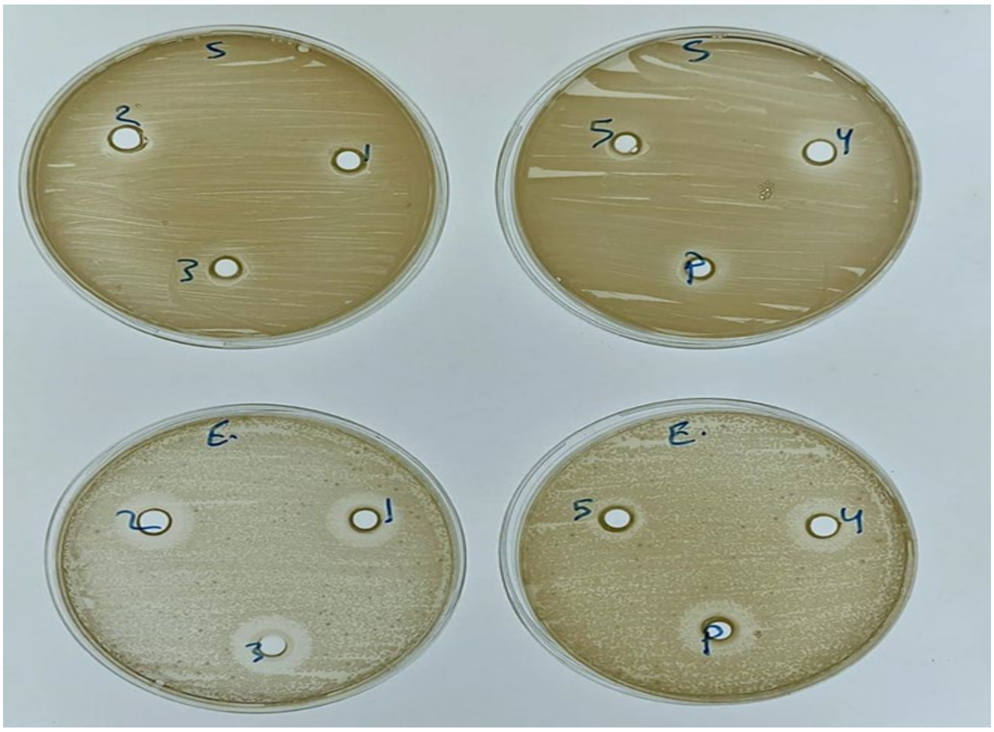

Figure 9 Shows the effectiveness of the prepared compounds against the bacteria(S) S.aureus at the top and the bacteria (E) E.coli at the bottom.

Table 4 The minimum inhibitory concentration (MIC) of the chitosan/PVA mix at various ratios is tested against Escherichia coli (E) and Staphylococcus aureus (S).

Components	Inhibition halo (mm)	
	Escherichia coli (E) 100%	S.aureus (s) ^{*1}100%
A1	10^{*2}	n.a
A2	11	n.a
A3	12	n.a
A4	10	n.a
A5	9	n.a
(Pure chaitosan)	10	n.a
Levofloxacin disc	+ve	+ve

- 1* Concentration of compounds. Calculated as a percentage
- n.a(No activity)
- 2* Diameter of inhibition (biological effectiveness) measured in mm.

4. CONCLUSIONS

FTIR reveals a wide range of molecular bands. The C–O–C bridge in chitosan undergoes a band shift, and its intensity diminishes as a result of the oxidative reduction of the glycosidic connection between polysaccharides. The intensity of CH2 bonding decreases as the PVA ratio increases, which is attributed to the formation of the mix. The optimal ratio, based on the results obtained from stress-strain hardness and thermal conductivity, was found to be 10% PVA. At this low PVA ratio, both the mechanical and thermal properties were improved. Additionally, the antibacterial activity was enhanced at a 15% PVA ratio, making it suitable for various medical applications. Additionally, it can be used in food packaging since it is biodegradable, impermeable to liquids, has improved mechanical qualities, and has antibacterial activity that prevents the spread of microorganisms in food.

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