



Properties Affected by Different Shape and Different Weight Percentages Nanoparticles, Embedded in Chitosan Polymer Thin Film

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ABSTRACT

Chitosan (CS) based thin films fabricated by incorporated with plasticizer (glycerol) at different weight ratios were prepared. This was carried out by employing a solvent-casting method incorporating with Halloysite nanoclay (nanotube) and Silica nanoparticle (spherical) into the films. Scanning Electron Micrographs (SEM) showed that nanoparticles were dispersed homogeneously throughout the polymer matrix in all of the chitosan-nanocomposite films; tensile test (UTM) showed that the mechanical strength of the films varies with the nanoparticle concentration. It was observed from the Thermal Gravimetry Analysis (TGA) results that there is no significant variation in the thermal degradation temperature of the films with the addition of the nanoparticles. The hydrophobicity increased with the addition of nanoparticles, as seen from the contact angle, moisture content and water solubility result.

Key words: Chitosan, glycerol, halloysite nanoclay, silica nanoparticles

INTRODUCTION

Chitosan (CS) polymers are natural Amino-polysaccharides having unique structures, multi-dimensional properties, highly sophisticated functions and wide ranging applications in biomedical and other industrial areas [1-3]. Being considered to be materials of great futuristic potential with immense possibilities for structural modifications to impart desired properties and functions, research and development work on CS have reached a status of intense activities in many parts of the world [4-5]. The positive attributes of excellent biocompatibility and admirable biodegradability with ecological safety and low toxicity with versatile biological activities such as antimicrobial activity and low immunogenicity have provided ample opportunities for further development [6-11]. It has become of great interest not only as an under-utilized resource but also as a new functional biomaterial of high potential in various fields [12-14].

In recent years, polymer-nanoparticle composite materials have attracted the interest of a number of researchers, due to their synergistic and hybrid properties derived from several components. Whether in solution or in bulk these materials are offer unique mechanical [15], electrical [16], optical [17-18] and thermal properties [15-18]. Such enhancements are induced by the physical presence of the nanoparticles and by the interaction of the polymer with the particle and the state of dispersion [15, 19].

In this work, the nanocomposite films are consisting of Inorganic halloysite nanoclay (nanotubes), silica nanoparticle (spherical) and organic polymer as chitosan (partially water soluble) [20].

MATERIAL AND METHODS

Chitosan

It is a linear polyamine copolymer of β -(1-4)-D-glucosamine and acetyl- β -(1-4)-D-glucosamine and it is obtained by alkaline N-deacetylation of chitin [21]. Chitin is the 2nd most abundant polysaccharide on the earth, present in the exoskeleton of arthropods such as insects, crabs, shrimps, lobsters, and certain fungal cell walls [22]. Compared with other polysaccharides, chitosan has several important advantages, including biocompatibility, non-toxicity, biodegradability, low immunogenicity, nontoxicity, etc. [10, 11 and 23]. These properties in combination with good mechanical properties make them good candidate materials for sutures that form the largest groups of material implants used in human body [8, 24].

Chitosan is readily soluble in dilute acidic solutions below pH 6.0. This is because chitosan can be considered a strong base as it possesses primary amino groups with a pKa value of 6.3. The presence of the amino groups indicates that pH substantially alters the charged state and properties of chitosan [12]. At low pH, these amines get protonated and become positively charged and that makes chitosan a water-soluble cationic polyelectrolyte. On the other hand, as the pH increases above 6, Chitosan amines become deprotonated and the polymer loses its charge and becomes insoluble. The soluble-insoluble transition occurs at its pKa value around pH between 6 and 6.5. As the pKa value is highly dependent on the degree of N-acetylation [25]. The degree of ionization depends on the pH and the pKa of the acid with respect to studies based on the role of the protonation of chitosan in the presence of acetic acid and hydrochloric acid [26, 27].

The dissociation constant K_a of the amine group is obtained from the equilibrium



Thus, $K_a = \frac{[R-NH_3^+][OH^-]}{[R-NH_2]}$ and $pK_a = -\log K_a$ [28]

For our experiment we used chitosan from shrimp shells (total impurities: $\leq 1\%$ insoluble matter, ign. residue: $\leq 2\%$ (as SO_4), loss: $\leq 10\%$ loss on drying, viscosity: < 200 mPa.s, 1 % in Acetic acid (20 °C)) was obtained from sigma-aldrich, India.

Plasticizer

We used here was glycerol. Glycerol is the simplest trihydric alcohol with a specific gravity of 1.26. It is a colourless, odourless, sweet, viscous liquid melting at 17.8°C boiling at 290°C. It decomposes at boiling point and produce corrosive fumes of acrolein. It is miscible in water and forms a solution in any proportion. It is completely soluble in alcohol and partially soluble in common organic solvents such as ether and ethyl acetate. Chemical formula: $CH_2(OH)CH(OH)CH_2OH$ (1,2,3-propanetriol).

For our experiment we used glycerol (minimum assay: 99.5%, Wt. per ml at 20°C: 1.257-1.262 gm, refractive index (nb20): 1.471-1.473, pH (10% aqueous solution): 6.0-7.0) from Ranbaxy, India.

Halloysite Nanoclay

It is clay a mineral, occurring as soft, smooth, and amorphous masses of white colour. Halloysite frequently has a unique tubular quality with very small diameter and hollow structure. It is aluminosilicate clay that forms naturally occurring nanotubes. Halloysite clay nominal chemical compositions are 50% silica and 50% clay $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$.

For our experiment, we used halloysite nanoclay from sigma-aldrich, India. The properties of this given nanoclays are nanopowder, diameter \times length: 30-70 nm \times 1-3 μ m, colour: 75-96, hunter brightness, refractive index: $n_{20/D}$ 1.54, pore size: 1.26-1.34 ml/g pore, volume surface area: 64 m^2/g , capacity: 8.0 meq/g, cation exchange capacity density: 2.53 (true specific gravity).

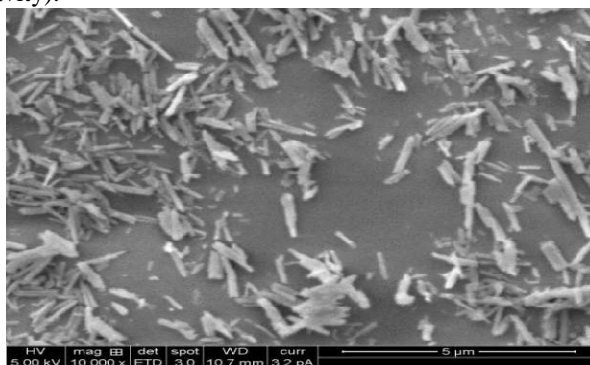


Fig.1 SEM image of Halloysite nanoclay

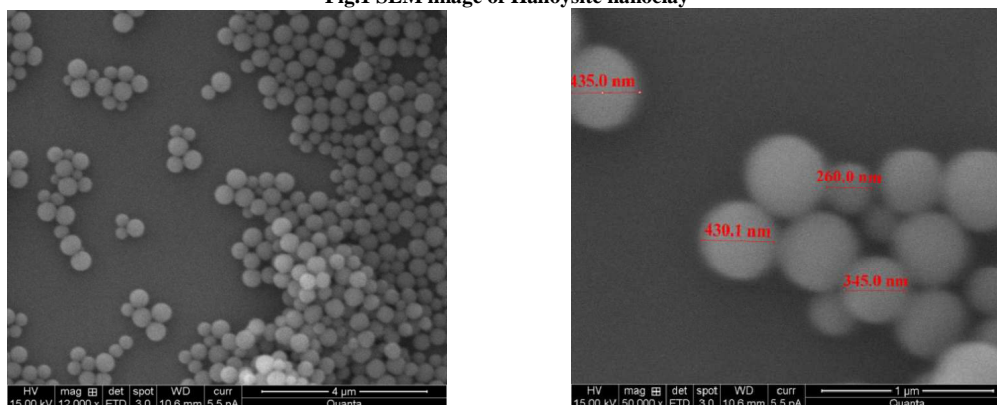


Fig.2 SEM images of silica nanoparticle

Silica Nanoparticles

We synthesized from Tetra-Ethyl Ortho-Silica (TEOS) in the presence of surfactants [29]. We used for to synthesis silica nanoparticles by adding 1.6 ml NH_4OH in 40 ml Ethanol and 3.2 ml water and sonicated for 10 mins. After sonication we added 2.4 ml TEOS and again sonicated for 10 mins and after sonication leave it for 2 h for forming the silica nanoparticles. After 2 h the solution is getting whitish for forming of silica nanoparticles, we collect the nanoparticles by centrifuging in 3000 rpm at 15°C for 15 mins for several times and then dried it in the furnace at 40°C and after that we got 0.70678 gm of silica nanoparticles.

Preparation of the films

We used solvent casting method for preparation of our films [30]. Polymer solution was prepared by dissolving 0.8 gm of polymer powder in 50 ml of aqueous acetic acid solution (1%, v/v) and 0.2 gm glycerol, using a magnetic stirring plate at 90°C for 20 min and then cooled to room temperature. Polymer-nanocomposite samples were obtained by dispersing selected amounts of nanoclay and nanoparticle (1 to 5% (wt/wt) on polymer powder) in 50 ml of 1% (v/v) aqueous acetic acid solution for 1 h at room temperature. This dispersion was added to the polymer solution, stirred for 1 h at room temperature and then for 30 min at 25°C in an ultrasonic bath. The dispersion was then poured onto petri dish (diameter = 9 cm) and dried at 40°C for 24 h, until the water was completely evaporated. Polymer films plasticized with glycerol was obtained by adding glycerol (20% (wt/wt) on polymer powder) to the polymer solution, while stirring for 20 min at 60°C . Thereafter the procedure for the film preparation was identical to that described previously. The types of the films are as follows: pure chitosan films, chitosan with glycerol (80:20) films, chitosan-halloysite nanoclay nanocomposite films (CS-HNC), chitosan-silica nanoparticle nanocomposite film (CS-SNP).

Thickness Measurements

Film thickness was measured to the nearest 0.001 mm using a held micrometre. Five values were randomly taken at different locations for each specimen of tensile tests, and the mean value was used in the determination of mechanical properties.

Tensile Properties

Each film-type samples were determined [31] with a Zwick micro tensile testing machine (screw driven micro tensile testing machine. It can do tension, compression and flexure test and attached with laser extensometer with load cell capacity of 2.5 KN). Rectangular specimens 50×10 mm were cut. Initial grip separation was set at 20 mm, and cross-head speed was set at 100 mm/min. The tensile strength and elongation measurements for each type of films were taken as follows: four sheets of each film type were used, with the mean values for tensile strength and elongation reported for each sample.

Scanning Electron Microscopy (SEM)

The morphology of the films depict where by using a scanning electron microscope (ESEM Quanta 200, FEI. W-Filament, low vacuum and humidity capability, Secondary E-T and solid state back scattered electron detector, ultra-thin window EDS System (EDAX), resolution at 20 kV:3 nm in high vacuum). For the powder samples, at first one drop of the powder (halloysite nanoclays, silica nanoparticle) suspension was placed on silica wafer and left it overnight for drying and for the thin films we took a small piece of samples and attached with the carbon tap and after that we gold sputtered by gold coating (JEOL, JFC-1100E, ion sputtering device, ion current: 20 Ma max.) before characterization. The samples were characterized in ESEM Quanta 200 electron microscopy at 5 kV with 15 mm working distance.

Water Solubility

We measured [32] by the content of dry matter solubilised after 24 h immersion in water. The initial dry matter content of each film was determined by drying to constant weight in an oven at 105°C . Three square of film (2×2 cm) were cut, weighed and immersed in 50 ml of water. After 24 h of immersion at 20°C with occasional agitation, the pieces of film were taken out and dried to constant weight in an oven at 105°C , to determine the weight of dry matter which was not solubilised in water. The measurement of solubility of the films was determined as follows:

$$\text{SOL} = (M_i - M_f)/M_i \times 100\% \quad (1)$$

Where, SOL is the percentage of soluble material, M_i is the initial mass and M_f is the final mass of the sample.

Moisture Content

We determined by three square of film (2×2 cm) were cut and weighted and then keep those film in an oven at 105°C for 24 h. The weight loss was measured after 24 h heating.

$$\text{MC} = (M_i - M_f)/M_i \times 100\% \quad (2)$$

Where, MC is the percentage of moisture content of the samples, M_i is the initial mass and M_f is the final mass of the sample.

Contact Angle - Polymer-nanocomposite thin film is one of the basic properties to study the wettability of packaging materials and is an indicator of the hydrophilic/hydrophobic properties of the material. For measurement of contact angle we used goniometer.

Thermal Stability Analysis

Completed with a NETZSCH (STA 409 PC). Samples were placed in the balance system and heated from 25 °C to 400 °C at a heating rate of 5 °C/min in Argon atmosphere. The onset temperature was calculated using proteus analysis software.

RESULTS AND DISCUSSION

Apparent Film Properties

Pure chitosan, chitosan with glycerol and chitosan-based nanocomposite films were observed to be flexible, free-standing and transparent. The CS-HNC films were seen with a slight yellowish tint and CS-SNP films are slight whitish.

Tensile Properties

The thickness of the polymer-nanocomposite films was not significantly different from that of pure films i.e. thickness was not affected by compositing with the nanoparticles used.

Tensile properties of Chitosan Films

As we know that with the using of plasticizer the polymer can get more plasticity. So, here we use glycerol as the plasticizer for our nanoparticle embedded films. With the increasing wt% of plasticizer, the tensile strength decreases but the film showed more plasticity. By adding of 60:40 ratio glycerols in chitosan films, loses 2.69 times tensile strength but gets plasticity around 11.87 times.

Table -1 Tensile Properties of Chitosan Films

Chitosan : Glycerol	Film Thickness (mm)	U.T.S (Mpa)	Elongation (%)
100:0	0.135±0.011	45.28±2.91	4.565±0.594
80:20	0.124±0.003	22.83±0.55	14.596±4.074
60:40	0.111±0.014	12.25±3.16	58.793±1.740

Tensile Properties of Chitosan Films Embedded with the Nanoparticles

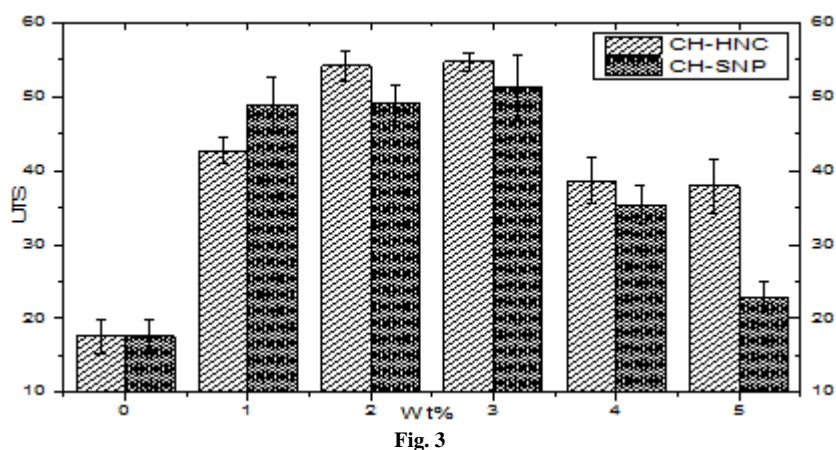
Tensile strength and elongation of the chitosan based nanocomposite films were increased and again decreased with the increasing of the weight percentages of the nanoparticles.

Table -2 Chitosan with Halloysite Nanoclay

Halloysite Nanoclay (wt%)	Film Thickness (mm)	U.T.S (Mpa)	Elongation (%)
0	0.092±0.003	17.57±2.36	9.110±0.260
1	0.086±0.003	42.64±1.79	12.496±0.886
2	0.081±0.007	54.19±2.06	13.156±0.782
3	0.089±0.004	54.70±1.27	17.880±0.756
4	0.084±0.001	38.65±3.03	4.640±1.253
5	0.091±0.002	37.95±3.66	5.583±1.510

Table -3 Chitosan with Silica Nanoparticles

Silica nanoparticle (wt%)	Film Thickness (mm)	U.T.S (Mpa)	Elongation (%)
0	0.092±0.003	17.57±2.36	9.110±0.260
1	0.090±0.013	48.90±3.70	5.852±2.800
2	0.100±0.010	49.13±2.53	6.970±2.000
3	0.082±0.002	51.21±4.33	6.740±2.920
4	0.096±0.005	35.42±2.66	6.797±2.888
5	0.110±0.004	22.91±1.98	9.280±3.504



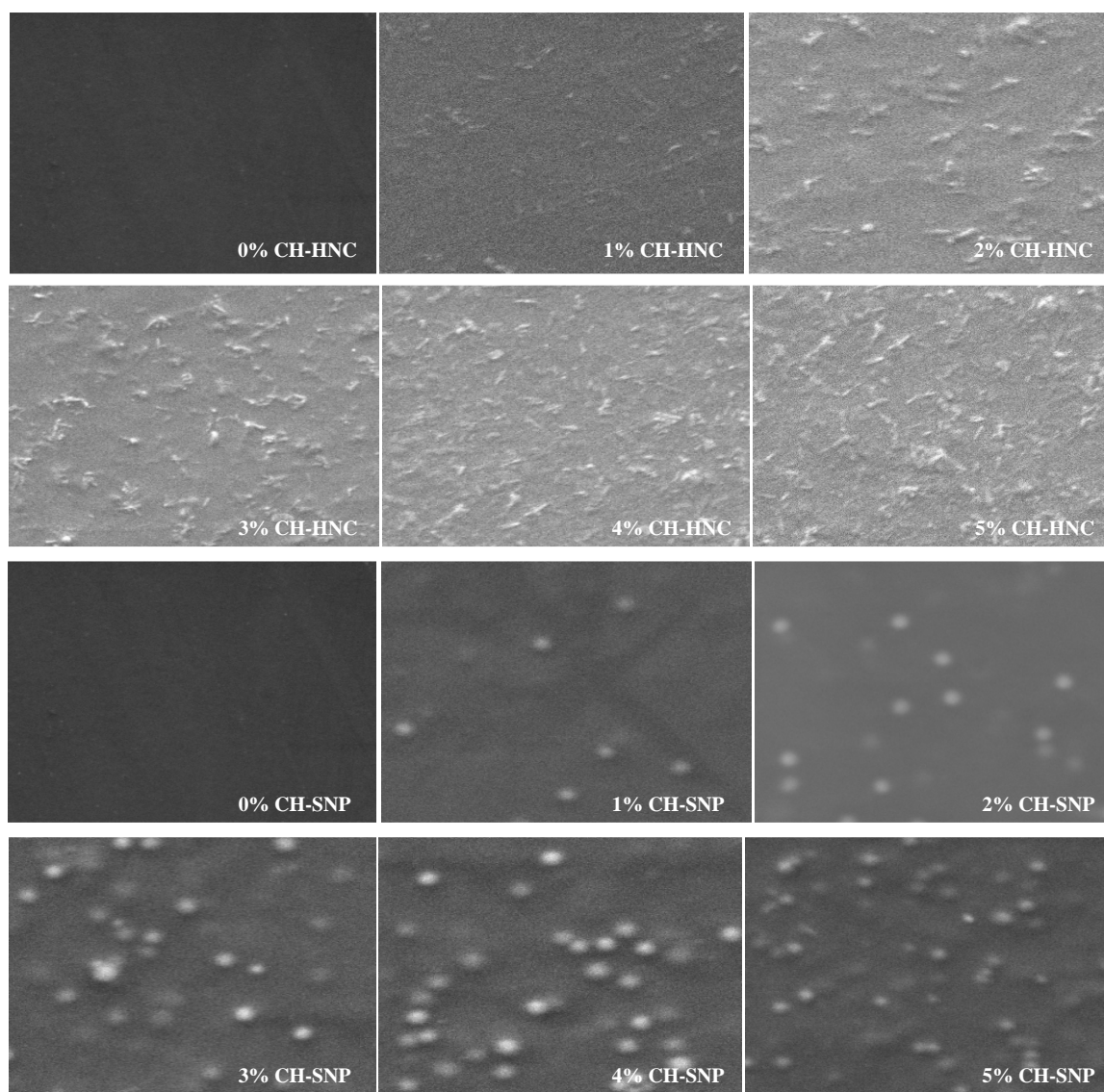


Fig.4 Scanning Electron Microscope (SEM) observation

Water Solubility Measurement

The solubility of chitosan in water is influenced by so many factors, i.e. the presence of plasticizer, nanoclays, and nanoparticles etc.

Water Solubility of Chitosan Films

Here we used glycerol as the plasticizer. The bonding with the plasticizer decreased the water solubility with an increase of plasticizer ratio.

Table -4 Water Solubility of Chitosan Films

Chitosan : Glycerol	Water Solubility (%)
100:0	24.627±0.769
80:20	20.830±1.077
60:40	18.467±0.355

Water Solubility of Chitosan Films Embedded with the Nanoparticles

Water solubility of chitosan based nanocomposite films decreased with the increase in the content of nanoparticle.

Table -5 Water Solubility of Chitosan Films Embedded with the Nanoparticles

wt%	avg. Water Solubility of CS-HNC (%)	avg. Water Solubility of CS-SNP (%)
0	20.830±1.077	20.830±1.077
1	19.210±0.802	18.570±0.681
2	18.640±0.203	18.477±0.464
3	18.157±0.286	18.427±0.100
4	17.973±0.323	18.207±0.196
5	17.927±0.881	17.630±0.389

From the above table we can say that the water solubility of the composite was related to the halloysite nanoclay concentration because there is no significant change in water solubility for silica nanoparticles with the increasing of weight percentages. With the addition of Halloysite nanoclay or silica nanoparticle to the film matrix, the observed decrease in water solubility can be attributed to the formation of hydrogen bonds between chitosan matrix and the nanoclay or nanoparticles.

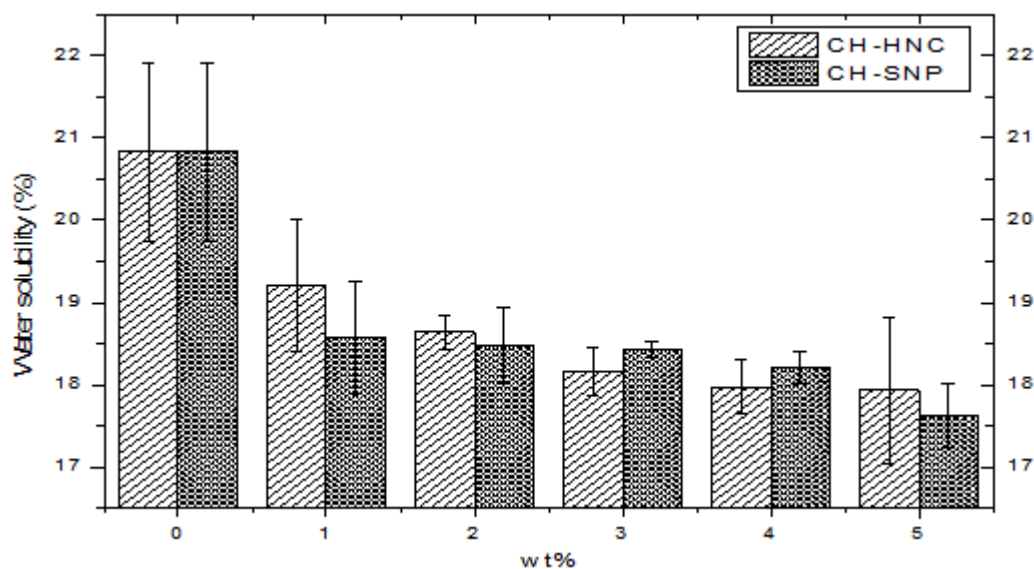


Fig. 5

Moisture Contents Measurement

The moisture content is increased or decreased in the nature of hydrophobicity or hydrophilicity of the polymer and the plasticizer and the nanoclay and the nanoparticles. The influence of the plasticizer is much more significant for the polymer films. Because of the hydrophilic nature of plasticizer (glycerol), the moisture content is increased with the increase of glycerol.

Moisture content of Chitosan Films

The pure chitosan film with the different ratio plasticizer showed changes in moisture content. From the table below we can see that the moisture content is increasing with increase of glycerol content for its hydrophilic nature.

Table -5 Moisture Content of Chitosan Films

Chitosan : Glycerol	Moisture Content (%)
100:0	16.847±0.121
80:20	25.147±0.884
60:40	40.810±1.107

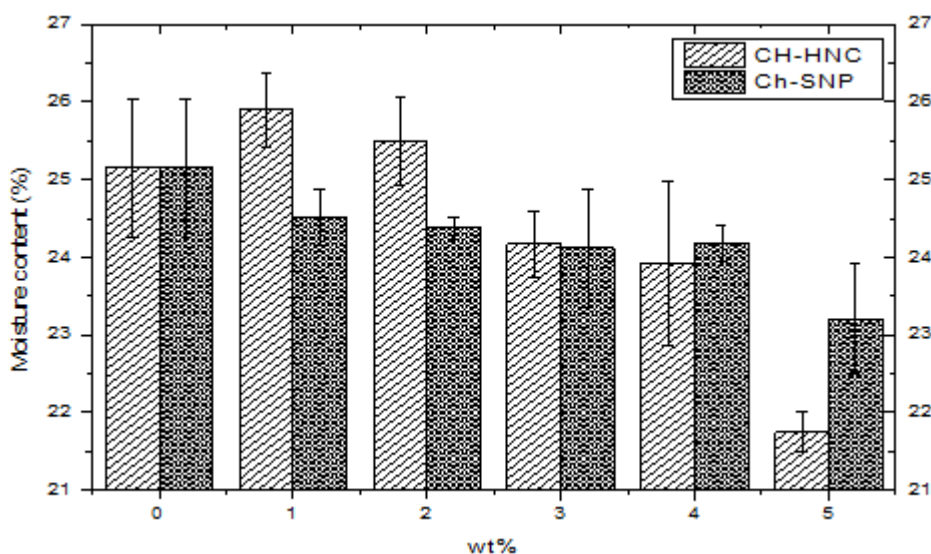


Fig. 6

From the above graph we can compare the effect of the nanoclay and the nanoparticle on moisture content for chitosan films. The silica nanoparticle has not much more influenced like nanoclay. We got less moisture content for Halloysite nanoclay in 5% weight films.

Table -6 Average Moisture Content

wt%	avg. Moisture Content of CS-HNC (%)	avg. Moisture Content of CS-SNP (%)
0	25.147±0.884	25.147±0.884
1	25.903±0.477	24.507±0.361
2	25.487±0.563	24.377±0.147
3	24.170±0.421	24.117±0.751
4	23.920±1.051	24.173±0.236
5	21.745±0.256	23.210±0.704

Contact Angle Measurements

The contact angle of water is one of the basic wetting properties of packaging films and is an indicator of the hydrophilic/hydrophobic properties of the film. Usually, the more hydrophilic a film is, the lower the contact angle value it has.

Table -6 Contact Angle of Chitosan Films

Chitosan : Glycerol	Contact angle (°)
100:0	98
80:20	60
60:40	52

Previously we discussed for the water solubility that the plasticizer is hydrophilic in nature so for that the contact angle decreased with the increase of plasticizer ratio.

wt%	Contact Angle of CS-HNC (°)	Contact Angle of CS-SNP (°)
0	60	60
1	65	61
2	68	63
3	73	66
4	74	67
5	76	68

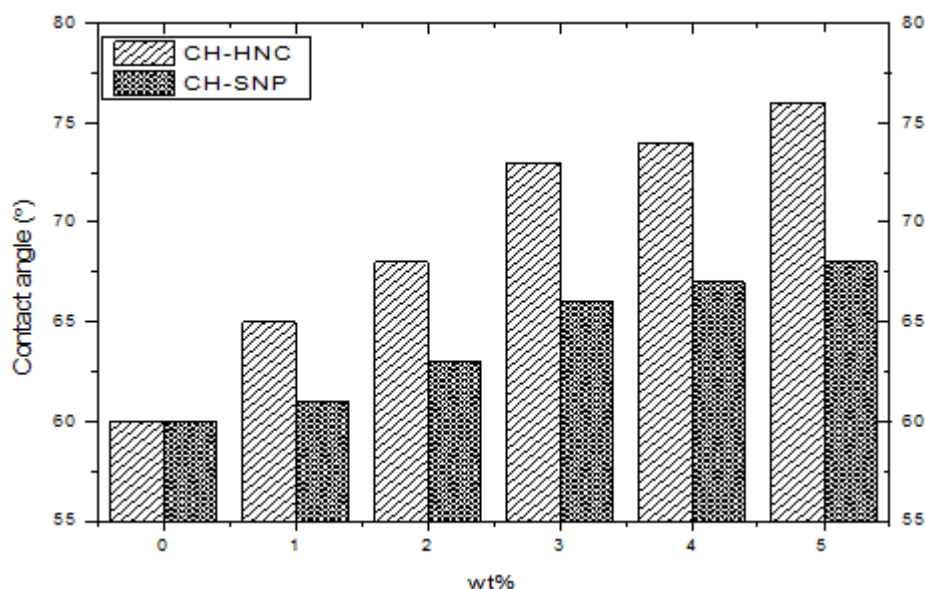


Fig. 7

For chitosan films the Halloysite nanoclay showing the maximum hydrophobicity. With the increase of Halloysite nanoclay the surface area of hydrophobicity increases, for that the contact angle is increasing but for silica nanoparticle (spherical) the surface area is not much more like Halloysite nanoclay (nanotube) in maximum amount.

Thermal Stability Analysis

We measured the thermal degradation temperature of the polymer films. Changes in the thermal stability of polymer films, with addition of nanoclays and nanoparticles were examined by TGA.

TGA of Chitosan Films

The degradation temperature of chitosan is not significantly influenced by the nanoclay and nanoparticles that much. Generally, the thermal stabilities of chitosan-nanocomposites were not enhanced as compared with pure chitosan film. The polymer chains were not intercalated into the galleries of the nanoclays and nanoparticles and hardly increased the thermal stability.

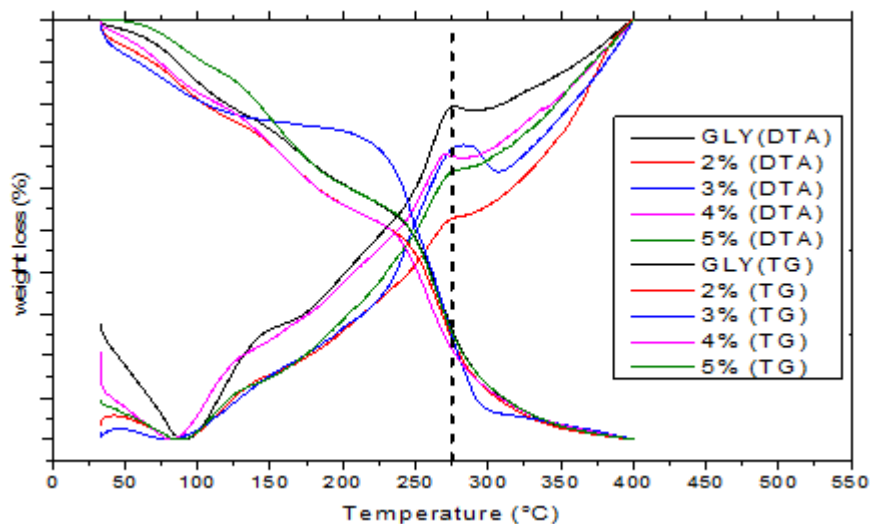


Fig. 8

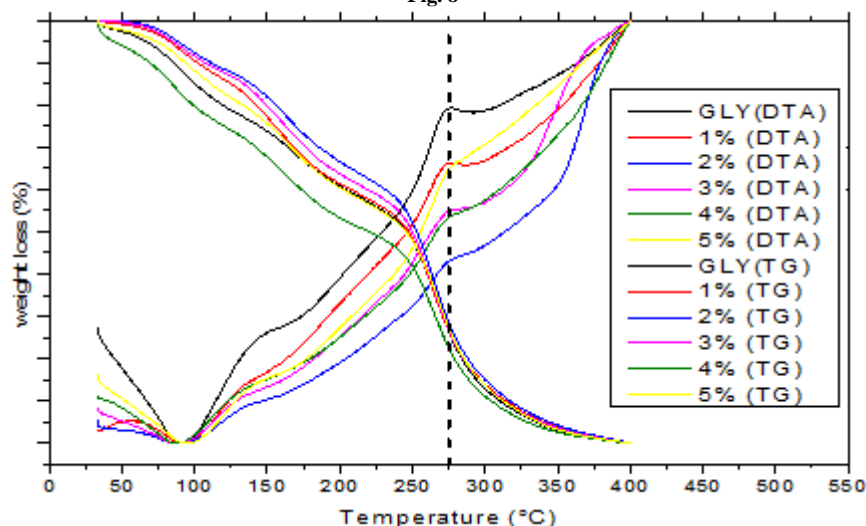


Fig. 9

So from above curve we can see that no degradation temperature is changing with the nanoparticles. All the chitosan films are degrading in between 270-275°C.

CONCLUSION

- Here we have used two types as well as two different shapes of nanoparticles (nanotube and nanosphere) for the Chitosan-Nanocomposite thin films and we got several changes in tensile strength, microstructure, water solubility, moisture content and contact angle.
- For both systems, we observed significant changes in tensile strength and elongation by changing the plasticizer ratio in chitosan films. For chitosan by using 60:40 ratio plasticizer we examined that the tensile strength decreased 2.69 times and elongated 11.87 times. So by using of plasticizer we can get more plasticised films but not strengthen films. If we consider 80:20 ratio plasticizer in chitosan films from that we got proper tensile strength and elongation. So for making the chitosan-nanocomposites we used 80:20 ratio plasticizers.
- For Halloysite nanoclay we got much more tensile strength than silica nanoparticles in chitosan films because of the good intercalation between the polymer-nanoparticles and for the surface area difference also. We got maximum strength for Halloysite nanoclay because the structure of Halloysite is mainly layered silicate structure and by adding on polymer the nanoclay exfoliated. So, the strength increased. But in the case of silica nanoparticle, that is a solid sphere only.

- Water solubility decreases with the increase of plasticizer. The pure chitosan films were much more soluble in water than chitin. With the addition of halloysite nanoclay or silica nanoparticle to the film matrix, the observed decrease in water solubility can be attributed to the formation of hydrogen bonds between chitosan matrix and the nanoclay or nanoparticles.
- Moisture content in chitosan films as influenced by the plasticizer is much more significant because of the hydrophilic nature of plasticizer (Glycerol). The moisture content is increased with the increase of plasticizer. We can compare from the results that the effect of the nano clay and the nanoparticle on moisture content for chitosan films, the silica nanoparticle has not much more influenced like nanoclay. We got less moisture content for halloysite nanoclay in 5% weight films because of hydrophobic nature of nanoclay. The nanoclay restricted the water molecule in absorption to the films.
- Contact angle of the films is directly related to the hydrophobicity and hydrophilic nature of the films.
- The degradation temperature of the chitosan films is not changing with the adding of nanoclays and nanoparticles.
- From the SEM picture we got that by the increasing of nanoclay and nanoparticles the films got much rougher surface.

From over all data we can conclude that, halloysite nanoclay has much more influence than silica nanoparticles for thin films.

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