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Na-Carboxmethylecellulose Properties Affected by Nanoparticles in Different Shape and Weight Percentages

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ABSTRACT

Na-carboxymethylcellulose (cmc) is biopolymer that offers immense structural possibilities for chemical and mechanical modifications to generate novel properties, functions and applications especially in biomedical area. In this work films fabricated from cmc incorporated with plasticizer at different weight ratios were prepared. This was carried out by employing a solvent-casting method incorporating halloysite nanoclay (nanotube) and silica nanoparticle (spherical) into the films. Scanning Electron Micrographs showed that nanoparticles were dispersed homogeneously throughout the polymer matrix in all of the cmc-nanocomposite films; tensile test showed that the mechanical strength of the films increased with increasing 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 hydrophilicity increased with the addition of nanoparticles, as seen from the contact angle, moisture content and water solubility results.

Key words: Na-carboxymethylcellulose (CMC), glycerol, halloysite nanoclay, silica nanoparticles

INTRODUCTION

Glucose unit in the cellulose chain has three hydroxyl groups, each of which is capable of hydrogen bonding to an adjacent molecule. Because of the abundance of hydroxyl groups, and their ability to hydrogen bond to a neighboring molecule, the chains are bound tightly together. Water molecules, at any temperature, cannot force their way in between the chains to hydrate them, thus cellulose is water insoluble. Na-carboxymethylcellulose is an anionic water-soluble polymer derived from cellulose. Due to its innocuousness, it is used as a stabilizer, binder, thickener, for suspension and as water retaining agent in food industry, pharmaceutical, cosmetic, paper, and other industrial areas [1 and 2]. 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 [3], electrical [4], optical [5 and 6] and thermal properties [3-6]. 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 [3 and 7].

In this work, the nanocomposite films are consisting of inorganic halloysite nanoclay (nanotubes), silica nanoparticle (spherical) and organic polymer as Na-carboxymethylcellulose (water soluble) and glycerol as the plasticizer.

MATERIAL AND METHODS

Na-Carboxymethylcellulose (cmc)

In where cellulose molecule have glucose unit in the cellulose chain has three hydroxyl groups, each of which is capable of hydrogen bonding to an adjacent molecule and cellulose connected together in a long, linear chain. Manufacture of cmc from cellulose by following:

Step (one) R-OH + NaOH = R-ONa + H_2O

Step (two) R-ONa +Cl-CH_2-COONa = R-O-CH_2-COONa

The above reaction is for the manufacture of cmc. It is essentially a two-step process. In the first step, cellulose is suspended in alkali to open the bound cellulose chains, allowing water to enter. Once this happens, the cellulose is then reacted with sodium monochloroacetate to yield Na-carboxymethylcellulose [8].

Plasticizer

We used here was glycerol. Glycerol is the simplest trihedric alcohol with a specific gravity of 1.26. It is a colorless, odorless, 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 Nanoclays

It is clay a mineral, occurring as soft, smooth, and amorphous masses of white color. 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 $Al_2Si_2O_5(OH)_4.2H_2O$. For our experiment, we used halloysite nanoclay from sigma-aldrich, India. The properties of this given nanoclays are nanopowder, diameter × length: 30-70nm × 1-3µm, color: 75-96, hunter brightness, refractive index: *n*20/D 1.54, pore size: 1.26-1.34ml/g pore, volume surface area: 64 m^2/g, capacity: 8.0meq/g, cation exchange capacity density: 2.53 (true specific gravity).

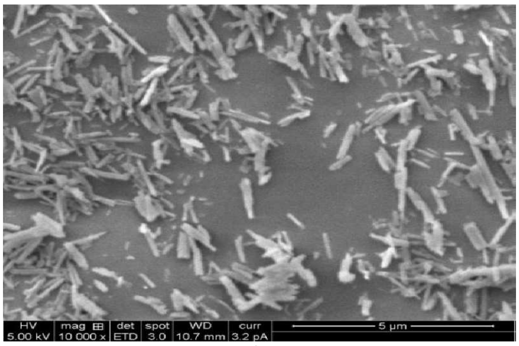

Fig.1 SEM image of halloysite nanoclay

Silica Nanoparticles

We had synthesized from Tetra-Ethyl Ortho-Silica (TEOS) in the presence of surfactants [9]. We used for to synthesis silica nanoparticles by adding 1.6ml NH_4OH in 40ml Ethanol and 3.2ml water and sonicated for 10mins. After sonication we added 2.4ml TEOS and again sonicated for 10 mins and after sonication leave it for 2h for forming the silica nanoparticles. After 2h the solution is getting whitish for forming of silica nanoparticles, we collect the nanoparticles by centrifuging in 3000rpm at 15°C for 15mins for several times and then dried it in the furnace at 40°C and after that we got 0.70678gm of silica nanoparticles.

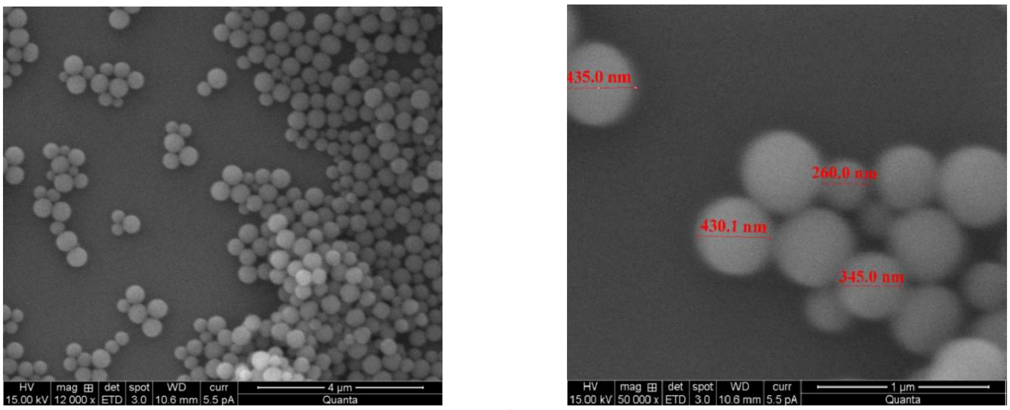

Fig.2 SEM images of silica nanoparticle

Preparations of the Films

We have done by solvent casting method [10]. Polymer solution was prepared by dissolving 0.8gm of polymer powder in 50ml of aqueous solution and 0.2gm glycerol, using a magnetic stirring plate at 90°C for 20min 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 50ml of aqueous solution for 1h at room temperature. This dispersion was added to the polymer solution, stirred for 1h at room temperature and then for 30min at 25°C in an ultrasonic bath. The dispersion was then poured onto petri dish (diameter = 9cm) and dried at 40°C for 24h, 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 20min 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 cmc films, cmc with glycerol (80:20 and 60:40) films, cmc-halloysite nanoclay nanocomposite films (cmc-HNC), cmc-silica nanoparticle nanocomposite film (cmc-SNP).

Thickness Measurements

Film thickness was measured to the nearest 0.001mm using a held micrometer. 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 [11] 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 2.5KN). Rectangular specimens 50 ×10mm were cut. Initial grip separation was set at 20mm, and cross-head speed was set at 100mm/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 20kV:3nm 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: 20Ma max.) before characterization. The samples were characterized in ESEM Quanta 200 electron microscopy at 5kV with 15mm working distance.

Water Solubility

It was defined [12] by the content of dry matter solubilised after 24h 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 × 2cm) were cut, weighed and immersed in 50ml of water. After 24h 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 solubilized in water. The measurement of solubility of the films was determined as follows:

$SOL = (M_i - M_f)/M_i \times 100\%$ 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

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

$MC = (M_i - M_f)/M_i \times 100\%$ 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

It was 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 cmc, cmc with glycerol and cmc-based nanocomposite films were observed to be flexible, free-standing and transparent.

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. 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. In the case of cmc polymer with the increasing the wt% of glycerol the plasticity is increasing and the tensile strength is decreasing. For adding 60:40 ratio glycerol in cmc polymer the elongation increases 6.94 times and tensile strength decreases 2.99 times. Tensile strength and elongation of the cmc based nanocomposite films were increased and again decreased with the increasing of the weight percentages of the nanoparticles.

Table-1 Tensile Properties of CMC Films

CMC : Glycerol	Films Thickness (mm)	UTS (Mpa)	Elongation (%)
100:0	0.089±0.003	51.42±3.87	3.263±0.486
80:20	0.092±0.003	17.57±2.36	9.110±0.260
60:40	0.080±0.000	12.88±1.02	25.930±3.020

Table-2 Tensile Properties of CMC Films Embedded with Halloysite Nanoclay

Halloysite Nanoclay (wt%)	Films Thickness (mm)	UTS (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

The maximum tensile strength was observed with the 3% halloysite nanoclay i.e. tensile strength increases 2.11times and the plasticity also.

Table-3 Tensile Properties of CMC Films Embedded with Silica Nanoparticles

Silica Nanoparticle (%)	Films Thickness (mm)	UTS (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

For silica nanoparticle we got the maximum tensile strength with the addition of 3%. The strength increases 1.91 times. But there is no significant change on plasticity with the increases of nanoparticles.

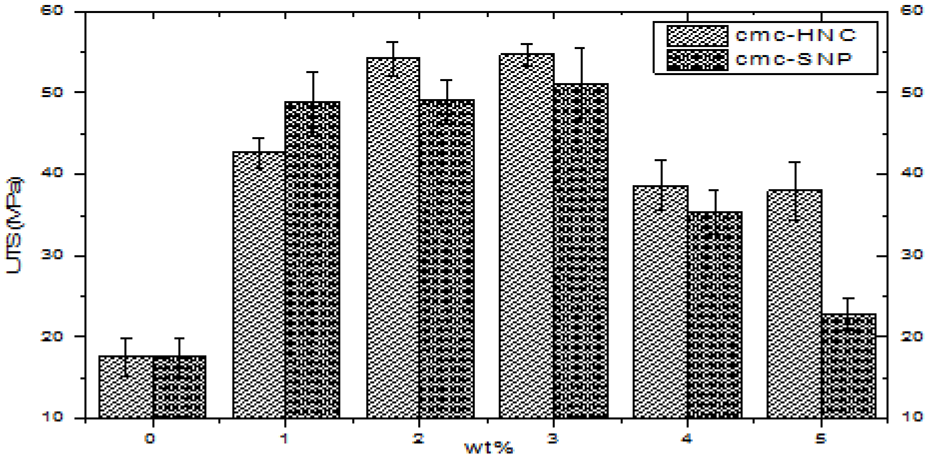

Fig.3 Tensile strength comparison of two different types of nanoparticles embedded films

Water Solubility Measurement

Cellulose is highly water soluble in nature. It was observed that with the addition of glycerol, halloysite nanoclay and silica nanoparticle there was no significant variation in the water solubility of cmc based nanocomposite films.

Scanning Electron Microscope (SEM) Observation

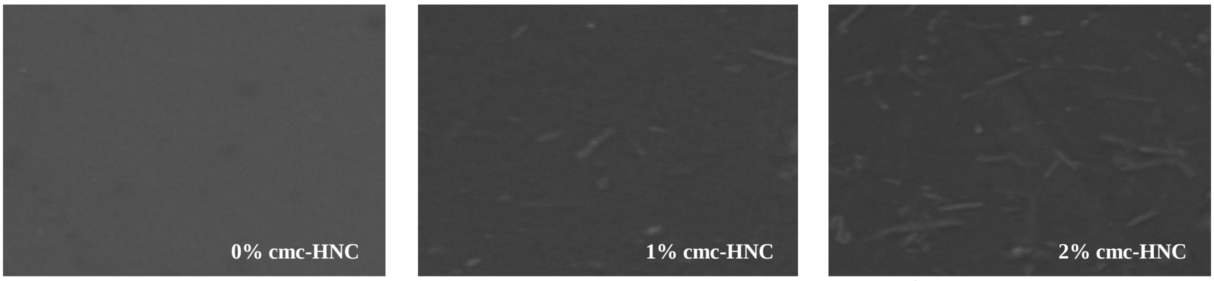

Fig.4 Halloysite nanoclay (0%, 1% and 2%) distribution embedded films

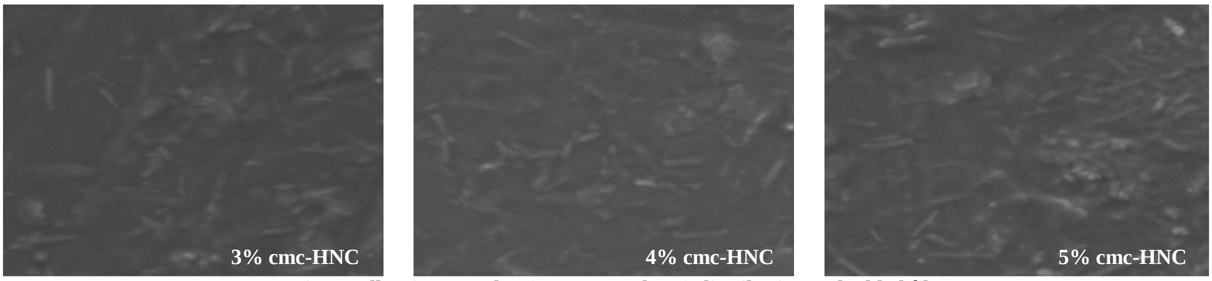

Fig.5 Halloysite nanoclay (3%, 4% and 5%) distribution embedded films

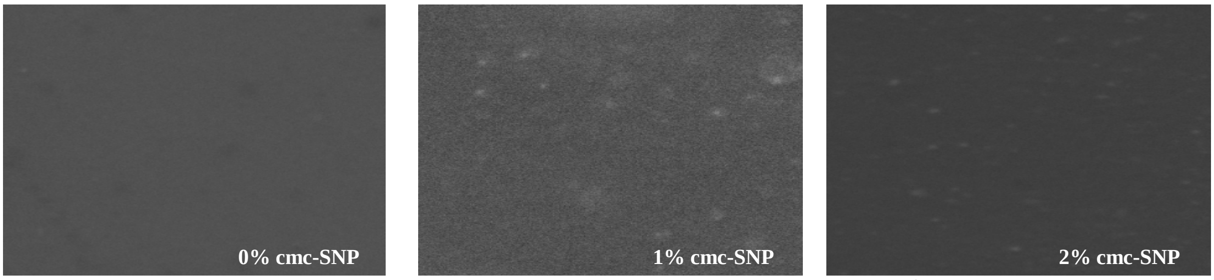

Fig.6 Silica nanoparticles (0%, 1% and 2%) distribution embedded films

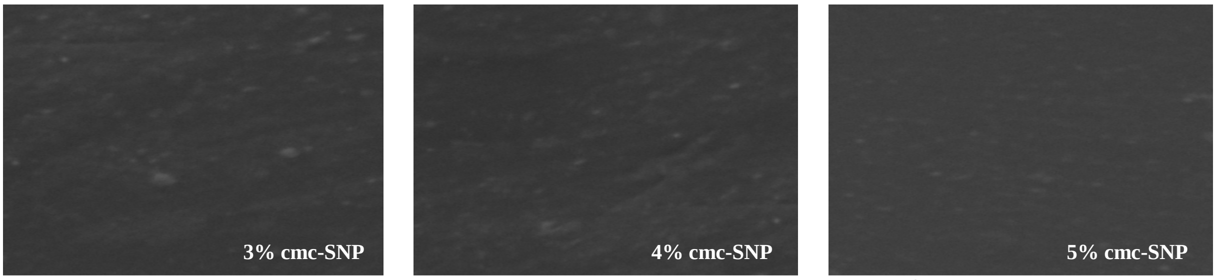

Fig.7 Silica nanoparticles (3%, 4% and 5%) distribution embedded films

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. The pure cmc film with the different ratio plasticizer showed changes in moisture content. From the table-4 we can see that the moisture content is increasing with increase of glycerol content for its hydrophilic nature. Due to the highly hydrophilic nature of cmc, moisture content increases with the increase of nanoclay weight. For silica nanoparticle addition also the moisture content increases with the increase of silica nanoparticles. The halloysite nanoclay holds much more water molecule than silica nanoparticle and cmc is highly hydrophilic in nature for that nanoparticle cannot showing there hydrophobic nature in cmc films.

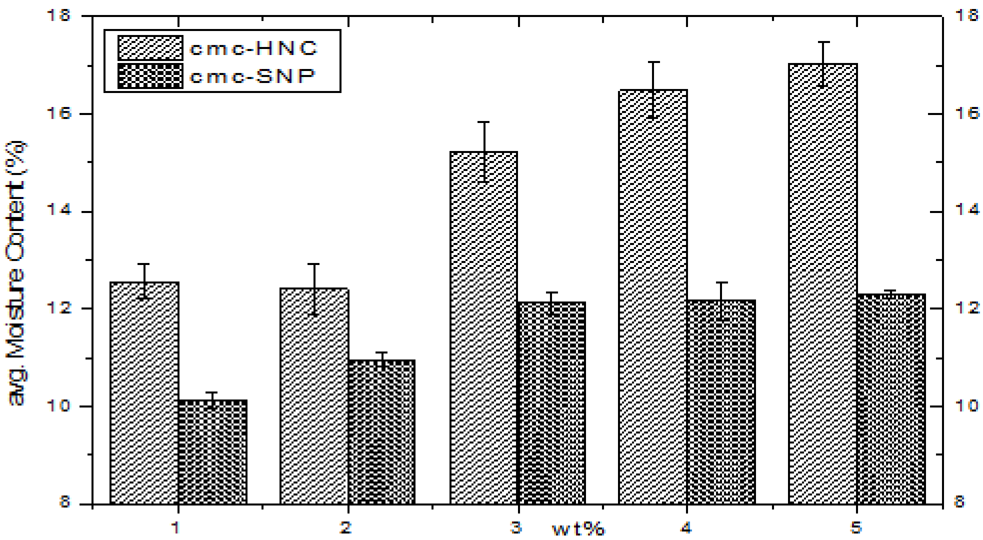

Fig.8 Moisture content comparison of two different types of nanoparticles embedded films

Tabile-4 Moisture Content of CMC Films

CMC : Glycerol	Average moisture content (%)
100:0	16.070±0.324
80:20	9.620±0.341
60:40	34.560±0.460

Table-5 Moisture Content of Two Types of Nanoparticle Embedded Films

wt%	Avg. moisture content for cmc-HNC	Avg. moisture content for cmc-SNP
0	9.620±0.341	9.620±0.341
1	12.563±0.336	10.133±0.157
2	12.407±0.500	10.953±0.145
3	15.226±0.607	12.127±0.237
4	16.483±0.567	12.173±0.396
5	17.023±0.446	12.307±0.074

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. For pure cmc film with the plasticizer that is showing totally hydrophilic in nature. But for 80:20 ratios plasticizer the film is showing hydrophobic in nature, for that the contact angle and the moisture content was also less.

For the hydrophilic nature of the cmc, it is showing the hydrophilicity with the increasing of the nanoclay also. For the silica nanoparticle also the cmc films retain its hydrophilicity and films get more hydrophilic with the increase of nanoparticles.

For increasing the amount of halloysite nanoclay the surface area is increasing with the comparison of silica nanoparticles. So for that halloysite nanoclay embedded film is showing more hydrophobic in nature. Although for the strong hydrophilic nature of cmc film the hydrophobicity cannot show by the nanoclay and the nanoparticles.

Table-6 Contact Angle of CMC Films

CMC : Glycerol	Contact Angle (°)
100:0	56
80:20	60
60:40	35

Table-7 Contact Angle Measurement of Two Types of Nanoparticle Embedded Films

wt%	Avg. contact angle for cmc-HNC	Avg. contact angle for cmc-SNP
0	60	60
1	54	42
2	50	40
3	44	39
4	43	36
5	39	35

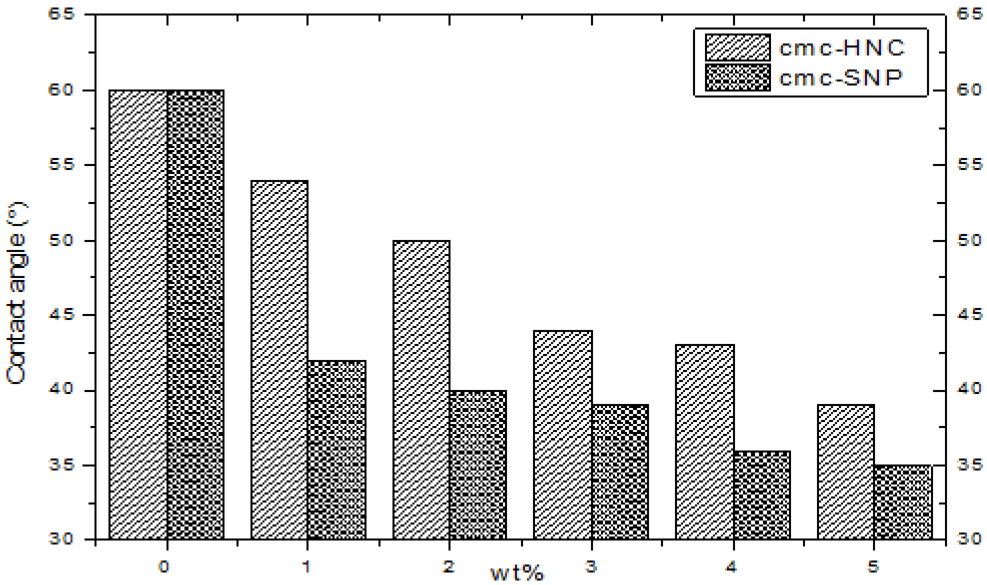

Fig.9 Moisture content comparison of two different types of nanoparticles embedded films

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. The degradation temperature of cmc is not significantly influenced by the nanoclay and nanoparticles that much. Generally, the thermal stabilities of cmc-nanocomposites were not enhanced as compared with pure cmc film. The polymer chains were not intercalated into the galleries of the nanoclays and nanoparticles and hardly increased the thermal stability. So from above curve we can see that no degradation temperature is changing with the nanoparticles. All the cmc films are degrading in between 280-285°C.

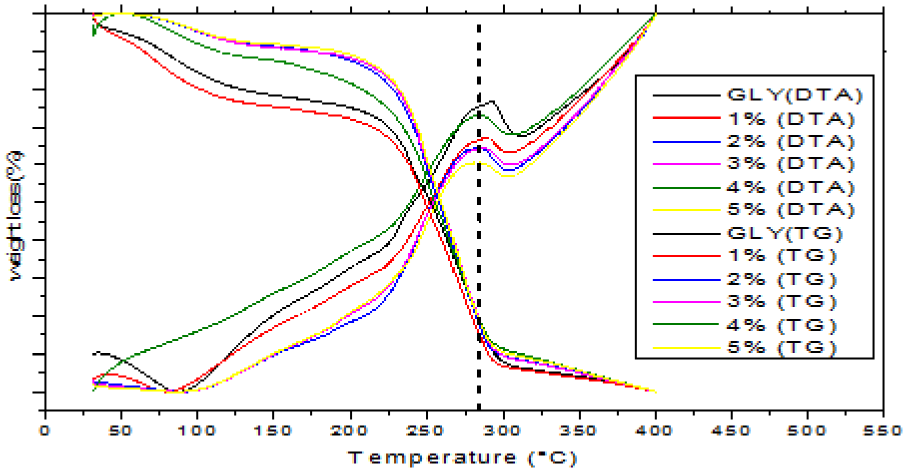

Fig.10 TGA of halloysite nanoclay embedded CMC films

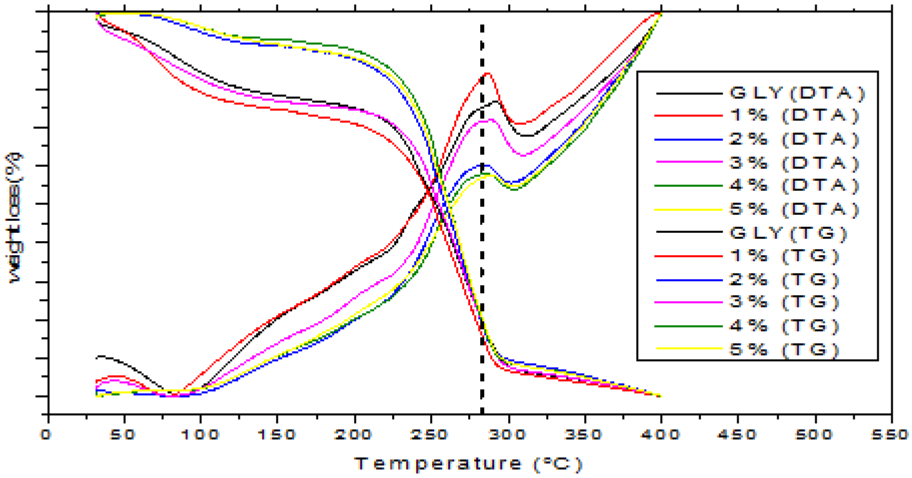

Fig.11 TGA of silica nanopartcles embedded CMC films

CONCLUSION

Here we have used two types as well as two different shapes of nanoparticles (nanotube and nanosphere) for the cmc-nanocomposite thin films and we got several changes in tensile strength, microstructure, moisture content and contact angle.

For both systems, we observed significant changes in tensile strength and elongation by changing the plasticizer ratio in cmc films. For cmc by using 60:40 ratio plasticizers we examined that the tensile strength decreased 2.99 times and elongated 6.94 times. So by using of plasticizer we can get more plasticised films but not strengthen films. If we consider 80:20 ratio plasticizers in cmc films from others then we can get proper tensile strength and elongation. So for making the cmc-nanocomposites we used 80:20 ratio plasticizers. For halloysite nanoclay we got high tensile strength than silica nanoparticles in cmc films because of the good intercalation between the polymer-nanoparticles and for the surface area difference and halloysite is mainly layered silicate structure and by adding on polymer the nanoclay exfoliated. Water solubility is not influenced embedded by nanoparticles for cmc films. Moisture content in cmc 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 nanoclay and the nanoparticle on moisture content for cmc 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 cmc 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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