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Study on the Effect of Nano TiO_2 on Mechanical Properties of Chitosan

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Abstract: *Owing to the importance of enhanced properties in various spectrums, a good number work has been carried on polymer nanocomposite materials. Augmentation of the properties of materials to fit a them into certain applications has led to the development in composite materials. Polymers due to their vast applicability are structurally exploited to strenghthen their properties which are of the essence. In this work we have impregnated nano powders of Titanium dioxide into the Chitosan polymer matrix in order to pull off a polymer nanocomposite. Attempts have been made to study a few mechanical properties of the nanocomposite like tensile strength, stiffness, modulus of elasticity, percentage elongation at fracture. Nanocomposite films were prepared by solution casting by adding different weights of nano Titanium dioxide to the solution containing 2g of Chitosan. It has been observed that the material propeties of neat Chitosan has undergone remarkable changes after it was doped with nano Titanium dioxide. The Young's Modulus of nano Titanium dioxide doped Chitosan decreased when compared to undoped material for all concentrations of the dopant. Percentage elongation at fracture is found to be having a sudden rise at a particular concentration (0.06gm) of Titanium dioxide in the Chitosan film. The stiffness TiO_2 doped Chitosan observes a notable fall in contrast to that of the neat Chitosan film.*
Keywords:*Chitosan, nano titanium dioxide, polymer nanocomposite*

I. Introduction

In this era of increasing material pollutants, material scientists are in a race of developing materials that exhibit optimum properties among which biodegradability or the eco-friendly nature of the materials has become inevitable. Chitosan, a mucopolysaccharide is one such polymer which has walked its way in fetching its place among the popular biopolymers due to its biodegradability, biocompatibility and adsorption properties. A constantly evolving area of study has emerged to investigate the various applications of polysacharides such as chitin, chitosan, hyaluronic acid, and alginate. Chitosan is a non-starch biopolymer derived from Chitin. Chitin or Chitosan being the next abundant natural biopolymer after cellulose, extensive research is being conducted on Chitosan based composites mainy due to its availability and diverse properties when combined with other materials. Chitin and Chitosan being insoluble in water, they are widely contained in shells of crabs and shrimp, cuticles of insects, in specific categories of fungi etc. Chitosan of varying types are available based on their varying degrees of deacetylation which also causes variation in their respective molecular weights. Various biological properties of Chitosan have attracted researchers and as a result they are being used in pharmaceutical, pharmacological, commercial, agricultural, and horticultural fields, in water filtration, cosmetic and paper industry etc [1]. Chitin has lower applicability when compared to Chitosan as it is insoluble in water and chemically rather unreactive. In the recent years, Chitosan-based drug delivery vehicles are attracting many researchers especially for developing safe and efficient Chitosan-based particulate drug delivery systems. Chitosan exhibits unique behaviour for drug delivery systems when compared to other polysacharides of its kind. Apart from this, investigations are being carried out on Chitosan to be used in membrane electrolyte and electrode is various fuel cells. Another property that has drawn the attention of the researchers towards Chitosan is its film forming characteristic. Chitosan is being utilized in manufacturing number of industrial and consumer products due to its gel forming properties and swellability in water.

On the other hand Titanium being the ninth abundant metal in the earth's crust is known for its toughness, high strength and can be typically thought of as being chemically inert. It is usually available in several kinds of rocks and mineral sands in the oxidized state as Titanium dioxide(TiO_2) which is a white, solid, non-hazardous, inorganic substance. Titanium dioxide is usually manufactured as a nanomaterial and as a pigment grade, both having similar production processes. Pigment grade TiO_2 (200nm-350nm) are used where white opacity and brightness are the parameters of interest as pigment grade TiO2 has excellent light-scattering properties. Nano TiO_2 (less than 100nm is size) provides ultraviolet absorption in spite of appearing transparent and is not inert. Applications of nano TiO_2 can be classified into two categories. Firstly application of nano TiO_2 as a catalyst or semiconductor and secondly as ultraviolet light attenuator. As photocatalysts, nano TiO_2 is being used in various engineering and chemistry appliactions and as semiconductors it is being applied in electronics field. Selective Catalytic Reduction (SCR) systems which are used in large industrial boilers, combustion plants and stationary or automotive diesel engines convert harmful nitrous oxides(NO_x) into harmless nitrogen and oxygen. Nano TiO_2 photocatalysts are highly dispersed and are sensitive to visible light and are used in manufacturing self- cleaning surfaces as on glass. Recenlty nano TiO_2 is being used in solar cells for its electron trasnfer properties. Material pollutants being a major concern today, research has been conducted to study the effect of nano TiO_2 on the environment [2]. This project analyzes the behavior of a nanocomposite polymer i.e. Chitosan doped with nano TiO_2. This study involves the preparation of neat Chitosan films, Chitosan films doped with nano TiO_2 powders and studying their mechanical properties. TiO_2 at high pressures underwent a rutile to baddeleyite transition which is a stable phase of ZrO_2 at ambient conditions resulting in increase in it's coordination number of titanium and decrease in it's volume [3]. In the work "Preparation and Characterization of Gelatin and Chitosan Films", Jeanette Mirian Diop[4] describes the optimal method of preparing the films in order to improve their mechanical properties. Results showed that Chitosan films that were washed with Sodium hydroxide (NaOH) were less succeptible to humidity and Chitosan films prepared with acetic acid (CH_3COOH) were easy to handle during film preparation and testing. Marino Quaresimin *et al.*, [5] discussed important issues regarding nano composite modelling and classified the available modelling strategies. These strategies for the assessment of nanocomposite mechanical properties is thought as a necessary tool for the development of new effective approaches. A molecular dynamics simulation has been used by Maenghyo Cho *et al.*, [6] who studied the effect of size of Al_2O_3nanoparticles on the mechanical properties of thermoset epoxy-based nano composites. Efficient estimation of particle size and epoxy network effects were made using the sequential bridging method. An effective interface concept was incorporated as a characteristic phase which could describe the particle size effects. The values calculated from the micromechanics model agreed with those of the simulation. Another study on epoxy nano composites by Hongwei He *et al.*, [7] revealed that surface modification of nano-particles, which can enhance the interfacial properties between nano-$CaCO_3$ and epoxy resin. This study also expressed that the mechanical and thermal properties of the nano composite enhanced. Esam A. El-Hefian, *et al.*,[8] examined the rheological properties of Chitosan in weak acid solutions. The parameters of interest being temperature, concentration, shearing time, and storage time. The results showed that shear thinning behaviour (pseudo-plastic non-Newtonian behaviour) was pronounced at temperatures from 20 to 50℃, but was more remarkable at lower temperature, the activation energy value derived from ln η vs. 1/T data was found to be 20.86kJ $mol^{-1}$and also the shear thinning behaviour was found to be pronounced at all concentrations. The TGA revealed that Chitosan decomposed in two different stages and this result was verified using DSC curves. Works have been cited where Chitosan was used as a dopant to dope polyhydroxybutyrate and the mechanical and thermal properties were investigated [9]. The DSC revealed increasse in the various thermal properties. TGA shows that the thermal stability of the polymer was enhanced when doped with chitosan. The Young's modulus of the polymer nanocomposite increased and was high at 40% concentration of chitosan in the composite Further increase in the concentration of chitosan decresed the ductility of the sample. Although a few studies are available on Chitosan-metal oxide composites, a work by F. Al-Sagheer and S.Muslim [10] demonstrates the mechanical and thermal properties of Chitosan-silica hybrid films and observed increase in the modulus of elasticity of the hybrid film in contrast with that of the neat film, increase in the glass transition temperature being directly proportional to the silica content in the hybrid film and also an increase in the thermal stability of the hybrid film. The transition of various properties of Chitosan were observed when Chitosan was doped with silica, a metal oxide. This casts-out the necessity of further research on Chitosan-metal oxide composites. In this work Chitosan films were branded by their properties like Modulus of Elasticity which is a measure of stiffness of the film, Tensile Strength which is the ability of the material to resist tensile derfomation, Yield Strength which is the stress at which the Chitosan film deforms permanently and Extension till Break or Elongation at fracture which is nothing but the extension of the film at its tensile strength.

II. Experimental Details

2.1 Materials and Equipment

Medium molecular weight Chitosan was purchased from Blue Line Foods (India) Pvt Ltd Mangalore. According to the vendor, the degree of deacetylation was between 75-85%. Nano Titanium dioxide was purchased from KMML Kollam, Kerala. Acetic acid was of reagent grade.

The thickness of the films was measured using a Mitutoyo made hand held micrometer. Lloyd universal testing machine with 5KN grips and cross head speed 25 mm/min, bench top thin film universal testing machine was used to study the mechanical properties of the thin films.

Care was taken to minimise the impact of inherent properties of the films like moisture content, physio-chemical properties, humidity of the atmosphere during testing which eventually would bring about variations in the results.

2.2 Nano Composite Preparation

The nanocomposite was prepared by solution casting method [11]. Thin films of neat Chitosan and Chitosan doped with different concentrations of nano Titanium dioxide were prepared.

The neat Chitosan film was prepared by adding 1gram Chitosan to 50ml of deioinzed water. This solution was stirried for about 0.5-1 hour using a magnetic stirrer. The pH levels of the solution was brought to the desired value by the controlled addition of acetic acid. The insoluble clumps in the solution were removed by filtration. Decanding method was adopted to extract the solvent. The clear solution obtained was cast into petri-dish for film formation. Curing process of the solution in the perti-dish took approximately about 4 days. Once dried, the films were gently peeled off from the glass plates.

The Chitosan films doped with nano TiO_2 were prepared as follows. 2gram Chitosan was added to 100mlof deionized water and stirred for about 12 hours while 0.02g, 0.06g, 0.1g, 0.2g, 0.4g, 0.6g & 1.0g of Titanium dioxide nano powder and acetic acid was added. The prepared clear solution was cast onto glass plates for film formation by drying it for about 4 days.

III. Result Analysis

3.1 Tensile Strength Analysis

TABLE 1 shows the variation of tensile strength in Chitosan with different concentration and also shows the variation when it is doped with Titanium dioxide.

Table 1. Variation of Tensile Strength

SL. NO.	MIXTURE	TENSILE STRENGTH
1.	Chitosan	19.51
2.	0.02 gm	12.82
3.	0.06 gm	13.05
4.	0.1 gm	13.26
5.	0.2 gm	17.34
6.	0.4 gm	8.51
7.	0.6 gm	11.95
8.	1.0 gm	8.97

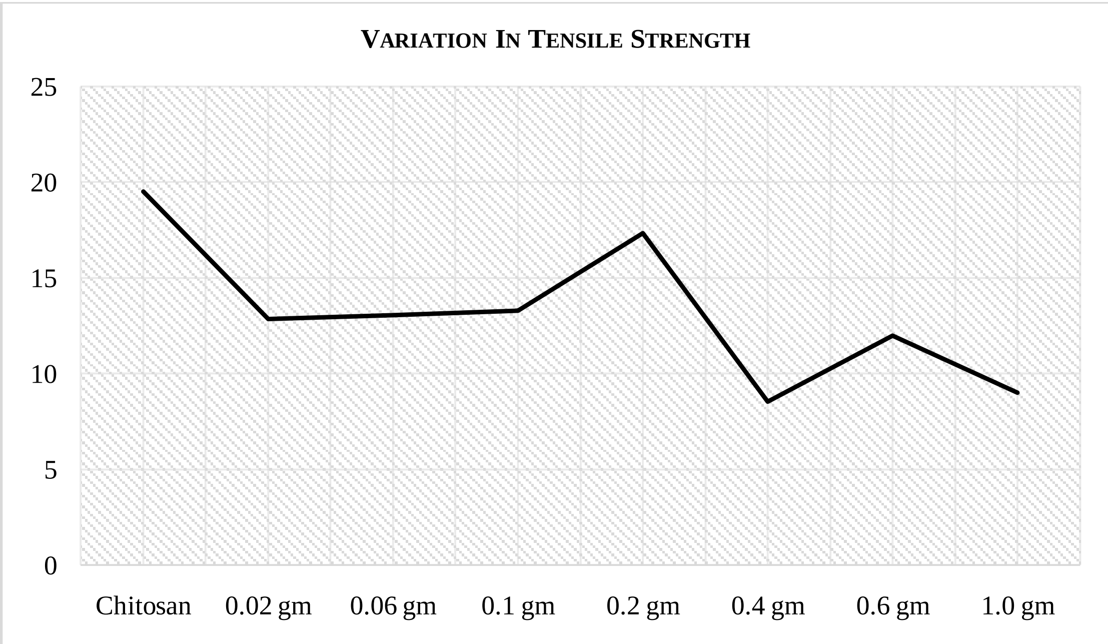

Figure 1. Variation of tensile strength with different concentrations of nano TiO_2.

TABLE 1 and Fig. 1 show that the tensile strength of 1%, 3%, 5%, 10%, 20%, 30% and 50% of Titanium dioxide doped in the Chitosan polymer matrix. From the above graph we have observed that the tensile strength of 1% Titanium doped Chitosan (12.82MPa) has decreased value than that of neat Chitosan (19.51MPa) and when Chitosan is doped with 10% of Titanium, the value of Tensile strength (17.34MPa) has been increased.

But when the same amount of Chitosan is doped with 20% of Titanium, we observe that the value of tensile strength has been dropped to a lesser value than expected. Here it is observed that the tensile strength of doped Chitosan films has decreased in comparison with neat Chitosan. Though the improvement of the property is observed at 10%, the property value observes decrement for 30%, 50% and 20% concentration of dopant repectively.

3.2 Stiffness

TABLE 2 shows the variation of stiffness in Chitosan with different concentration and also shows the variation when it is doped with Titanium dioxide.

Table 2 Variation of Stiffness

SL. NO.	MIXTURE	STIFFNESS
1.	Chitosan	16504.93
2..	0.02 gm	3915.98
3.	0.06 gm	1946.10
4.	0.1 gm	7298.32
5.	0.2 gm	7576.69
6.	0.4 gm	2811.52
7.	0.6 gm	4668.71
8.	1.0 gm	7094.38

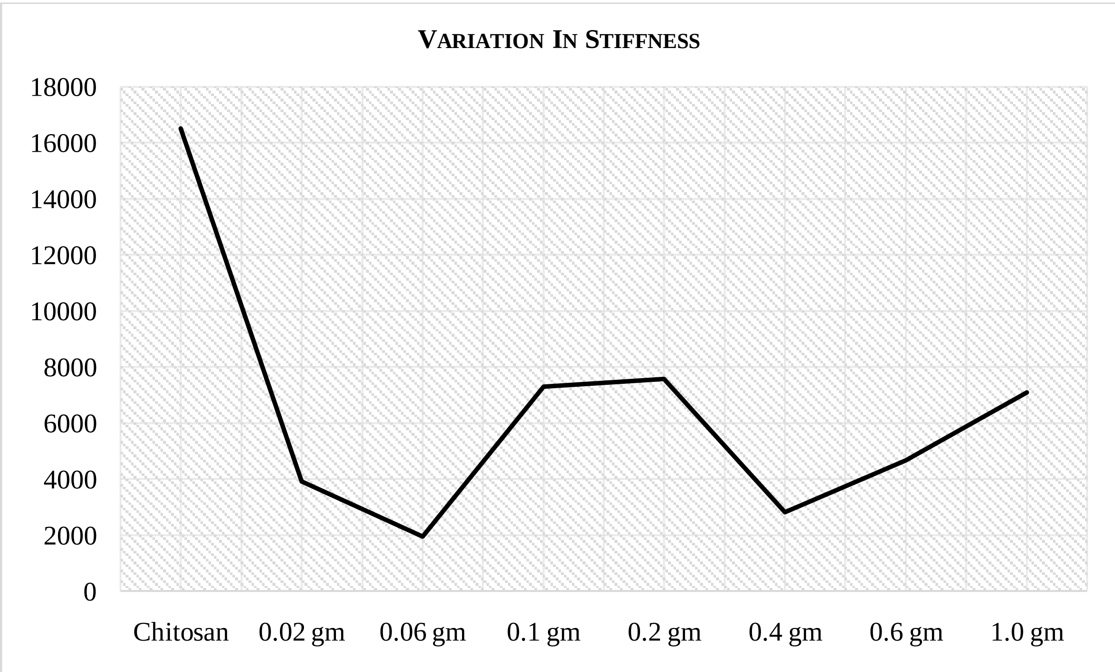

Figure 2. Variation of stiffness with different concentrations of nano TiO_2.

The data shown above corresponds to the stiffness values for 1%, 3%, 5%, 10%, 20%, 30% and 50% of Titanium dioxide in Chitosan polymer matrix. From the graph we observe that the stiffness for 1% Titanum dioxide doped Chitosan (39.15kN/m) has decreased to a lower value than that of the value of neat Chitosan (165.04KN/m). When Chitosan is doped with 10% of Titanium dioxide, the value of Stiffness (75.76KN/m) has been increased to almost twice as that of the value for 1% Titanium dioxide. The value of stiffness finds a sudden drop at 20% and gradually catches up for 50% concentration of nano TiO_2(70.94KN/m). On the whole we can conclude that the neat Chitosan is stiffer that the doped films.

3.3 Young's Modulus

TABLE 3 shows the variation of Young's Modulus in Chitosan with different concentration and also shows the variation when it is doped with titanium dioxide.

Table 3. Variation of Young's Modulus

SL. NO	MIXTURE	YOUNG'S MODULUS
1.	Chitosan	200.06
2..	0.02 gm	47.47
3.	0.06 gm	23.59
4.	0.1 gm	88.46
5.	0.2 gm	91.84
6.	0.4 gm	34.08
7.	0.6 gm	56.59
8.	1.0 gm	85.99

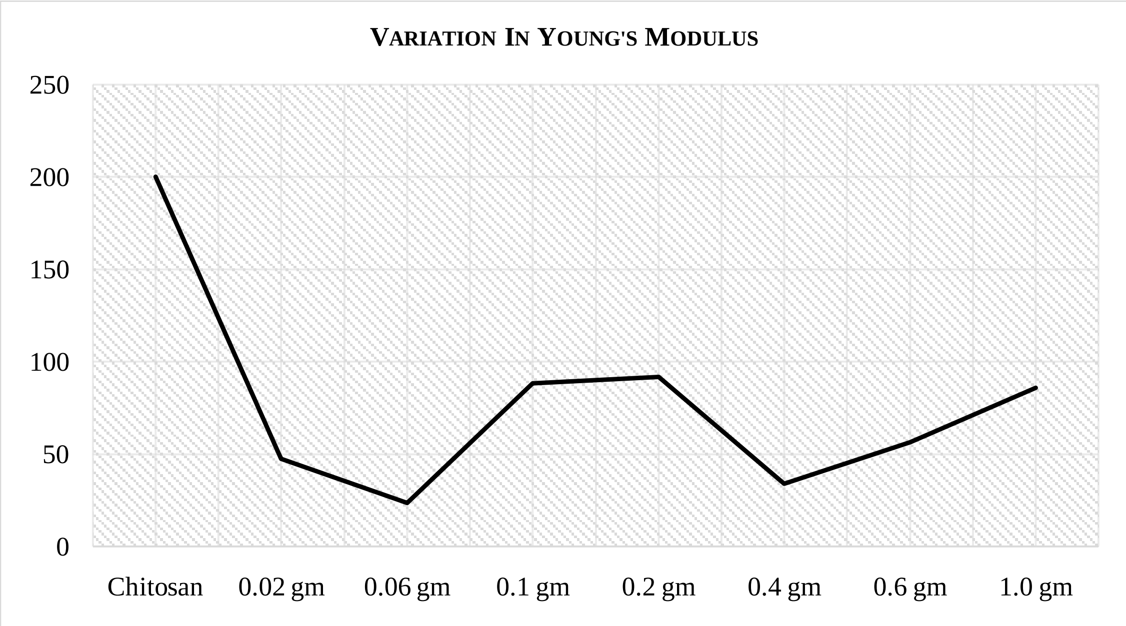

Figure 3. Variation of Young's Modulus with different concentrations of nano TiO_2.

TABLE 3 and Fig. 3 show the variation of Young's modulus of 1%, 3%, 5%, 10%, 20%, 30% and 50% of Titanium dioxide doped with Chitosan. From the above graph we have observed that the Young's modulus of 1% Titanium dioxide doped Chitosan (47.46MPa) has decreased to almost three times than that of the value of Chitosan (200.05MPa) and when it's doped with 10% of Titanium dioxide the value of Young's Modulus (91.83MPa) has been increased more than two times than that of the 1% Titanium dioxide. But when the same amount of Chitosan is doped with 20% of Titanium dioxide, we have observed that the value of Young's modulus has been dropped to a lesser value than expected. A similar trend has been observed for stiffness. This proves that Young's Modulus is the measure of stiffness for a given material.

3.4 Percentage Total Elongation at Fracture

TABLE 4 shows the variation of percentage total elongation at fracture in Chitosan with different concentration and also shows the variation when it is doped with Titanium dioxide.

Table 4. Variation of Percentage Elongation

SL. NO	MIXTURE	% ELONGATION
1.	Chitosan	35.52
2..	0.02 gm	39.15
3.	0.06 gm	81.39
4.	0.1 gm	33.10
5.	0.2 gm	39.01
6.	0.4 gm	30.35
7.	0.6 gm	33.22
8.	1.0 gm	22.89

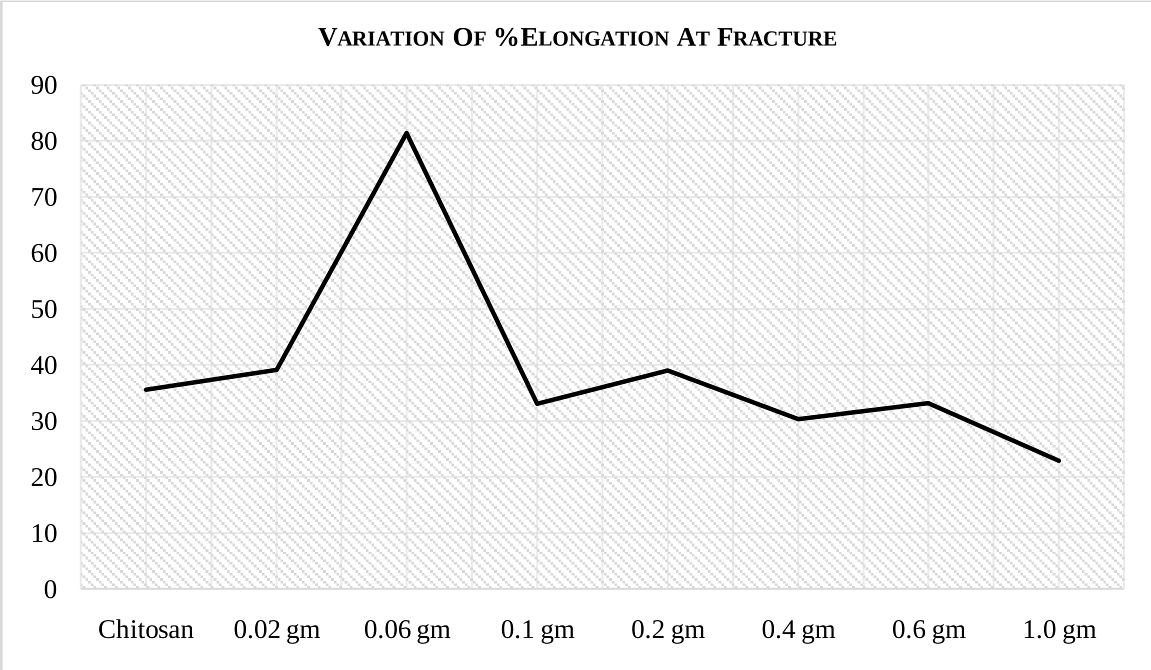

Figure 4. Variation of Percentage elongation at fracture with different concentrations of nano TiO_2.

The table and the graph above show the percentage elongation at fracture for 1%, 3%, 5%, 10%, 20%, 30% and 50% of Titanium dioxide doped with Chitosan. Percentage elongation at fracture is nothing but the ductility of that material. More ductile a material is, more desirable it becomes. From the above graph we have observed that the percentage total elongation at fracture has not varied significantly for most of the concentration except for 0.06 gram of doping. The property value touches a peak for Chitosan doped with 3% of Titanium dioxide. The values for percentage elongation at fracture further observes depression and slight variations for increase in concentration of nano TiO_2. Still it has enhanced the percentage total elongation at fracture, to a value much better than that of the neat Chitosan film prepared.

IV. Conclusions

From the obtained results we can arrive to the following conclusions:

- Notable changes have been observed in the properties of Chitosan films doped with nano particles in comparison with neat Chitosan films.
- It has been observed that increase in the concentration of nano particle doping has resulted in decrease in the respective property values, percentage elongation at fracture being an exception.
- The tensile strength of neat Chitosan reduced when doped with Titanium dioxide nanopowder.
- Chitosan doped with TiO_2 nano powder was found to be less stiff when compared to neat Chitosan for all concentation of doping.
- The values of young’s modulus of doped Chitosan films dip when compared to that of neat Chitosan film.
- Percentage Elongation at Fracture has considerably increased for doped film at a doping concentration of 8% (0.06gm) than that of the neat Chitosan film.

From the above observations, one can conclude that the most optimum concentration for enhanced property is 1%. The use of Acetic acid instead of sodiumhydroxide and hydrochloric acid made the film preparation relatively easy. It should also be kept in mind that preparatin of the samples using solution casting method will not assure the quality of the sample as there is a possibility of the nano particles being settled at the bottom of the petridish based on the viscosity of the liquid in which the nano particles have been dispersed. Also it is difficult to maintain the uniformity of thickness of the samples and the uniform distribution of the nano particles throughout the samples when it comes to solution casting method.

Since nano TiO_2 is relatively harmful to the environment, a study may be conducted on the biodegragability toChitosan-nano TiO2 nano composite. Also various thermal properties of the nano composite may be studied.

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