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## A review analysis on morphology of chitosan film reinforced by nanoparticles

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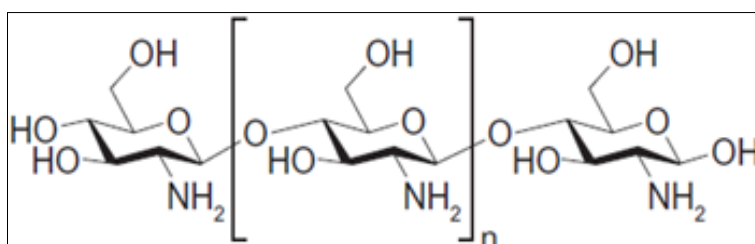
### Abstract

Synthetic petroleum-based polymers have been widely used in a variety of packaging materials but have become a major source of waste disposal problems due to their poor biodegradability. The use of renewable resources to produce edible or biodegradable packaging materials can reduce waste disposal problems. One of the approaches is to use renewable biopolymers such as polysaccharides, proteins, lipids, and their composites, derived from plant and animal resources.

**Keywords:** Chitin, nano composites, transmission electron micrograph

### Introduction

Chitin, a structural polymer in shellfish, insects, and microorganisms, is next to cellulose, the most abundant biopolymer [1-4]. It is basically a copolymer containing  $\beta$ -(1, 4)-2-acetamido-D-glucose and  $\beta$ -(1, 4)-2-amino-D-glucose unit. The structure of chitosan is shown below:



Chitin has been known to form microfibrillar arrangements in living organisms. These fibrils are usually embedded in a protein matrix and have diameters from 2.5 to 2.8 nm [5]. On commercial scale, chitin is being supplied by Sigma-Aldrich. Marches sault *et al.* [6] showed that acid-hydrolyzed chitin spontaneously dispersed into rod-like particles that could be concentrated to a liquid crystalline phase and self-assemble to a cholesteric liquid crystalline phase above a certain concentration.

Nano composites are an attractive class of materials providing novel performance. Due to some of their remarkable properties at low filler loading (less than 10 wt %), they are being increasingly adopted by industry whilst displacing the use of conventional filler materials. Chitosan as a nano scale filler is capable of enhancing mechanical and thermal properties of nano composites, including modulus, strength, impact performance, and heat resistance [7-9]. Chitosan can be added as a filler or other nanoparticles can be added in chitosan to improve the desired properties.  $\text{CaCO}_3$  is one of the most common and inexpensive inorganic fillers that has been used in the nano composite preparation process. Another possible approach to modify biopolymer film properties is to make hybrid films with organic polymers and nanosized clay minerals such as layered silicates, which are known as nano composite films [10-13]. Nano composite films, consisting of inorganic nano layers of layered silicate, such as montmorillonite (MMT) clay and organic polymers, have recently evoked intense research interest in the material and polymer science areas [14-16]. Partly because of their high aspect ratios and high surface area, the clay particles, if properly dispersed in the polymer matrix at a loading level of 1-5 wt%, impart unique combinations of physical and chemical properties that make these nano composites attractive for making films and coatings for a variety of industrial applications. Moreover, biodegradability is retained; that is, after final degradation, only inorganic, natural minerals (clay) will be left [17, 18].

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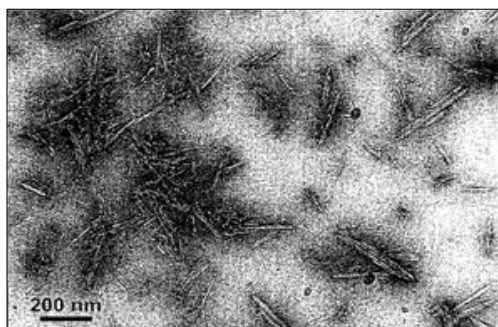
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## Preparation

There are several methods to prepare nanosized chitin/chitosan. We are discussing the preparation of chitin whisker, chitosan-based nanofibers as well as nano porous chitosan material in this section.

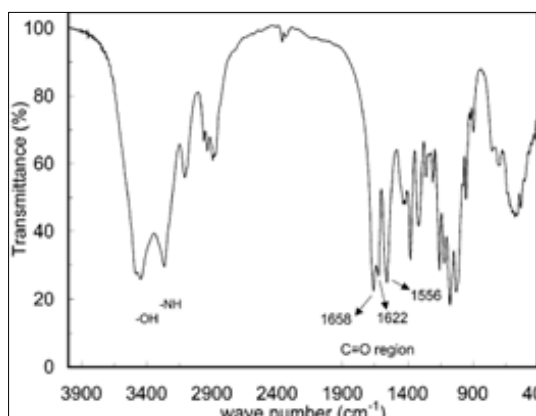
### Chitin whisker by acid hydrolysis

Chitin whisker suspensions are prepared by hydrolyzing the purified chitin sample with 3 N HCl at the boiling temperature for 1.5 h under stirring [19]. After acid hydrolysis, the suspensions are diluted with distilled water followed by centrifugation and the process is repeated three times. Next, the suspensions are dialyzed for 24 h against distilled water until a pH of 6 is reached. The pH is then lowered to 3.5 by adding HCl and it is subjected to ultrasonic treatment. A typical transmission electron micrograph obtained from a dilute suspension of hydrolyzed squid pen chitin is shown in Figure 1.



**Fig 1:** Transmission Electron Micrograph of Chitin (Reprinted from Ref. [19]).

Figure 2 shows an infrared spectrum for a film of chitin whiskers obtained from evaporation of the whisker suspension. In the carbonyl region, the spectrum presents three strong absorption peaks at 1658, 1622, and 1556  $\text{cm}^{-1}$  characteristic of anhydrous R-chitin [20].



**Fig 2:** FTIR Spectra of Chitin. (Reprinted from Ref. [21]).

### Chitin Nano fiber by Electros pinning

Electro spinning is a fiber-forming process by which either polymer solutions or melts are charged by high voltage to form fine jets. It was first reported by Formhals in 1934 [41]. These nanofibers can form nonwoven textile mats, oriented fibrous bundles and even three-dimensional structured scaffolds, all with large surface areas and high porosity [23]. These nanofibers are of considerable interest for various kinds of applications. Chitosan is soluble in most acids. The protonation of chitosan changes it into a polyelectrolyte in

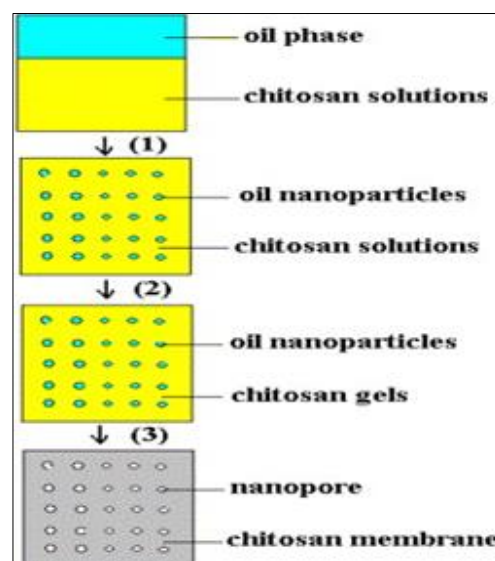
acidic solutions. The repulsive forces between ionic groups within polymer backbone that arise due to the application of a high electric field during electro spinning restrict the formation of continuous fibers and often produce beads [24]; so it is difficult to fabricate pure chitosan nanofibers. An electro spun nano fibrous mat of pure chitosan was successfully prepared by Ohkawa and coworkers [25] using trifluoroacetic acid (TFA) as electro spinning solvent. Under optimized conditions, homogenous chitosan fibers with a mean diameter of 330 nm were prepared.

### Nano porous chitosan by emulsion-mediated templating method

Liu *et al.* reported the preparation of nano porous chitosan materials in both membrane and bulk form with pore diameter ranges of 10-50 nm [26]. The method utilized is a novel emulsion-mediated templating method. Figure 3 shows the schematic diagram for preparation of nano porous carbon. The first step includes preparation of the inert-oil/chitosan solution emulsion system followed by crosslinking and gelling process of chitosan solution phase containing inert-oil nano beads. Finally, rinsing away of the inert-oil nano beads and forming the nano porous chitosan materials.

### Mechanical and thermal properties of chitosan film reinforced by nanoparticles

Four gram of chitosan powder was dissolved in a mixture of acetic acid aqueous solution and glycerin by heating for about 20 min at 90 °C. The castings were dried at ambient conditions ( $\sim 23$  °C) for  $\sim 48$  h and then peeled off the glass plates. Chitosan-based nano composite films were prepared by reinforcement with four different types of nanoparticles, such as Na-MMT, Cloisite 30B, nano silver, or Ag-zeolite. Table 1 shows the results of thickness, tensile strength (TS), and elongation (E) for chitosan and chitosan nano composite films. TS and E of chitosan films are  $32.9 \pm 0.7$  MPa and  $54.6 \pm 3.0\%$ , respectively. TS of all the nano composite films increased significantly, whereas E, for all except the chitosan/Cloisite 30B film, decreased significantly by compositing with nanoparticles. This was mainly attributed to a possible strain-induced alignment of the nanoparticle layers in the polymer matrix [13].



**Fig 3:** Schematic Representation of the Formation of Nano porous Chitosan Materials by Emulsion Templating Method (Reprinted from Ref. [26])

**Table 1:** Mechanical Properties of Neat and Nanoparticle Reinforced Chitosan Film (Reprinted from Ref. [27])

film type	Thickness (µm)	TS (MPa)	E (%)
Neat chitosan	64.0±6.0a	32.9±0.7b	54.6±3.0ab
Na-MMT	70.0±9.2a	35.1±0.9ab	50.3±11.7bc
Cloisite 30B	63.3±2.3a	36.8±3.3ab	66.3±5.3a
Nano-silver	64.7±9.0a	35.9±1.9ab	46.3±7.6bc
Ag-ion	61.3±5.0a	38.0±3.4a	38.9±1.4 Ac

Abdolmohammadi *et al.* prepared the nano composites of polycaprolactone (PCL)/chitosan/CaCO<sub>3</sub> by using a melt-blending technique [28]. PCL pellets were first added to the mixing chamber, which had been heated and stabilized at 100 °C. Then, after 2 min of heating, chitosan was added in four equal portions at 2-min intervals to the molten PCL. This was followed by the additions of 0.5, 1, 3, 5, or 7 wt % of CaCO<sub>3</sub> nanoparticles into the PCL/chitosan (90/10 wt %). To prepare a sheet of composite with a thickness of 1 mm, compression molding was carried out by hot pressing. These research groups illustrated that by increasing the amount of CaCO<sub>3</sub> nanoparticles in PCL/chitosan, tensile modulus increased. The increase in tensile modulus must be caused by rigidity of the filler and strong interaction between the polymer and filler due to the large interfacial area between particles [29, 30]. The enhanced composite modulus as a result of nano filler loading has also been reported by several other research groups [31, 32].

The thermal behaviour of nanosized reinforced PCL/chitosan film shows two stages of degradation. The onset decomposition temperature for PCL is 223 °C and for PCL/chitosan it is 231.45 °C. At 1 wt % of nanosized CaCO<sub>3</sub> the onset decomposition temperature increases to 258.76 °C. Calcium carbonate nanoparticles raise the temperature at which the degradation process initiates. Two stages of degradation of the PCL/chitosan blend have been observed. The first stage at T<sub>max1</sub> (283 °C) corresponds to chitosan backbone degradation resulting from saccharide ring dehydration, and the second stage at T<sub>max2</sub> (382 °C) corresponds to PCL decomposition [33]. The nano composites possess higher thermal stability compared to the PCL/chitosan composite, due to better adhesion between reinforced CaCO<sub>3</sub> nanoparticles and matrix and the hindered diffusion of volatile decomposition products resulting from homogeneous dispersion of nanoparticles within the nano composites [34].

#### Morphology of chitosan film reinforced by nanoparticles

Figure 4 shows morphology of cross-sectional surface of chitosan film. These films are modified with several nanoparticles such as Cloisite 30B, nano silver, and Ag-Ion. All these films showed island-sea morphology, that is, the nanoparticles were dispersed throughout the chitosan matrix except for Na-MMT which appeared to have intercalated or layered silicate morphology. In the case of NC films with nano silver, aggregated particles were observed in part of the film matrix.

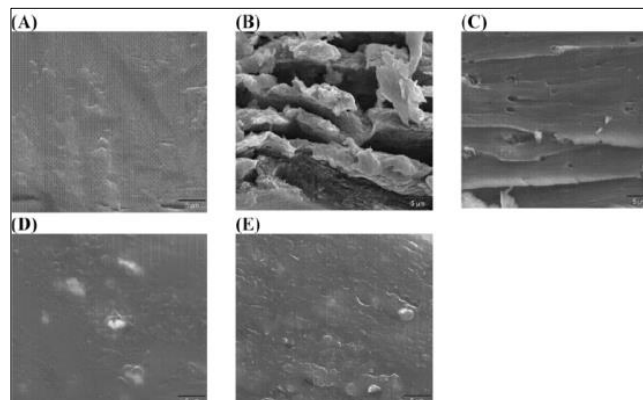
#### Applications

The applications of chitosan based nano composites are broadly divided into two categories. One relates to commodity plastics and other to medical applications.

#### Bio plastics and Bio composites

Polypropylene (PP) and polyethylene (PE) are virtually the source of all commercial commodity plastics. Both polymers display mechanical properties which make them important

and irreplaceable materials. The unique mechanical properties of PP and PE result from long carbon chain. Also, both these polymers are completely hydrophobic. Chitosan-based plastics can be used instead of synthetic polymers. However, one has to see the end-use applications as the chitosan-based plastics will be slightly hydrophilic and we know that mechanical properties get decreased once the material absorbs water. Nano composites are relatively a new class of composites that exhibit ultrafine phase dimensions of 1–1000 nm. Because of the nano metric size effect, these composites have some unique outstanding properties with respect to their conventional micro composite counterparts.



**Fig 4:** SEM of Cross Sections of Films from Chitosan and Chitosan-Based Nano composites. (A) Neat Chitosan, (B) Chitosan/Na-MM,; (C) Chitosan/Cloisite 30B, (D) Chitosan /Nano silver, (E) Chitosan/Ag-Ion (Reprinted from Ref. [27])

#### Medical Field

Electro spun nanofibers have been proven to be excellent supports for enzyme immobilization because they can provide large surface area-to-volume ratios, pore sizes tailored to protein molecule dimensions, functionalized surfaces, multiple sites for interaction or attachment, and low mass-transfer limitation [35]. The chitosan nano fibrous membrane was explored as support for enzyme immobilization due to the characteristics of excellent biocompatibility, high surface/volume ratio and large porosity.

Nanofibers containing chitosan have the advantage of filtering material based on the high surface/volume ratio, large porosity and functionality. They can be potentially applicable in a wide variety of filtration applications ranging from water purification media to air filter media [36]. Pure chitosan nano fiber mats fabricated by electro spinning using trifluoroacetic acid (TFA) as solvent have been used for absorbing metal ions [37]. Similar nonwoven fiber mats with fiber diameter as low as 80±35 nm for air and water filtration were also made by electro spinning high molecular weight chitosan/PEO blends [38]. From animal studies, the chitosan membrane has been found to be better than gauze and commercial collagen sponge wound dressing in wound healing rate. These obtained nano fibrous electro spun mats are promising for wound healing applications. A wound dressing material composed of silver nanoparticles (AgNPs) and chitosan has been fabricated using a nano meter and self-assembly technology [39]. It could significantly increase the rate of wound healing.

The development of bio inspired or biomimetic materials is Essential and has formed one of the most important fields in today's tissue engineering research. The nanofibers are of potential interest for bone tissue engineering applications.

A nano fibrous catalyst was fabricated by electro spinning of chitosan grafting acrylic acid copolymer (CS-g-AA)



supporting nano palladium <sup>[40]</sup>. The diameter of nano fiber was about 70-200 nm, the size of metal particles were in a range of 10-40 nm, and palladium particles dispersed on nanofibers homogeneously. The catalyst was applied to catalyze alpha-octene hydrogenation in normal temperature and pressure.

### Conclusions and perspectives

The chitosan-based nano composites and nanofibers have potential use in the areas of commodity plastics as well as enzyme immobilization, filtration, wound dressing, tissue engineering, drug delivery and catalysis because chitosan is a nontoxic, antibacterial, biodegradable and biocompatible biopolymer.

During the past few years, enormous progress has been made in the area of chitosan-based nano composites and also electro spinning to produce various nanofibers containing chitosan with unique shape and unique properties. However, there are many problems that need to be solved for large-scale manufacturing of chitosan-based new nanofibers and nano composites. The applications of the chitosan-based products are still at the laboratory level and will become true in near future by the efforts of researchers.

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