

SYNTHESIS AND CHARACTERIZATION OF SILANE MODIFIED IRON (III) OXIDE NANOPARTICLES REINFORCED CHITOSAN NANOCOMPOSITES

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Abstract

Silane modified iron (III) oxide ($\text{Si-Fe}_2\text{O}_3$) nanoparticles reinforced chitosan (CS) nanocomposite membranes were prepared by sol-cast transformation method. The iron (III) oxide nanoparticles and nanocomposite membranes were investigated by UV (Visible) spectroscopy, FT-IR spectroscopy, XRD, SEM and TEM. The size and shape of iron (III) oxide and $\text{Si-Fe}_2\text{O}_3$ nanoparticles were determined by XRD and TEM. The $\text{Si-Fe}_2\text{O}_3$ nanoparticles were reinforced homogeneously within the chitosan matrix which could be assigned due to the hydrogen bonding between CS and $\text{Si-Fe}_2\text{O}_3$. The mechanical properties of nanocomposites were investigated. The results showed that the tensile and elongation properties of the $\text{Si-Fe}_2\text{O}_3$ nanoparticles reinforced chitosan nanocomposite increases upto 6 wt.% and then declines.

Index Terms: $\text{Si-Fe}_2\text{O}_3$ nanoparticles reinforced chitosan, XRD, SEM, TEM, Mechanical Properties

1. INTRODUCTION

Chitosan, a de-N-acetylated form of chitin, the second most abundant natural polymer obtained from the shells of crab, shrimp and krill, consists mainly of $\beta(1-4)$ -2-amino-2-deoxy-D-glucose units. Chitosan is non-toxic, biodegradable and has excellent film forming properties, which find applications in various fields (Muzzarelli et al., 1989). Chitosan-based films are prepared by wet casting followed by infrared (IR) drying (Tharanathan et al., 2002) and no significant differences were observed in their mechanical and barrier properties in comparison with those prepared under conventional methods of drying (Srinivasa et al., 2004). The molecular weight of chitosan has a profound influence on the thermal, mechanical, and permeability properties of the films (Butler et al., 1996; Chen and Hwa, 1996). Currently, the research on the combination of CS and metal oxide has focused on titanium dioxide, as titanium dioxide has excellent photocatalytic performance and is stable in acidic and alkaline solvents (Yang et al., 2009; Zainal et al., 2009). Surface modification of magnetic particles by organic compounds is used to disperse magnetic powders in the matrix and can be achieved via major

avenues: organic vapor condensation, polymer coating, surfactant adsorption, and direct siliconization. (Takafuji et al., 2004). Among them, the direct siliconization of magnetic particles using a silane-coupling agent is attractive because it enables easy control of surface properties. In this work $\text{Si-Fe}_2\text{O}_3$ nanoparticles reinforced chitosan nanocomposites membrane were prepared successfully. The obtained nanocomposite membranes were studied using FT-IR, XRD, TEM, SEM, and Mechanical properties.

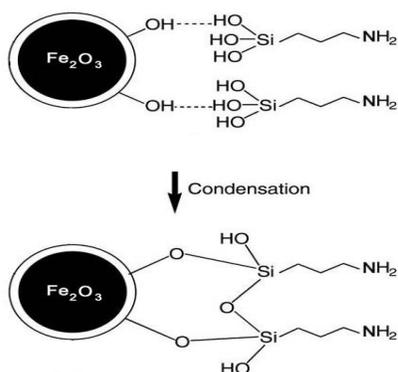
2. EXPERIMENTAL

Material

Chitosan, molecular weight 6.7×10^5 g/mol was procured from Indian Sea Foods, Cochin, India. Iron (III) oxide (Fe_2O_3) nanoparticle (<50 nm) having m.p 565°C , density 5.12 was purchased from Aldrich Inc., USA. (3-glycidyloxypropyl)trimethoxysilane (GPTS), boiling point = 217°C , density = 0.946 g.cm^{-3} , $M_w = 221.3$ was procured from Aldrich Inc. USA. Solvents were obtained from Merck India Ltd, India.

Preparation of Si- Fe₂O₃ nanoparticles

The siliconization of iron (III) oxide nanoparticles with 3-aminopropyltrimethoxysilane was carried out in a 250 ml 3-necked flask, equipped with a reflux condenser, nitrogen inlet tube, dropping funnel, on a thermostated silicone bath. The reactions were performed in inert atmosphere, at dichloroethane reflux temperature (81°C) for 24h. 20 ml dichloroethane, 0.3 g dibutyltin dilaurate (catalyst), 0.6367g iron (III) oxide nanoparticle (2.7 mmol) and 4.73g 3-aminopropyltrimethoxysilane (21.4 mmol) were added. The unreacted solvent and monomers were separated by vacuum distillation on a rotavaporator at 35°C. Siliconized iron (III) oxide nanoparticles, washed with small amounts of toluene for the removal of siloxane oligomers formed during the reaction and with acetone for the separation of catalyst, were dried in vacuum at 35°C for 24 h (Scheme 1).



Scheme 1: Preparation of siliconized iron (III) oxide nanoparticles.

Preparation of chitosan/Si-Fe₂O₃ composite membrane

Chitosan was dissolved in 2% acetic acid solution (2% m/v). Si-Fe₂O₃ nano particles were dispersed into the prepared chitosan-acetic acid solution by ultrasonic irradiation for 60 min after magnetic stirring. According to the percentage of Si-Fe₂O₃ nanoparticles added, the resulting suspensions were termed as CS0, CS1, CS2, CS4, CS6 and CS10 for 0%, 1%, 2%, 4%, 6% and 10%, respectively. After sonication, the nanocomposite blends were poured into a glass plate and dried at 60 °C for 8 h. The glass plates were cooled and subsequently immersed in alkali solution to finally get the chitosan-Si Fe₂O₃ composite membrane. The membrane were further soaked in distilled water for 24 h to remove the residual solvent.

3. TEST METHODS

UV-analysis

The structure of the nanocomposite blend films were measured using UV-vis spectrophotometer (UV-2450, Shimadzu, Japan)

FT-IR analysis

Fourier transform infrared (FTIR) spectra (transmission) were recorded on a Shimadzu-1800S spectrophotometer in the range of 4000–400 cm⁻¹ at room temperature.

XRD Analysis

Wide angle X ray scattering (WAXS) were temperature by using X[’]-Pert Pro diffractometer recorded at room, with Cu K α radiation, 40kV, 100mA. The diffraction patterns were determined over a range of diffraction $2\theta = 10 - 80^\circ$.

TEM analysis

Transmission electron microscope (TEM) was used to characterize the morphology (size and shape) of the as received Fe₂O₃ and Si-Fe₂O₃. TEM was carried out in a JEM 100CX (JEOL) with an accelerating voltage of 100 keV.

Morphology

Surface morphology of fractured surface of the samples was performed using scanning electron microscope (Quanta-200, FEG).

Mechanical studies

Mechanical property of elongation-at-break was measured with a constant force applied to two ends of 10 × 20 mm piece of chitosan/Si-Fe₂O₃ composite membrane, following the guidelines of ASTM standard Method D 882-91 (ASTM, 1995a). Elongation-at-break was calculated as the ratio of the final length at the point of sample rupture to the initial length of a specimen, which was repeated five times for each type of membrane.

4.RESULT AND DISCUSSION

UV- analysis

The UV-vis absorption spectra of pure CS membrane and Si-Fe₂O₃ nanoparticles reinforced chitosan nanocomposite membranes were shown in Figure 1. As shown in Figure 1a, the absorption peak of pure CS membrane was not obvious in that there were not conjugated double bonds in the CS molecules. Compared with the pure CS membrane, the absorption band of the composite membranes was observed at about 343 nm, lower than that of the macrocrystalline Fe₂O₃ (about 370 nm). (Haase et al., 1988) the absorption band would

be blue-shifted with the decrease of the diameter of nanoparticle (Kubo et al., 1962; Kawabata et al., 1966) Therefore, Si-Fe₂O₃ nanoparticles reinforced in the nanocomposite membranes were nanometric, which agreed well with the XRD analysis.

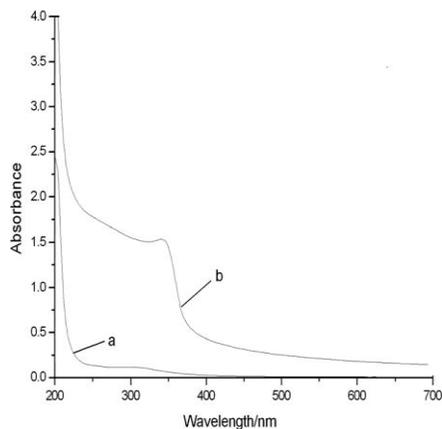


Fig-1: UV- Spectroscopy of
(a) Pure chitosan
(b) Si-Fe₂O₃ reinforced chitosan nanocomposite

FT-IR spectroscopy

Fig.2. shows characteristic FT-IR absorptions of iron (III) oxide and siliconized iron (III) oxide nanoparticles. Iron (III) oxide nanoparticle spectrum (Fig. 2a) presents the characteristic absorption bands of Fe-O at 640.39, 563.23 and 440 cm⁻¹, a broad band at 3448.84 cm⁻¹ due to Fe-OH and a deformation vibration of -OH bond at 1635.65 cm⁻¹ (Durdureanu-Angheluta et al., 2008; Harabagiu et al., 2009). The covalent bonding of aminopropylsilane groups is mainly due to their self-polycondensation leading to core-shell nanoparticles. The presence of Fe-O-Si bonds cannot be seen in the FT-IR spectrum because it appears at around 640.39 and 563.23 cm⁻¹ and therefore overlaps with the Fe-O vibration of iron (III) oxide nanoparticles, however, the bands were wider and sharper than iron (III) oxide nanoparticles alone (Feng et al., 2008; Ma et al., 2003). But, the adsorption of silane polymer onto the surface of iron (III) oxide nanoparticles (Fig. 2b) was confirmed by bands at 1114.89 and 1047.2 cm⁻¹ which correspond to the Si-O-H and Si-O-Si groups (Ma et al., 2003). The absorption bands at 890.4 cm⁻¹ and 780 cm⁻¹ are due to the stretching of Si-O-H and vibrations of -OH on the surface of iron (III) oxide nanoparticles. Furthermore, the two broad bands at 3448.84 cm⁻¹ and 1635.69 cm⁻¹ can be ascribed to the N-H stretching vibration (White et al., 2000; Heiney et al., 2000). These results indicate the formation of siliconized iron (III) nanoparticles.

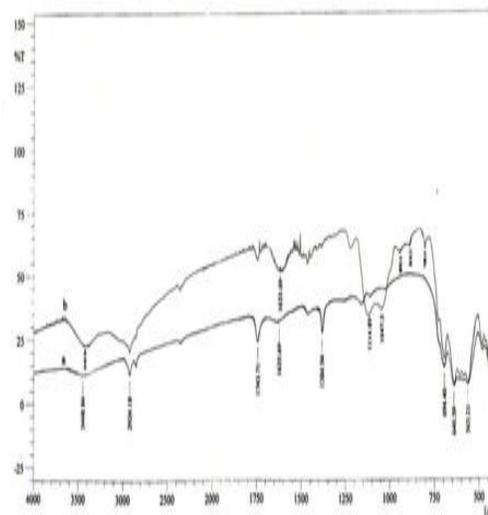


Fig-2: FT-IR spectra of
(a) iron (III) oxide
(b) siliconized iron (III) oxide nanoparticles

XRD Analysis

Figure 3 shows the X-ray diffraction patterns of pure CS membrane and Si-Fe₂O₃ nanoparticles reinforced nanocomposite membranes. The typical peaks of CS membrane (Fig. 3a) appeared at 10.4^o, 12.8^o, and 19.9^o, (Urbanczyk et al., 1994; Samuels et al., 1981) while these peaks became weak in the XRD pattern of Si-Fe₂O₃ nanoparticles reinforced chitosan nanocomposite membranes (Fig. 3b). Other diffraction peaks at 31.6^o, 34.3^o, 36.2^o, 56.5^o, 62.8^o, and 67.8^o of Si-Fe₂O₃ nanoparticles reinforced chitosan nanocomposite membranes were assigned to the (1 0 0), (0 0 2), (1 0 1), (1 1 0), (1 0 3), and (1 1 2) planes of Si-Fe₂O₃ as shown in Figure 3b. These data revealed the successful inclusion of Si-Fe₂O₃ nanoparticles in nanocomposite membranes. The Si-Fe₂O₃ nanoparticles size of 14 nm was calculated by using the Debye-Scherrer equation. Moreover, the presence of Si-Fe₂O₃ nanoparticles impeded the order of polymer chains by both steric effect and intermolecular hydrogen bonds. So, the introduction of Si-Fe₂O₃ nanoparticles in chitosan decreased the crystallinity of composite membranes and increased the flexibility of polymer chain (Dong et al., 2000).

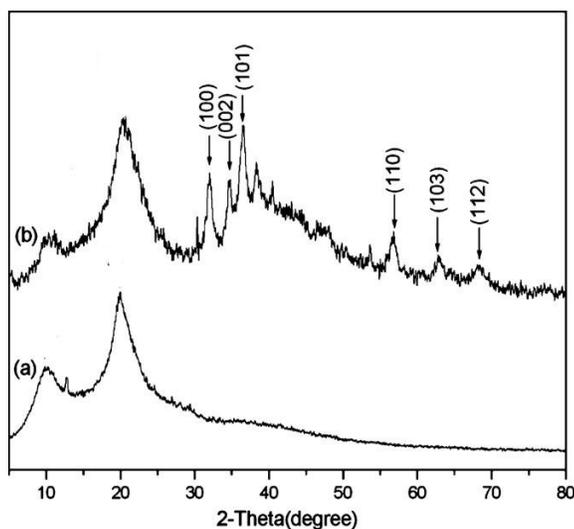


Fig-3: XRD of
(a) Pure chitosan
(b) Si-Fe₂O₃ reinforced chitosan nanocomposite

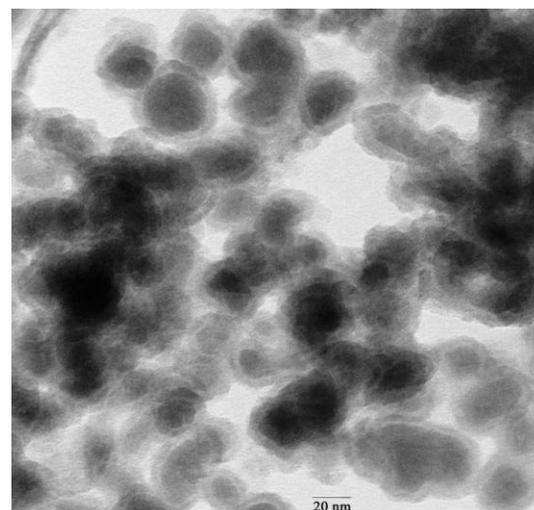


Fig-4: (b) Si- Fe₂O₃ nanoparticle

TEM Analysis

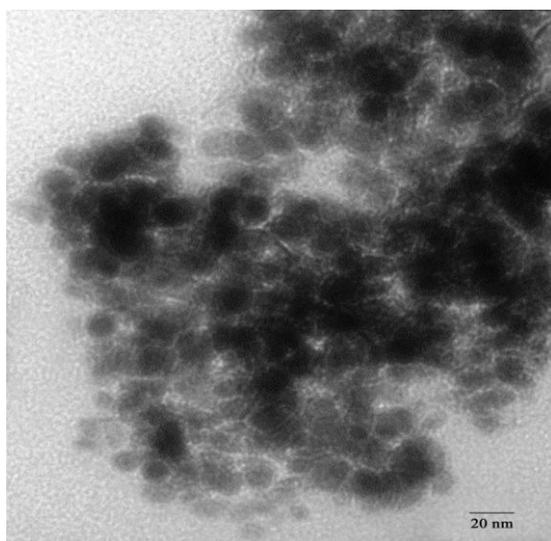


Fig-4: (a) Fe₂O₃ nanoparticles

TEM study on the iron (III) oxide and Si-Fe₂O₃ nano-particles were done to know the shape and size of the particles. The TEM images shown in Fig. 4a and 4b confirmed the presence of well-dispersed nano-sized spherical particles of Fe₂O₃ nanoparticles and Si-Fe₂O₃ nano particles with diameters ranging from 14 to 20 nm. The size of the nanoparticles determined from TEM agrees with XRD .

Morphology

Scanning electron microscope microphotographs of the fractured surfaces of pure CS and Si-Fe₂O₃ nanoparticles reinforced chitosan nanocomposite membranes are displayed in Figure 5. Compared with the surface of pure CS membrane (Fig. 5a), the nano- composite membrane shows uniform granular morphology which was attributed to the homogeneous dispersion of Si-Fe₂O₃ spherical nanoparticles within CS matrix by hydrogen bonding. Moreover, the nanocomposite membranes (Fig.5b) presented shows a homogenous and smooth cross-section with thickness of approximately 4 μm.

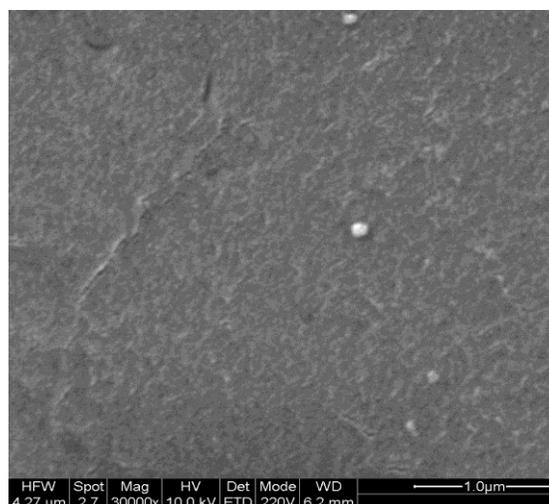


Fig-5: (a) SEM photograph of pure chitosan

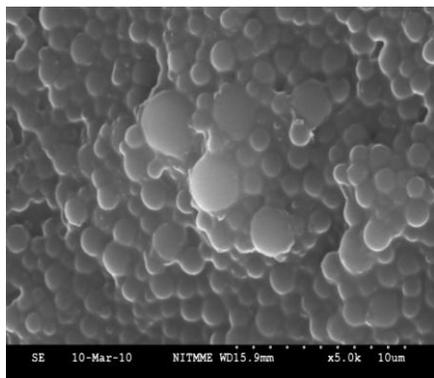


Fig-5:(b) SEM photograph of 4wt.% Si-Fe₂O₃ reinforced chitosan nanocomposite

Mechanical properties

Table 1 presents the tensile strength and the elongation at break of the nanocomposite membranes. As shown in Table 1, all the mechanical properties of Si-Fe₂O₃ nanoparticles reinforced chitosan nanocomposite membranes were better than those of pure CS membrane up to Si-Fe₂O₃ content of 6 wt %. The tensile strength of nanocomposite membranes was higher than that of pure CS membrane upto Si-Fe₂O₃ content of 10 wt %. Moreover, compared with other nanocomposite membranes, the mechanical properties of nanocomposite membrane containing 1 wt % Si-Fe₂O₃ was highest. But, as the Si-Fe₂O₃ amount increases, the mechanical properties of the composite membranes declines. These mechanical behaviors were explained as follows: chitosan contained a large number of ring structures. The intramolecular and intermolecular hydrogen bonds were formed by the –OH and –NH₂, which seriously hindered the rotation and movement of the molecular chain.

Sample	Tensile strength (MPa)	Elongation at break (%)
CS	43.5	33.8
CS-1	79.8	66.9
CS-2	77.2	61.4
CS-4	72.4	49.7
CS-6	55.7	38.1
CS-10	50.3	29.4

Table 1 Mechanical properties of pure CS membrane and Si-Fe₂O₃ reinforced chitosan nanocomposite

When Si-Fe₂O₃ was introduced, the intermolecular hydrogen bonds were weakened and new hydrogen bonds were formed between CS and Si-Fe₂O₃, which made the rotation and

movement of molecular chain easier. Therefore, the tensile strength and the elongation at break of the nanocomposite membranes greatly enhanced. However, the nanocomposite membranes became brittle with doping excess Si-Fe₂O₃. Therefore, incorporation of appropriate Si-Fe₂O₃ amounts into the chitosan membrane would enhance its mechanical properties.

5. CONCLUSIONS

The Si-Fe₂O₃ nanoparticles reinforced chitosan nanocomposite membranes were prepared. The obtained nanocomposite membranes were characterized by UV, FT-IR, XRD, TEM and SEM. Tensile strength and elongation at break of the nanocomposite membrane were also studied. Reinforcement of Si-Fe₂O₃ nanoparticle increases the tensile strength of chitosan membrane. Homogenous spherical structure shows Si-Fe₂O₃ nanoparticles were well dispersed in chitosan matrix by hydrogen bonding.

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