Research Article

Thermal and Mechanical Properties of Chitosan/SiO₂ Hybrid Composites

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Chitosan-silica (CSSi) hybrid films have been fabricated by sol-gel process using tetraethoxysilane (TEOS) as precursor. The structure of the resulting hybrid has been characterized by Fourier transform infrared spectroscopy (FTIR). Fracture surface has been revealed through a field emission-scanning electron microscopy/energy dispersive spectrometer (FE-SEM/EDS) to probe the dispersion degree and the size of SiO₂ particle. Study of morphology using a SEM micrograph and the High Resolution Transmission Electron Microscopy (HRTEM) images of the nanocomposite films suggests that the SiO₂ nanoparticles are within the range of 2–7 nm in diameter and are uniformly dispersed in the polymer matrix. Thermal properties of these composite materials have been studied as a function of silica, indicating that thermal stability of the chitosan film is enhanced. Dynamical mechanical thermal analysis (DMTA) has been carried out to measure the shift in the glass transition temperature (T_g) of the composites from the maxima of the α transition curves. The glass transition temperature and the storage modulus show an increase with increasing silica content. The maximum increase in the T_g value, that is, 159.37°C, is seen with 30 wt% silica. A gradual increase of 3.0 GPa in the modulus relative to the pure polymer is observed.

1. Introduction

Bio-nanohybrid materials are part of an interdisciplinary field between Life Sciences, Material Sciences, and Nanotechnology. They are gaining importance in areas such as biosensors, structural materials, catalysts, separation methods [1], and regenerative medicine [2].

Chitosan is a biopolymer derivative of chitin, a polysaccharide found abundantly in nature in crustacean exoskeletons of crab, shrimp, and lobster as well as in cuttlebone of cuttlefish. It is a linear chain of linked 2-acetoamido-2-deoxy- β -D-glycopyranose units. Chitosan possesses unique functional and biomedical properties. It is biodegradable, biocompatible, nontoxic, heat resistant showing adsorption properties and is easily accessible by recovering from marine waste [3]. It is especially attractive due to its film forming characteristic and finds multiple uses in applications of coatings, drug delivery, nutrients, controlled release of food ingredients, separation techniques, optical material, and so forth.

Organic/inorganic hybrids exhibit characteristics of both organic polymers and ceramics [4, 5]. These are easily produced through sol-gel chemistry [6–8] which is a very versatile method allowing incorporation of inorganic component like metal alkoxide namely, Si [9, 10], Ti [11, 12], Zr [13] or even bioactive materials to modify final chemical and physical properties of materials at low processing temperatures. The narrower distribution of particles and the reduced particle size due to in situ development of the metal oxide network leads to better strength and increased glass transition temperatures.

Chitosan which has hydroxyl and amine functional groups rapidly bonds to other groups. Thus the silicon precursor shows quick in situ development of the silica network in the presence of ethanol and water via the sol-gel route forming glassy, homogeneous and transparent films compatible over a wide composition range [14]. It is therefore expected that chitosan/silica hybrids should have increased interfacial interaction, greater ceramic nature, and

improved thermal, mechanical, optical and adsorbing properties. Chitosan is soluble in weak organic acid which renders it unsuitable for adsorbing in an acidic environment. Many studies have been conducted using chitosan or chitosan adsorbed onto conventional silica for metal ion removal and chelating agent. Lai et al. [15] prepared chitosan silica thick films with in situ silica from zero to hundred percent silica via the sol-gel process, to investigate the interfacial interaction of the two phases and its capability to chelate Cu(II) and Fe(III) to a large degree under wide environmental variation.

Attempts to arrive at an accurate glass transition temperature and effect of DDA on the T_g has been studied in the past, but information on the change in viscoelastic behavior of composites due to reinforcement has been wanting. In the present study, transparent chitosan-silica (CSSi) hybrid films with various silica contents have been prepared via in situ incorporation of silica by the sol-gel process at room temperature. These composites have been characterized for their viscoelastic nature, thermal stability, and optical sensitivity. Their modified morphology has been studied through X-ray mapping and SEM to show the nature of the nanophase silica particles and their homogeneous distribution.

2. Experimental

2.1. Materials. Practical grade chitosan (CS) was obtained from Aldrich. The Brookfield viscosity provided by the supplier was >200.00 cps. Tetraorthosilicate (TEOS) from Aldrich had purity of 98%. All other chemicals were of analytical grade and used as such.

2.2. Preparation of the Hybrid Films. Chitosan was dissolved in 2% acetic acid deionized aqueous solution to produce a 2 wt% chitosan solution. This solution was stirred for 48 hours at room temperature to form a homogeneous mixture. Required amount of this solution was taken in a 50 mL bottle, and measured amount of TEOS was added to it. This was stirred for 1 hour at room temperature. Stoichiometric amount of an equal mixture of ethanol and water was added to the solution and allowed to stir for 18 hours at room temperature. The water to TEOS ratio was 1 : 4. The solution was cast in Teflon petri dishes and dried at 50°C for 17 hours. The films were then dried under vacuum for another 48 hours at 50°C. Flexible chitosan-silica (CS-Si) hybrid films of 5, 10, 20, and 30 wt% silica were prepared.

2.3. Characterization of the Hybrid Films. Fourier Transform Infrared spectroscopy (FTIR) spectroscopic analysis was carried out on Perkin-Elmer FTIR-2000 spectrophotometer to monitor the physical bonding between the CS polymer matrix and silica network formation in the sol-gel process. The morphology of the hybrid films was studied using field emission scanning electron microscopy model *Leo Supra 50VP FESEM*. The films were fractured with liquid nitrogen, sputter coated with gold by means of Balzer's SCD 050 sputter coater, and mounted on aluminum mounts before analysis. Cross-sectional view of the hybrids was studied to

determine the modification in morphology. Samples prepared in the similar manner were then subjected to Elemental X-ray Microanalysis which was conducted using a JSM-6300 J scanning electron microscope which was attached to an Energy Dispersive X-ray Spectroscopy operated at 20 kV for analyzing material science specimens. Samples of 10% and 20% silica loading were degraded at 430°C for 9h to ensure that all the organic matter had decomposed, prior to imaging in HRTEM. The microscope used was JEOL's HRTEM-3010 equipped with a 300 kV electron gun. UV-vis spectroscopic analysis was carried out on Varian Cary 5. Absorption was measured in the 400–800 nm range. The dynamic mechanical thermal analysis (DMTA) on the hybrid films was carried out using DMA Q-800 (TA, USA). The measurements of storage modulus and $\tan \delta$ were made under tension mode in the temperature range 50–210°C at heating rate of 2°C/min using a frequency of 2 Hz under inert atmosphere. Thermogravimetry (TG) was performed on a 10 mg sample from ambient to 800°C at a heating rate of 10°C/min in a dynamic (30 mL/min) synthetic air atmosphere using TGA-50 Shimadzu automatic analyzer.

3. Results and Discussion

3.1. Structural Characterization. The interaction between chitosan and TEOS suggested the formation of hydrogen bonds between amide groups of chitosan and silanol groups, ionic bonds between chitosan amino groups and silanol groups, and covalent bonds due to esterification of chitosan hydroxyl groups on silanol groups of silica network [1]. Schematic suggestion of the CS-Si hybrid preparation is represented in Figure 1.

FTIR analysis was carried out to observe the interaction between the polymer matrix and the silica network formation. The spectra for the pristine CS and its hybrid composite with 20 wt% silica are shown in Figures 2 and 3. Characteristic absorbance for CS shows the Amide I (C=O) stretch at 1645 cm^{-1} , C-N stretch at 1616 cm^{-1} and at 1576 cm^{-1} ; the bending due to Amide II (N-H) is evident. The C-H bond interaction due to Amide II is clear with the band at 1402 cm^{-1} . C-O-C antisymmetric stretching is seen at 1152 cm^{-1} , and the C-O skeletal stretch characteristic of polysaccharides is observed at 1060 and 1084 cm^{-1} . The N-H control band for the amide vibration is seen as a single peak at 3249 in Figure 3. The incorporation of in situ silica shows an overall reduction in intensity including in the N-H regions, also shifting the peak to a slightly lower frequency and marking the increased interfacial interaction between the matrix and the inorganic phase. The appearance of the new absorption band at 969 cm^{-1} related to the Si-OH bonds is observed due to formation of H-bonds between silanol groups of silica network and amide- and oxy-groups of chitosan. The broad shoulder due to Si-OH also appears in the region of 3300–3370 cm^{-1} [16]. This region also overlaps the influence of phase interaction on the amine groups which show a clear band at 3334 cm^{-1} in pristine chitosan. A broad and strong band appears in the region between 3400 and 3200 cm^{-1} due to hydrogen bonding. This is evident in

FIGURE 1: Schematic representation for preparation of chitosan siloxane (CS-Si) hybrids.

FIGURE 2: FTIR spectra for A: pristine chitosan, B: CS-Si 20%.

FIGURE 3: FTIR spectra for A: pristine chitosan, B: CS-Si 20%.

Figure 3 in the region of the broad and pronounced peak of 3278 cm^{-1} where interaction between the carbonyl group of chitosan and the silica network occurs. Specific bands in the region of $1000\text{--}1250\text{ cm}^{-1}$ [17] showing characteristic absorption for Si-O-Si are clearly seen in the modified system. The appearance of the Si-O-C bands at 1069 cm^{-1} and at 795 cm^{-1} is seen in the hybrid film spectra which

are not visible in the pure spectra indicating that there is a definite interaction between the phases.

3.2. Morphological Studies. The FE-SEM micrograph of fractured surfaces of hybrids with 10 and 20 wt% silica is shown in Figure 4. The silica particles are in the form of white round beads, and their dispersion within the matrix is clearly

FIGURE 4: High magnification FE-SEM micrographs for CS-Si hybrid films with silica contents wt% (a) 10, (b) 20.

FIGURE 5: High Resolution Transmission Electron Microscopy images showing the individual particle size for CS-Si composites with (a) 10% and (b) 20% silica loading.

visible. The size of the individual silica particle within the hybrid films approximately ranges from 2 to 7 nm which is confirmed by the HRTEM results as depicted in Figure 5. As the concentrations of SiO_2 increase, the uniform and dense structure of silica in the polymer matrix is clearly observed in hybrids. This explains the interfacial interaction within the matrix and the clear, successful dispersion of the reinforcement material. Figure 6 presents the Si-mapping analysis of the hybrid membrane. The electron beam penetrates 2-3 microns below the surface of sample to reveal the embedded silica distribution. The bright spots representing the silicon element clearly reflect a homogeneous distribution of silica in CS polymer domains. The nanometer level dispersion of silica in chitosan also indicates that there should also be an influence on the mechanical and thermal properties of the polymer.

3.3. Optical Properties. Figure 7 shows the increasing nature of UV-vis light absorbance by the hybrid films in proportion to silica content. The absorbance values of the pure and hybrid CS-Si films tested for transparency via UV-Vis

spectroscopy in the 400–800 nm range are tabulated in Table 2. Transparency of films usually varies due to varying thicknesses. Films in the range of 0.85 ± 0.03 mm have been measured. The pure film is almost transparent with absorbance closest to zero at 0.067. It decreases further in the 800 nm range to show greater transparency at 0.049. Since the composite films have almost comparable thicknesses, the variation in absorbance is due to the spatial distribution and the size of the silica particles in the matrix. In the 5% CS-Si composite, the size of the ceramic particle is still smaller than the wavelength of light thus permitting light to transmit more easily. Also the distribution of the network is more uniform and homogeneous. With an increase in silica content the network becomes more extensive and bulky causing the smaller particles to agglomerate reducing the overall homogeneity of the system. As the size of the particles increases and the distribution is more overlapped, the absorbance increases as is evident in the 20% CS-Si hybrid result. Thus the pure film is more transparent when compared to the 20% hybrid film which is almost opaque. The films are off white in color.

(a)

(b)

FIGURE 6: Elemental X-ray mapping of CS-Si hybrids silica wt%; (a) CS-Si, 10%; (b) CS-Si, 20%.

FIGURE 7: UV-visible spectra for the CS-Si hybrids.

3.4. Viscoelastic Properties. The variation in dynamical mechanical thermal properties of the CS-Si hybrids has been studied to determine the change in glass transition temperature and the viscoelastic stability of the polymer on incorporation of the silica enhancement. The storage modulus (E') of the polymer increases with the increase in

FIGURE 8: Temperature variation of storage modulus for CS-Si nanocomposites at 2 Hz. Silica wt% 0 (●), 5 (○), 10 (■), 20 (□), 30 (◆).

TABLE 1: Viscoelastic properties of chitosan-silica hybrids.

SiO ₂ (wt%)	CS-Si hybrids		
	Storage modulus (GPa) at 50°C	T_g (°C)	Tan delta (δ)
0	3.67	152	0.15
5	4.42	154	0.14
10	4.82	156	0.11
20	6.00	157	0.094
30	6.70	159	0.083

silica content, and its temperature variation is depicted in Figure 8. The storage modulus at 50°C is 3.67 GPa for the pure polymer and increases to 6.70 GPa for the 30% CS-Si hybrid film. Initially with the increase in temperature, the storage modulus drops linearly in the rubbery region from 110°C till 150°C for the pure polymer. The rate of decrease is considerably lower for hybrids with silica in this region. Increasing the temperature increases the segmental motion of the polymer and there is a sharp increase in $\tan \delta$ which corresponds to the α relaxation temperature associated with the glass transition temperature T_g (Figure 9). In the pure polymer this is seen at 152°C, and enhanced polymer silica interaction causes it to reach 159°C for the 30% CS-Si composite. The addition of silica restricts the mobility of the chains, and thus the glass transition temperature increases. But effectively the loss factor ($\tan \delta$) reduces, which is the ratio of the loss modulus to the storage modulus, showing enhanced ceramic nature of the polymer hybrids (Figure 10). The value of $\tan \delta$ progressively decreases from 0.15 for the pure polymer to 0.08 for the 30% CS-Si composite. The viscoelastic data is presented in Table 1.

3.5. Thermogravimetric Analysis of Nanocomposites. To study the effect of silica reinforcement on thermal stability of the CS nanocomposites, thermogravimetric analysis was carried out under synthetic air in the temperature range of 50–750°C

FIGURE 9: Temperature variation of $\tan \delta$ for the CS-Si nanocomposites at 2 Hz. Silica wt% 0 (•), 5 (○), 10 (■), 20 (□), 30 (◆).

FIGURE 10: Variation of $\tan \delta$ with silica content for CS-Si hybrids.

FIGURE 11: Thermogravimetric curves for the CS-Si nanocomposites showing various silica contents.

TABLE 2: UV-vis absorbance for the CS-Si hybrids.

CS-Si films	400 nm	600 nm	800 nm
Pure	0.067	0.049	0.049
5%	0.338	0.264	0.246
20%	0.358	0.284	0.266

(Figure 11). The initial weight loss observed between 100 and 160°C appears to be due to the loss of absorbed water on the surface of chitosan and side product of subsequent condensation of the Si-OH groups [18]. Chitosan shows slower weight loss in the region between 160°C and 270°C due to the decomposition of low molecular weight species. Thermal decomposition is more marked in the region between 170°C and 450°C relating to the complex dehydration of the saccharide rings, depolymerization, and decomposition of the acetylated and deacetylated units of the polymer [19]. Incorporation of silica network and its interaction with the polymer increases the thermal resistance of the hybrids and consequently the thermal decomposition temperature. The mass of residue retained at 750°C corresponds to the amount of silica content incorporated in the hybrids indicating that the sol-gel reaction was successful.

4. Conclusions

Chitosan-based silica hybrids have been prepared by the sol-gel process. Both organic and inorganic phases show increased interfacial interaction which is depicted in the FTIR spectra. The absorbance is proportional to the increase in silica content which is clear in the UV-vis range. Field emission scanning electron microscopy, high resolution transmission electron microscopy, and elemental X-ray mapping clearly depict the nanodimensional morphology of the particles in the matrix and a very homogeneous distribution throughout the matrix with a particle size in the range of 2–7 nm. The glass transition temperature and storage modulus (E') determined through DMTA indicate better cohesion between the phases, and the shift to higher temperature suggests increased interfacial interaction and an increase in the ceramic nature of the polymer due to a decrease of the area under the curve seen in the $\tan \delta$ values. The thermal stability of the composites increases with the increase in silica concentration and the residue corresponds to the content used for reinforcement suggesting that the sol-gel reaction is complete.

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