Original Article

Characterization of selenium oxide nanofiller effect on the spectroscopic and thermal properties of Cs/PAM nanocomposites

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ABSTRACT

Nanocomposite samples of chitosan (Cs)/polyacrylamide (PAM) blend incorporated with different concentrations of selenium oxide (SeO₂) nanoparticles were fabricated and investigated. The results of Cs/PAM-SeO₂ nanocomposites show an exchange in the physical and thermal properties. The X-ray diffraction shows the semicrystalline nature for pure Cs/PAM blend which decreased with the increase of Se contents, causing a decrease in the degree of crystallinity inside Cs/PAM films. The absence of Se peaks for doped films indicates that Se was finely dispersed in polymeric matrices. The FT-IR spectra display a change in the intensities of some bands compared with the spectrum of the virgin Cs/PAM, which indicates that an interaction and complexion between Cs/PAM and selenium nanoparticles took place. The UV–vis measurements revealed that the values of the direct and forbidden direct optical energy gap (Egd and Eg) decreased after the addition of Se nanoparticles. The TG, DTG and DSC analysis were used to investigate the thermal properties of the nanocomposites. The TG thermograms show two regions at ≈100 °C varied from 2.8 to 4.6 % weight loss due to the evaporation of water and moisture absorbed, and the other from 244 to 433 °C related to ≈9.5% to ≈55.2 % weight loss. The shifts of TG curves result in a higher temperature indicating that, with the addition of Se, the thermal stability increases with increasing Se content. The values of the change of activation entropy (∆S°), change of activation enthalpy (∆H°), and Gibbs free activation function (∆G°) were calculated. The small increase of both ∆H° and ∆G° reveals that the total energy was increased with respect to the reagents and compound formation activated.

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1. Introduction

The study of the spectroscopic and thermal properties of polymeric materials has received attention owing to various applications [1,2]. The microstructural, optical, and thermal
properties of the polymer and/or polymer blend can be modified with the addition of nanofillers [3,4].

Natural polymers such as chitosan (CS), which are natural aminoascarides, have been widely used in various biomedical applications, due to their unique structures [5]. CS is derived from chitin and it has attracted great attention as a non-toxic, biodegradable functional polymer for diverse applications [6]. Chitosan is a heteropolymer, containing every amine group (NH₂) and the hydroxyl group (OH) on its spine. CS is different from chitin because it contains a free amino group (NH₂) [7,8] and is obtained by deacetylation of chitin. By performing a minimum deacetylation, the obtained free amino-group corresponding to chitosan polymer [9], while the CS monomer is the amino-D-glucose. Background information about the structure of the band gap energy for polymeric materials can be obtained simply by analyzing their optical absorption spectra [10].

Chitosan can form pure films, fibers, and reciprocal bonding. Therefore, Cs films are manufactured as protective materials for food packaging, but their widespread application was limited by insufficient mechanical and antimicrobial properties [11,12]. The high-water vapor permeability of Cs films makes them an excellent choice for moisture-sensitive packaging applications. Thus, further modifications in Cs films are inevitable for the industrial exploitation of this biologically talented polymer [13]. Cs is a natural polymer that has a basic polysaccharide and it is widely used because of the presence of functional groups of NH₂ and OH [14,15]. It has a high solubility in many media and high viscosity. It can form films when prepared with nanoparticles. It is used to prepare homogeneous nanocomposites by doping nanoparticles [16,17]. However, the weak mechanical and electrical properties are a significant drawback. Researchers have used several strategies to improve these properties of chitosan. CS is characterized by the easy ability to form blends with many polymers. CS is one of the most promising biopolymers in many fields. The presence of the amino group and the hydroxyl group in its basic structure increases useful properties that are applicable in many areas, such as the industrial and biomedical industries [18].

Polyacrylamide (PAM) is a polymer of medical interest and has been widely studied by pharmaceuticals for its hydrogel-compatible blood applications [19]. PAM is well known for the hydrophilicity and idioicy that made it a favorable material in many applications, such as biomedical pharmacy and water separation [20,21].

When the materials are on the microscale, it has relatively limited mechanical, thermal and electrical properties. Nanomaterials have recently emerged raising considerable attention from the researchers because of their ability to demonstrate unique properties used in practical and technological applications.

In addition to these and other features, nanoparticles suffer from some limitations, since their small size and large area can lead to the accumulation of particles, making physical handling difficult in solid and liquid forms. To reduce these defects, there have been many attempts to manufacture nanocomposites using compound polymerization with synthetic polymers, such as polyethylene glycol (PEG) and polyvinylpyrrolidone (PVP), epoxy/phenol formaldehyde (DGEBA/novolac) resin blends, and/or natural polymers such as chitosan [22–25].

Nanomaterials are multifunctional materials with a high ability to exhibit new, unique properties, and properties extending to the micrometer level. Nanoparticles exhibit a wide range of performance characteristics compared to their individually prepared components. Therefore, they currently make a better option on practical and industrial scales. In the present and future research, the polymeric nanocomposites are of paramount importance as new promising materials due to their wide uses in chemical field, antimicrobial activity, environment treatment and water purification applications [26–29]. The insertion of nanoparticles into polymeric materials enhances and adds new properties to the polymeric nanocomposite when compared to the basic individual components [30,31]. The polymer blend between Cs and PAM with new properties has generated a lot of interest due to the potential improvement in structural and thermal properties of the individual polymer.

Selenium (Se) has been utilized in photo-electrochemical and photovoltaic cells as well as photosensors. This is due to its semiconducting properties with a small band gap and its high light sensitivity [32–34].

The thermogravimetric (TG) is widely used in materials science, especially for polymeric materials because of its ability to assess thermal stability and determine the amount of components in polymers. Moreover, in recent years, multipurpose thermal analysis coupled with spectroscopic instruments, such as X-ray and Fourier transform infrared (FT-IR), has become very common. It can be used to estimate both the volatilization ratio during gases decomposition and volatility values of polymeric material during heat treatment, which facilitates the estimation of the sample composition [35–37]. The present paper deals with the synthesis and characterization of novel Cs/PAM-SeO₂ nanocomposites samples. The change of the structure was done by X-ray diffraction, FT-IR, ultra violet-visible (UV–vis) and TG analysis to measure the prepared nanocomposites.

2. Experimental work

2.1. Materials

The chitosan (Cs, (C₆H₁₁NO₄)ₙ) and poly acrylamide (PAM, (CH₂₂CHCONH₂)ₙ) were purchased from Sigma-Aldrich company.

Selenium oxide nanoparticles (SeO₂) were prepared as follows. A 200 m mole of sodium selenite and 100 m mole ascorbic acid were first selected. Then, the ascorbic acid was added step by step to the sodium selenite solution at room temperature for about 30 min, using magnetic stirring. The final solution could react until the color change from colorless to light orange due to SeO₂ nanoparticles. The solution of SeO₂ nanoparticles was washed 5 times using distilled water and G₃H₂O to get rid of any impurities that may have accumulated during the reaction. The films were dried in an oven at 65 °C. Pure SeO₂ nanoparticles was inserted in the desiccator until use.

The virgin Cs/PAM blend and Cs/PAM were doped with various concentrations of Se nanoparticles by casting technology preparation of the films using common solvent distilled solution of water and 1% acetic acid to both polymers. The solutions were mixed and stirred constantly until it became a homogeneous solution. After that, the required amounts of Se nanoparticles (0, 0.2, 0.4, 0.8 and 1.0% weight) were first dispersed by stirring in distilled water. Polymer solution further dispersed the SeO₂ nanoparticles by using a magnetic drive until it turned into a highly viscous homogeneous solution. The resulting solution has been carefully poured in a Petri dish. The final produced films were kept in a dryer, which were filled with silica gel. It has remained in the final product dryer, which was filled with silica gel dryers for further drying. The possible interaction is estimated by a chem draw program between Cs/PAM incorporated with SeO₂ to obtain the Cs/PAM-Se nanocomposites as shown in Scheme 1.

2.2. Characterization techniques

The prepared polymer films were characterized by several techniques. XRD patterns of the Se nanoparticles (NPs) pure blend and the blends loaded with various contents of Se NPs were obtained using PANalytical’s X’Pert diffractometer by Cu-Kα radiation (λ = 1.540 Å) operating with scanning rate of 5°/min and 2θ = 10–80°. FT-IR absorbance spectra were measured using FT-IR-430, JASCO, Japan spectrometer at 4 cm⁻¹ with a wavenumber from 4000 to 400 cm⁻¹. The UV–vis spectra were carried out in the wavelength range of 190–800 nm. The thermogravimetric (TG) and differential scanning calorimetric (DSC) analysis were recorded by NETZSCH, STA 409 PC at temperatures ranging from 30 to 700 °C and a heating rate of 10 °C/min under the constant flow of nitrogen.

3. Results and discussion

3.1. X-ray study

The microstructure of virgin Cs/PAM polymer blend and the Cs/PAM doped with different concentrations of SeO₂ nanoparticles are evaluated using XRD and presented in Fig. 1. The spectrum of X-ray of pure Cs/PAM blend exhibited a broad peak at 2θ ≈ 21.5°, which can be linked to its semi-crystalline nature resulting from an intramolecular and intermolecular interaction between the components of the prepared nanocomposites [38]. The X-ray diffraction spectrum shows broader and smaller peaks, without any sharp Bragg’s peaks. This confirms that it is amorphous in nature [39]. The spectra are mainly performed to confirm the presence of elemental selenium nanoparticles in the polymeric medium. The XRD spectrum of pure Se nanoparticles showed a characteristic peak at 2θ ≈ 23.6, 29.78 and 43.9° [40]. The semicrystalline regions of pure behavior arise from the order of the contracting polymer molecules in the presence of hydrogen bonds between the inter molecules. This indicates that the presence of selenium oxide nanoparticles is reduced from selenite ions present in the polymeric medium. The intensity of this XRD peak decreased as it becomes broader after the addition of SeO₂ nanoparticles, which indicates a decrease in the crystallinity degree of the polymer blends. This confirms the fact that the presence of the Cs/PAM blend restricts crystalline behavior and weakens the relative content of the Se nanoparticles [41]. The main peaks of pure Se nanoparticles are not clearly observed in the spectra, which is ascribed to a well dispersed SeO₂ in the polymer blend matrices.

3.2. FT-IR analysis

Fig. 2 presents the FT-IR spectra of Cs/PAM doped with different concentrations of Se nanoparticles ranging from 4000 to 400 cm⁻¹. The intramolecular and intermolecular interactions can take place inside the Cs/PAM blend due to the presence of hydrogen bonds, which occur due to the presence of OH and NH₂ groups in chitosan (Cs) and amide groups in polyacrylamide (PAM). The spectrum of pure Cs/PAM shows strong absorption bands at the range between 3300 and 3600 cm⁻¹ assigned to NH stretching vibrations, and at 1666 cm⁻¹ due to CO= vibrational mode and amide I absorption bands at 1647 cm⁻¹ and amide II around 1562 cm⁻¹ [42]. Two bands at 1100 cm⁻¹ and 600 cm⁻¹ are assigned to the C=O stretching, and CO= stretching modes of the Cs moiety [43].

Small transformations of major characteristic bands in the nanocomposite spectra indicate that hydrogen bonds give new bands. These shifts confirm an interaction between polymer Cs/PAM blend and Se nanoparticles, which confirms that these groups react with Se nanoparticles [44]. From the spectra, it is evident that the spectra of both virgin Cs/PAM and the Cs/PAM-Se nanocomposites films are nearly similar. For clarity, the spectra of the nanocomposites films prove that Cs/PAM blend and Cs/PAM-Se nanocomposites films had similar functional groups.

3.3. UV–vis spectroscopy

The ultra violet and visible (UV–vis) spectra of the virgin Cs/PAM and Cs/PAM containing various concentrations of nanoparticles at a wavelength from 190 to 1100 nm are recorded in Fig. 3. The absorption edge below 300 nm is produced because of electronic excitation in the carbonyl group (C=O) in PMMA structure related to π→π* transition. The position of this edge is shifted towards longer wavelengths by increasing Se contents. This shift confirms the complexation between the Cs/PAM and SeO₂ nanoparticles, which is attributed to change in the crystallinity after the addition of Se. The band at about 300 nm observed in the spectra is attributed to the forbidden n→π+ transition. The spectrum of pure Cs/PAM displays the shoulder-like band at about 297 nm due to the presence of carbonyl groups inside the blend [45].

For doped samples, the spectra show a shift in the UV absorption edge towards higher wavelength conforming reduction of the optical band gap. Moreover, there was a decrease in the absorbance. The various optical energy band gaps (E₀) of the nanocomposites are determined [46,47] using Eqs. 1 and 2 as:

\[(ahv)^2 = B (hv - E₀) \text{ for direct transition} \]  
\[(ahv)^2 = B (hv - E_d) \text{ for direct forbidden transition} \]

where α is the absorption coefficient, h is Planck’s constant, ν is the frequency, hν is the energy of the photon, B is constant, and m is 1/2, 2, 3/2 and 3 corresponding to direct, indirect, direct and indirect prohibited transformations respectively.

Figs. 4 and 5 show the plot of (ahv)² and (ahv)³/² against hν for Cs/PAM-Se nanocomposites. The values of both direct optical (E₀) and the forbidden direct (E₀) are clearly seen using the linear portion induction of the high energy curves of the photon energy axis at the zero-absorption level, as seen from the disconnet lines in the curves [48,49].

The calculated values of E₀ and E₀ of the polymer nanocomposite films are recorded in Table 1. The lower values of the optical band gaps (E₀ and E₀) for doping samples are observed. This reduction of both E₀ and E₀ is discussed according to invoking occurrence of local cross-linking inside the amorphous regions in Cs/PAM blend causing an increase in the degree of order in these regions. Another cause of this reduction may be that a drop, for example, is due to the difference of non-bonding oxygen. Non-oxygen bonds with a much larger ionic character have much less bond energy. Thus, the oxygen bonds do not fill a higher polarization, leading to a
decrease in the non-bridging oxygen bonds. This decrease of non-oxygen bonds has higher polarizability, which leads to a decrease in $E_g$. The calculated value of the energy band gap is associated with defects inside the nanocomposites after the addition of Se nanoparticles. So, the maximum value of Se content confirms the maximum defect (a disorder in the nanocomposites) causing a decrease in the $E_g$, especially for forbidden direct optical band gap $E_{gd}$. The rise in the amorphous regions (disorder) in the samples cause a decrease in the optical band gaps for all nanocomposites. A broad band appeared at 297 nm of the spectra; the intensity of this band increased as the Se nanoparticles concentration increased. The formation of new levels of energy in the forbidden band gap, which is attributed to the increase in the amorphous region of Cs/PAM, facilitates the transfer of electrons from the top of valence band (LOMO) to the bottom of conduction band (HUMO) through these new localized states. Therefore, there were less band gaps with increased Se contents.

### 3.4. Thermal analysis

The thermogravimetric (TG) analysis, derivative thermogravimetric (DTG) and DSC thermograms of the pure Cs/PAM doped with 0.2, 0.4 and 0.8 wt.% of Se nanoparticles using heating rate $10\degree C \ min^{-1}$ are shown in Fig. 6 (a-d). In the TG thermograms it is observed two regions at 100 $\degree C$, which varied between 2.8 and 4.6 % weight loss due to evaporation of water and moisture absorbed; and from 244 to 433 $\degree C$ related to $\approx 9.5–55.2 \%$ weight loss. This confirms the vaporization inside the nanocomposites. A strong hydrogen bonding is formed between molecules due to the presence of the amide group (NH$_2$) and hydroxyl group (OH) in chitosan, above 312 $\degree C$. Significant change is observed during the TG-thermograms because of the changes in the structure for prepared nanocomposites and the changes in the mechanism of its thermal degradation by deacetylation of Cs process [50]. At temperature above 455 $\degree C$, the weight loss is attributed to the decomposition of the acetylated and deacetylated units in the compounds. In the derivative thermogravimetric (DTG) and DSC thermograms, there are two exothermic peaks seen at about 292.3 $\degree C$ (related to 24.4 % weight loss) and at 433.5 $\degree C$ (related to 47.4 % weight loss), respectively. The first peak in DTG curves relates to deacetylation and depolymerization of polymer blend especially Cs, but the second peak in DSC thermograms is related to the residual cross-linked degradation of the blend.

The significant variations of the positions and heights of DTG peaks are attributed to the addition of Se nanoparticles. With the increase of Se contents, the behaviour of thermal decomposition increased in the range 292–433 $\degree C$, with the shift towards the higher temperature in the DTA thermal curves. The temperature corresponding to maximum values of loss of the peaks are shifting towards higher values. Furthermore, temperatures over 500 $\degree C$ are followed by a slow further mass loss up to the final temperature, where the TG thermograms tend to become flat. The shifts of TG curves of Se towards a higher temperature indicate that the addition of Se causes an increase in the thermal stability with increasing of Se nanoparticles content.

#### 3.4.1. Calculation of the activation energy

To estimate the activation energy of the main decomposition in the TGA thermograms, the variation in reaction range (a) is calculated as [51]:

$$\alpha = \frac{m_i - m_f}{m_i - m_{\infty}}$$  \hspace{1cm} (3)

where $m_i$ is the initial mass, $m_f$ is the mass at different temperatures $t$ and $m_{\infty}$ is the final mass.
The thermal activation energy (E) is estimated using Coats and Redfern method as [52,53]:

\[
\ln \left( \frac{-\ln (1 - \omega)^{1-n} - 1}{(n - 1)T^2} \right) = \ln \left( \frac{AR}{AE} \right) (1 - \frac{2RT}{E}) - \frac{E}{RT} \tag{4}
\]

where \( T \) is the absolute temperature, \( R \) is the gas constant (8.3136 J/mol K), and \( n \) is a correlation parameter from the model. For \( n = 1 \), Eq. (4) becomes:

\[
\ln \left( \frac{-\ln (1 - \omega)}{T^2} \right) = \ln \left( \frac{AR}{AE} \right) (1 - \frac{2RT}{E}) - \frac{E}{RT} \tag{5}
\]

According to Eq. (5), we plot the relationship between expression \( \ln \left( \frac{-\ln (1 - \omega)}{T^2} \right) \) on the left side against the temperature \(( \frac{1}{T} \)) of each sample. This relation gives straight lines, as represented in Fig. 7. The slope of each curve is \( E/R \); then, \( E = -R \times \text{slope} \). The data in Table 2 represents the estimated values of the activation energies (E) of the samples. The values of \( E \) increased with an increase of Se content, which means that there is a variation in the reaction due to the interaction.

The thermodynamic activation properties are: the change of activation entropy \( \Delta S^* \) (which is defined as the degree of the order), the change of activation enthalpy \( \Delta H^* \) (known as the total thermal motion), and Gibbs free activation function \( \Delta G^* \) (which is the stability of the system). These are estimated as follows [54–56]:

\[
\Delta S^* = R \ln \left( \frac{A_h}{K_B T_p} \right) \tag{6}
\]

\[
\Delta H^* = E^* - RT_p \tag{7}
\]

\[
\Delta G^* = \Delta H^* - T_p \Delta S^* \tag{8}
\]
where $K_b$ is Boltzmann constant, $h$ is Planck’s constants and $T_p$ is the peak temperature of DTG thermograms.

According to the Coats-Redfern method, the values of the calculated thermal parameters ($E$, $\Delta S^*$, $\Delta H^*$ and $\Delta G^*$) are tabulated in Table 2. The values of the thermal parameters show a small increase attributed to the random separation of the molecule series in the polymer matrices, while the activation energy has decreased values. As we see in the table, the negative values of $\Delta S^*$ indicate more and more activated states ordered. Changes in the activation of the universal $\Delta S^*$ were observed in quite a few of the samples, confirming that the formation of the activation complex is preferred attributed to the low latent energy barriers. Moreover, the higher value of $\Delta S^*$ indicated that the stabilization is not entropically driven due to higher free energy.

4. Conclusion

A solution casting technique was used to synthesized novel polymeric nanocomposites films based on chitosan/polyacrylamide (Cs/PAM) blend incorporated with different concentrations of selenium oxide (SeO$_2$) nanoparticles. The films of nanocomposites were characterized and investigated using X-ray diffraction, FT-IR and UV–vis spectroscopy. The thermal properties and thermal parameters were studied using TG, DTG and DSC analysis. No X-ray peaks were observed for pure Se, indicating that Se was well dispersed in polymer blend matrices and also due to the semi crystalline nature of Se. The FT-IR spectra display a small shift of some bands due to the presence of OH and NH groups. The UV–vis analysis revealed that the values of the optical energy gap decreased after the addition of Se nanoparticles. The TG thermograms have two regions at $\approx 100 ^\circ C$ attributed to evaporation of water and moisture absorbed, and the other region ranging from 244 to 433 $^\circ C$. The shifts of TG curves towards a higher temperature indicate that the addition of Se causes an increase in the thermal stability with the increase of Se content. The values of the changes in the activation entropy ($\Delta S^*$), change of activation enthalpy ($\Delta H^*$), and Gibbs free activation function ($\Delta G^*$) were calculated using Coats-Redfern method. The little increase of both $\Delta H^*$ and $\Delta G^*$ was attributed to the formation of the activation complex, which is preferred due to the low latent energy barriers. The higher value of $\Delta S^*$ indicated that the stabilization is not entropically driven due to higher free energy.

REFERENCES


