



Characterization of Chitosan and Polyethylene glycol Blend Film



Afaf Sarhan

Polymer Research Group, Physics Department, Faculty of Science, Mansoura University, ET-35516, Mansoura, Egypt.

CHITOSAN-polyethylene glycol (Cs/PEG) blend films with different mass ratios have been synthesized utilizing simple blending and casting technique. Molecular structure, electronic transitions and surface morphology of the developed blends have been inspected utilizing a series of Fourier Transform Infrared (FTIR) spectroscopy, ultraviolet-visible (UV-Vis) spectroscopy, scanning electron microscopy (SEM). Moreover, both of the microhardness and swelling ability of the blends with different mass ratios have been evaluated. Both of UV-Vis and FTIR results postulates the presence of a distinct sort of interaction between both of chitosan (Cs) and polyethylene glycol (PEG) which could emanate from the newly formed intermolecular hydrogen bonds between Cs and PEG. It was also found that increasing PEG mass ratio in the blend results in increasing the value of the direct bandgap. SEM micrographs of the blend revealed changing the surface morphology of chitosan after the addition of PEG.

Keywords: Chitosan, Polyethylene glycol, Band gap, Hardness, Swelling .

Introduction

Chitosan an aminoglucoopyran, is a natural polysaccharide comprising of randomly distributed *N*-acetylglucosamine and β -(1,4)-linked glucosamine residues [1, 2]. It is obtained through *N*-deacetylation of chitin with strong alkaline [3] which is a one of the most abundant natural polymers as a component of the exoskeletons of crustaceans [4]. Presence of amino groups and hydroxyl groups in chitosan make it hydrophilic and gave it its polycationic property [5]. Advantageous features of chitosan [6], including good film forming, biocompatibility, biodegradability, hydrophilicity, nontoxicity, non-antigenicity, and biocidal activity [7, 8] in addition to bioadherence.

These remarkable features of chitosan broaden its range of application in all fields especially in medical one as chitosan is regarded as good candidate as biomaterial [9, 10]. Nevertheless, The mechanical properties and some of physicochemical characteristics

of chitosan are not adequate to match all these applications. To overcome this shortcomings and improving the physical/chemical properties of chitosan incorporation chitosan with other natural or synthetic polymer [11-13] and inorganic nanoparticle [14] have been studied. Incorporation chitosan with polyethylene glycol is a good example for improving mechanical properties of chitosan by both blending and copolymerization [15, 16]. Zhang et al. [17], established that blending proper ratios of chitosan and PEG resulted in a Cs/PEG blend with upgraded biological properties such as improved biocompatibility protein adsorption, cell adhesion, growth and proliferation compared with the pure ones. Kolhe et al. [18], demonstrated that Cs/PEG blend revealed improved ductility compared with Cs/EG copolymer reflecting the efficiency of utilizing the blending technique.

Polyethylene glycol (PEG), a linear polymer derived from ethylene oxide, finds a broad range of application in both biomedical and industrial sections [19-22]. It is regarded as one of the

extremely investigated polyether owing to its preferable features like high hydrophilicity, remarkable biocompatibility with cells low toxicity as well as non-immunogenicity [23, 24]. The presence of hydroxyl groups (OH) in PEG structure facilitate its solubility in both hydrophilic as well as hydrophobic solution. Hydroxyl group considered as electron donor hence it has the ability to interact with organic compounds (with hydrophobic nature) via the formation of hydrogen bonding [25].

The objective of this study is to probe the impact of blending polyethylene glycol with chitosan via investigating the molecular structure, the electronic transition and the electronic structure, and the surface morphology along with the swelling ability and the hardness. Hence, a series of Fourier Transform Infrared (FTIR) spectroscopy, ultraviolet-visible (UV-Vis) spectroscopy, scanning electron microscopy (SEM) have been used in the characterization of the resultant blends.

Materials

Medium molecular weight chitosan (Cs) powder with a degree of deacetylation (75%-85%) was supplied by Sigma-Aldrich (Saint Louis, USA). Polyethylene glycol (Mw = 7000-9000) purchased from Bio Basic (Canada). Glacial acetic acid was purchased from El Nasr pharmaceutical chemical (Cairo, Egypt) and used as received. De-ionized water was utilized for the preparation of all samples.

Methods

Chitosan/PEG blends with different chitosan/PEG ratios (0/100, 20/80, 40/60, 60/40, 80/20, 100/0) were prepared via employing solution casting technique. In a typical procedure, Cs powder was dissolved into 2% glacial acetic acid solution and subjected to stirring in order to obtain completely dissolved and transparent solution. Then adequate amounts of PEG were added to this solution and stirred again until obtaining a clear solution. The solution was left un distributed for 2 hours before casting to avoid air bubbles formation and then cast on a and dried in electrical oven at 60°C. The prepared blend films had regular thickness which ranged between 115 µm to 185 µm by the aid of digital micrometer.

Characterization

FTIR spectra of the chitosan/PEG blend films as well as the neat components were measured

employing a Mattson 5000 spectrometer. The measurements were conducted in the wavenumber range of 400-4000 cm⁻¹ at 298 K. UV-Vis absorption spectra measurements of the chitosan-polyethylene glycol blend were conducted in the range of 200-800 nm using were performed in the range 200-900 nm using a dual UV-Vis Unicomp spectrometer, Mattson, UK. The morphology of the prepared blend films as well as the neat Cs were investigated by scanning electron microscope (SEM) (JEOL JSM 6510 Iv) operates under high vacuum, at room temperature.

Hardness Test

In order to evaluate the values of the surface microhardness of Cs/PEG blends as well as pure Cs, digital Vickers microhardness tester (Model FM-7, Tokyo, Japan) was utilized. The measurements were conducted at 10 and 100 g of indentation load for 5 sec indentation time.

Swelling studies

In order to evaluate the swelling behavior or the medium uptake ability of chitosan-PEG film samples as well as pure chitosan film, all the prepared samples were cut into (2.5 cm×3 cm) and weighted. Then, they were immersed in de-ionized water and buffer solution PH7 at 37°C for different time periods. The swelling behavior was tested by immersing the weighted film samples in de-ionized water and buffer solution PH7 at room temperature for predetermined intervals. Afterwards, the weights of the samples were measured after blotting them with a tissue paper in order to remove any water on the surface. The swelling percentage (swelling %) was calculated by utilizing the formula:

$$\text{Swelling \%} = \frac{\text{Wet weight} - \text{Dry weight}}{\text{Dry weight}} \times 100$$

Results and Discussion

FTIR spectroscopy

Figure 1. displays the FTIR spectra of pure chitosan, polyethylene glycol and chitosan-polyethylene glycol blend films. Spectra of pure chitosan demonstrates absorption band at 3500 cm⁻¹ which can be ascribed to both the O-H and the N-H stretching vibration of chitosan [26, 27]. The band located between 3350 and 3066 cm⁻¹ may be assigned to N⁺-H vibration stretch owing to the protonation of amino group in chitosan which combined with peak about 1571 cm⁻¹ arising from N-H bending vibration in amide group [28]. The two peaks at 2115 and 1380 cm⁻¹ refers to stretching vibrations of carbodiimides and CH₃ [28] in amide group of chitosan respectively.

On the other hand, the neat PEG shows its characteristic absorption bands located at 2887, 1647, 1469, 1281 and 962 cm^{-1} were attributed to C-H stretching vibration of alkane, C=C stretching vibration of alkenes, C-H bending vibration of alkanes, C-O stretching vibration of ether and C-H bending [29, 30].

The effect of blending PEG and Cs can be investigated via comparing the FTIR spectra of the different blend films with the respective ones of pure Cs and PEG. As shown in Figure 1b blend film with mass ratio 90/10 (Cs/PEG) exhibit FTIR spectra identical to that of pure

chitosan. Upon increasing the mass ratio of PEG in the blend, most of its characteristic absorption bands become more evident. Although there is no evidence for developing new bands or vanishing of characteristic bands relevant to both of the neat Cs and PEG, slight change in intensity and slight shift in the position of some characteristic bands of Cs and PEG has been observed in the spectra of blends. This postulates the presence of a distinct sort of interaction between both of Cs and PEG which could emanate from the newly formed intermolecular hydrogen bonds between Cs and PEG [18, 29].

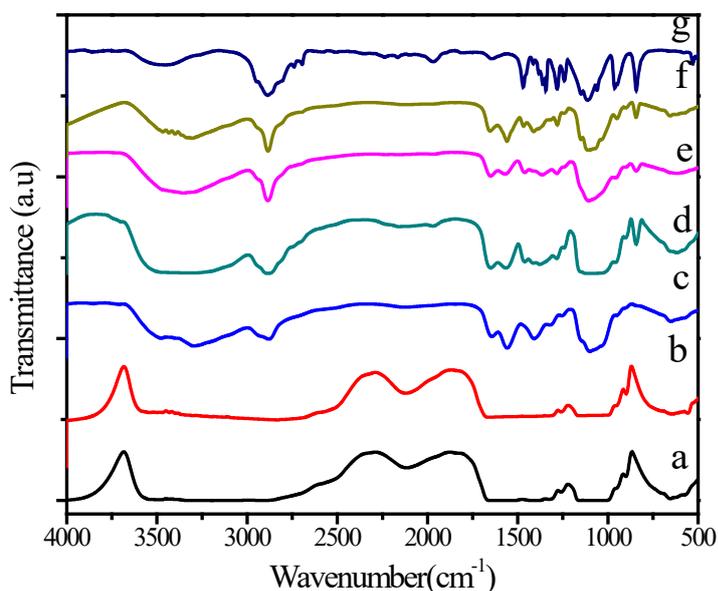


Fig. 1. FTIR spectra of (a) chitosan and Cs/PEG blend with different weight ratio (b) (Cs/PEG) 90/10, (c) (Cs/PEG) 80/20, (d) (Cs/PEG) 70/30, (e) (Cs/PEG) 60/40, (f) (Cs/PEG) 50/50 and (g) polyethylene glycol.

UV-Visible Spectra

UV-Vis spectra of chitosan polyethylene glycol (Cs/PEG) blends and its components are shown in Figure 2. Pure chitosan spectra exhibit weak absorption band at 299 nm which attributed to $\pi-\pi^*$ transition of C=O group of chitosan [31]. On the other hand, polyethylene glycol spectra did not show any absorption band. With regard to blend film of 90/10 and 50/50 mass ratio, their UV-Vis spectra similar to that of pure Cs. Further increasing in PEG mass ratio in the blends (80/20, 70/30 and 60/40) lead to increase in band intensity with small shift to low wavelength (blue shift) with reference to spectra of pure chitosan. The changes observed in the UV-Vis spectra of the blends signalize

the formation of inter/intra molecular hydrogen bonding fundamentally between polyethylene glycol with chitosan which is concomitant with FTIR results [30].

The values of optical band gap (E_g) of (Cs/PEG) blends as well as both of pure Cs and PEG are deduced by Tauc's relation and supplied by Davis and Mott [32]: $\alpha h\nu = (\alpha h\nu - E_g)^n$ where ($h\nu$) is the photon energy, h is plank's constant, ν is the frequency, A is a constant, n is equal 1/2 for direct band gap and the absorption coefficient (α) obtained by the relation [33]: $\alpha = 4\pi K/\lambda$

where k is the absorption index or absorbance and λ the wavelength. Plotting the relationship

between $(\alpha h\nu)^2$ versus the photon energy ($h\nu$) show straight portion, band gap can be calculated by extrapolating this straight portion [$(\alpha h\nu) = 0$]. Table 1 represents calculated values of the direct band gap of chitosan polyethylene glycol with different mass ratio compared with their neat component. It is remarkable that increasing polyethylene glycol ratio leads to increases in energy gap.

Scanning electron microscopy (SEM)

For the sake of inspecting the surface morphology of the resultant Cs, PEG and Cs/PEG blends, SEM micrographs were recorded and depicted in Figure 3. SEM micrograph of pure chitosan exhibited smooth and uniform surface, this result is coincident with the literature

[34]. After the incorporation of PEG with Cs, the surface of blend films manifested some changes [29]. For blend film with 80/20 mass ratio, its SEM micrograph shows coarsening and observed reduction in film homogeneity. Further increasing in PEG ratio (70/30, 6/4 and 50/50) show obvious improvement in surface homogeneity and a few small pores. Such changes can be tentatively ascribed to the fact that both of Cs and PEG has its own phase so when PEG was added to Cs matrix, they exhibited a tendency of self-gathering throughout the course of solution volatilization by virtue of the restricted compatibility [29]. Consequently, migration was occurred and holes were formed on the blend films surfaces.

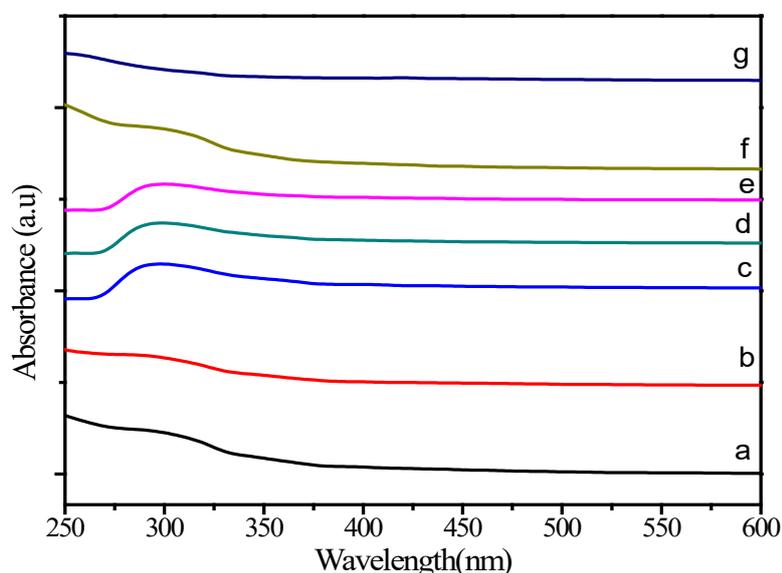


Fig. 2. UV-Vis spectra of (a) chitosan and Cs/PEG blends with different weight ratio (b) (Cs/PEG) 90/10, (c) (Cs/PEG) 80/20, (d) (Cs/PEG) 70/30, (e) (Cs/PEG) 60/40, (f) (Cs/PEG) 50/50 and (g) polyethylene glycol.

TABLE 1. Calculated values of the direct band gap of Cs, PEG and Cs/PEG blends with different mass ratio.

Band gap (ev) for direct allowed transition	Mass ratio of the blend film (CS/PEG)
4.691	Pure C _s
4.997	90/10
5.285	80/20
5.366	70/30
5.269	60/40
4.276	50/50
4.132	Pure PEG

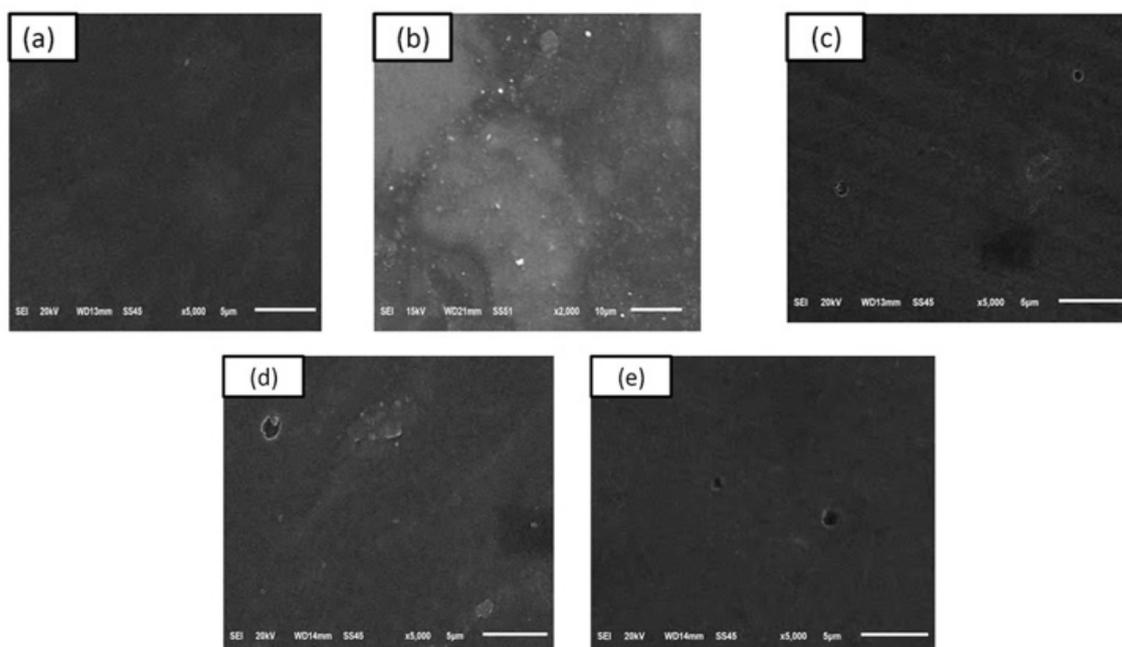


Fig. 3. SEM Micrographs of (a) chitosan and Cs/PEG blends with different weight ratio (b) (Cs/PEG) 80/20, (c) (Cs/PEG) 70/30, (d) (Cs/PEG) 60/40, (e) (Cs/PEG) 50/50.

Hardness

The hardness of any material reflects its ability to resist being permanently deformed as a response to applying a load on it. The Vickers hardness and maximum shear stress of Cs/PEG blends with different mass ratio as well as pure Cs are listed in Table 2. It can be noted that increasing polyethylene glycol ratio in blend results in increasing both Vickers hardness and maximum shear stress except for blend with 70/30 (CS/PEG) mass ratio.

Swelling studies

Investigation of the swelling behavior of polymeric materials is of a particular interest

of due to its significance in determining the appropriateness of such materials for many biomedical applications [26, 35]. Figure (4a, b) illustrates the swelling ratio of blend film in deionized water and buffer solution with PH7 with time respectively. As shown in Figure (4a, b), increasing polyethylene glycol mass ratio in blend result in observed decrease in maximum swelling ratio for both water and PH7. It is worth to mention that it was expected that increasing polyethylene glycol ratio must lead to increase in swelling due to hydrophilic property of it. Such decrease in maximum swelling ratio can be explained by the presence of a hydrogen bonding between both of Cs and PEG.

TABLE 2. Values of Vickers hardness and maximum shear stress of pure chitosan a well as chitosan polyethylene glycol blend film with different mass ratio.

(τ_m) kg/mm ²	H _v Kg/mm ²	Composition Ratio (CS/PEG)
1.468	4.45	Pure C _s
1.683	5.10	90/10
2.227	6.75	80/20
0.858	2.60	70/30
1.650	5.00	60/40
3.102	9.40	50/50

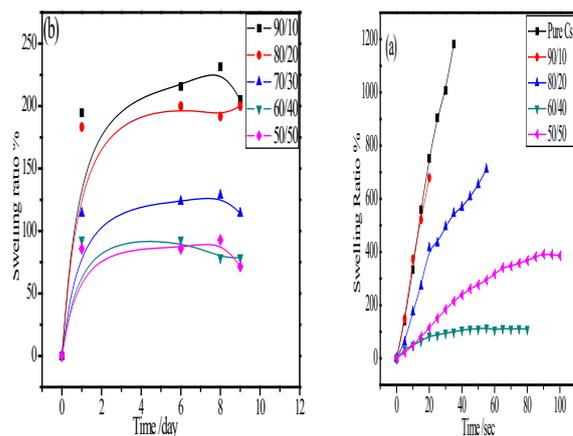


Fig. 4. Swelling study of chitosan and Cs/PEG blends with different weight ratio.

Conclusions

By employing simple blending and casting technique Cs/PEG blends have been prepared and characterized by a group of FTIR spectroscopy, UV-Vis and SEM. The structural characterization results assumed the presence of a distinct sort of interaction between both of Cs and PEG. The changes in the surface morphology of chitosan which is noticed after the addition of polyethylene glycol strengthen this postulation. Additionally, it was found that increasing PEG mass ratio in the blend results in increasing the value of the direct bandgap and in turn increasing insulating character of the blend.

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توصيف مخاليط الكيتوزان و البولى ايثيلين جليكول

عفاف سرحان عبدالرازق سرحان

قسم الفيزياء- كلية العلوم- جامعة المنصورة- مصر

يهدف هذا البحث الى تحضير أفلام من مخاليط الكيتوزان و البولى ايثيلين جليكول Cs/PEG بنسب وزنية مختلفة باستخدام تقنيات الخلط و الصب البسيطة. وقد تمت دراسة كلا من التركيب الجزيئي و الانتقالات الإلكترونية, والشكل الظاهري للمخاليط المحضرة باستخدام أطياف الأشعة تحت الحمراء ($FT-IR$), الأشعة فوق بنفسجية (UV) و الميكروسكوب الإلكتروني الماسح (SEM) بالاضافة الى قياس كلا من الصلابة و قدرة الانتفاخ للمخاليط المختلفة. و قد أوضحت نتائج كلا من الأشعة فوق بنفسجية و أطياف الأشعة تحت الحمراء وجود تفاعل بين الكيتوزان و البولى ايثيلين جليكول الذي يمكن أن ينبع من روابط الهيدروجين الجزيئية المتكونة حديثاً بين الكيتوزان و بولى ايثيلين جليكول. وقد وجد أيضاً أن زيادة نسبة البولى ايثيلين جليكول في المخاليط يمكنه ان يؤدي إلى زيادة قيم فجوة الطاقة. كما أظهرت نتائج الميكروسكوب الإلكتروني الماسح للمخاليط المختلفة تغير في الشكل الظاهري للكيتوزان بعد اضافة بولى ايثيلين جليكول.