



Scholars Research Library

Der Pharma Chemica, 2015, 7(10):357-361
(<http://derpharmachemica.com/archive.html>)



ISSN 0975-413X
CODEN (USA): PCHHAX

Chitosan membrane as an oil carrier: Spectroscopic and modeling analyses

Diaa Atta, Ahmed Fakhry and Medhat Ibrahim*

Spectroscopy Department, National Research Center, 33 El-Bohouth St. 12311 Dokki, Giza, Egypt

ABSTRACT

Chitosan is loaded with olive oil and then subjected to Fourier transform infrared spectroscopic study. FTIR spectra of chitosan as well as the loaded chitosan show that olive oil is weakly bonded with chitosan. Both spectra are nearly identical which could be an indication that, chitosan is an ideal structure for loading olive oil. Molecular modeling at B3LYP/6-31g(d,p) level of theory is utilized to investigate the physical as well as electronic differences between chitosan and oil loaded chitosan. Glycine is chosen as a model molecule for olive oil. Calculated total dipole moment indicates that; chitosan became highly interacting with its surrounding as far as olive oil loading is concerned. It indicates that, olive oil/chitosan interaction requires only -0.1372 au, meaning that, small amount of energy is needed for such interaction, which confirms the FTIR and the model molecule results that such interaction is weak.

Keywords: Chitosan, Olive oil, Glycine, FTIR and B3LYP/6-31g(d,p).

INTRODUCTION

Natural-polymer in the form of films shows extensive applications as alternatives to plastic packaging owing to their biodegradability and biocompatibility [1].

Furthermore, these films may be used as carriers for many additives, such as antioxidants and antimicrobials agents. Accordingly, extensive research works are directed to maintain food quality, minimize the growth of undesirable microorganisms on the surface of food and provide extra protection against oxidative agents by utilizing such films with additives in the so called "active packaging [2-4]. Chitosan is one of the most famous natural polymers which are derived after the deacetylation of chitin. It is dedicated for many applications as it is well known as non-toxic, biodegradable and biocompatible polymer [5]. It is well known with its antimicrobial activity [6-7]. It is stated that, chitosan could be effectively utilized for the delivery and encapsulation of drugs, vitamins, proteins, genes, nutrients, essential oils and phenolic compounds [8-9]. Carumcopticum essential oil (CEO) was successfully encapsulated in nano chitosan using emulsion-ionic gelatin with two cross linkers namely TPP and HMP [10]. Chitosan as well as other natural polymers was subjected to FTIR and molecular modeling studies in order to elucidate their molecular structure [11], and their interaction with biological molecules in order to investigate their functionalities [12-15]. Based upon these considerations this study is conducted for carrying on olive oil upon chitosan membrane. FTIR and molecular modeling at B3LYP/6-31g(d,p) are utilized to understand the mechanism of interaction between olive oil and chitosan surface.

MATERIALS AND METHODS

The chitosan film membrane has been prepared by the casting method [16]. Chitosan film and another one loaded were prepared with Extra Virgin Olive Oil (EVOO). For pure chitosan film we dissolved 25 g of low molecular weight (15kD) chitosan (from ABCO Laboratories, USA) in 25 ml of 7% acetic acid (from ADWIC, Egypt). The chitosan solution stirred for 1 hour then filtered and casted in Petri dish finally stored in room temperature for 48 hours. For the EVOO loaded Chitosan film a 2 microliters of EVOO have been added after the chitosan solution filtration and stirred for another 2 hours then the solution was casted also in a Petri dish for 48 hours.

The FTIR have been measured by ATR technique based on FTIR spectrometer (VERTEX 70, Bruker Optics, Germany). The obtained data is analyzed by OPUS software (Bruker Optics)

3. CALCULATION DETAILS

The amino acid glycine is proposed as a model molecule for olive oil, and then interacted with chitosan through the NH_2 of chitosan. Calculations were carried out on a personal computer, performed using Gaussian09 program [17]. The initial geometry optimizations of chitosan interacted with glycine was performed to get approximate minimum energy structures. The lowest energy conformations obtained and optimized with the B3LYP/6-31g(d,p) method [18-20]

RESULTS AND DISCUSSION

The assignment of the spectrum of chitosan was discussed in many studies [11-13]. The assignment will be mentioned here in order to indicate the effect of oil upon the spectrum of chitosan. As shown in Figure 1 the FTIR absorption spectrum of chitosan shows a broad band around 3378 cm^{-1} which is assigned as the OH stretching vibration. Then the band arising from CH stretching is located at 2936 cm^{-1} and 2871 cm^{-1} . The band at 1650 cm^{-1} was due to the OH of chitosan [21]. The band at 1589 cm^{-1} is due to the scanty amount of $\text{O}=\text{C}-\text{NH}_2$. Peaks around 1429 cm^{-1} and 1384 cm^{-1} are assigned to the CH_2 and CH_3 vibrations respectively. The region from 1152 cm^{-1} to 1033 cm^{-1} is the characteristic bands of C-O-C linkage. Finally, the C-N fingerprint band appears at 894 cm^{-1} . The structure of chitosan remains unchanged as a result of loading with olive oil. Regarding effect of oil one can conclude that, the intensity of CH bands of chitosan has increased as a result of coupling between chitosan and olive oil. The band at 1750 cm^{-1} has appeared for chitosan loaded with oil according to the $\text{C}=\text{O}$ stretching vibrations. The CH stretching bands became more intense as a result of loading chitosan with olive oil. The band at 1589 cm^{-1} which is assigned as the scanty amount of $\text{O}=\text{C}-\text{NH}_2$ is shifted to 1657 cm^{-1} as a result of loading chitosan with olive oil.

The coincidence between both spectra has suggested that chitosan is an ideal structure for loading olive oil. As stated earlier, chitosan shows the ability to interact with amino acids through four sites through its hydrogen bondings. Molecular modeling calculations indicate that the NH_2 group is the most favorable place for interactions. Based on this fact, chitosan is proposed to interact with glycine as a model molecule for olive oil. Figure 2 shows the optimized model molecule for the interaction between chitosan and glycine through the NH_2 of chitosan. The model indicates that, the interaction is weak. Correlating this with FTIR absorption bands in figure 1 one can observe that, the olive oil is weakly bonded with chitosan.

Table 1 shows the calculated total dipole moment of the studied structures. Chitosan shows 3.49 Debye while glycine has 6.94 Debye. The model indicating the interaction between chitosan/glycine shows 4.40 Debye indicating that chitosan became highly interacting with its surrounding as far as glycine interacts with it. The SCF energy is calculated for chitosan and glycine as well as their complex in order to calculate the interaction energy. The interaction energy is the difference between the sum of SCF energies of chitosan and glycine and the SCF energy of their complex chitosan/glycine. The interaction between chitosan and glycine required -0.1372 au . This indicated that, small amount of energy is needed for such interaction, which confirms the FTIR and the model molecule results that such interaction is weak.

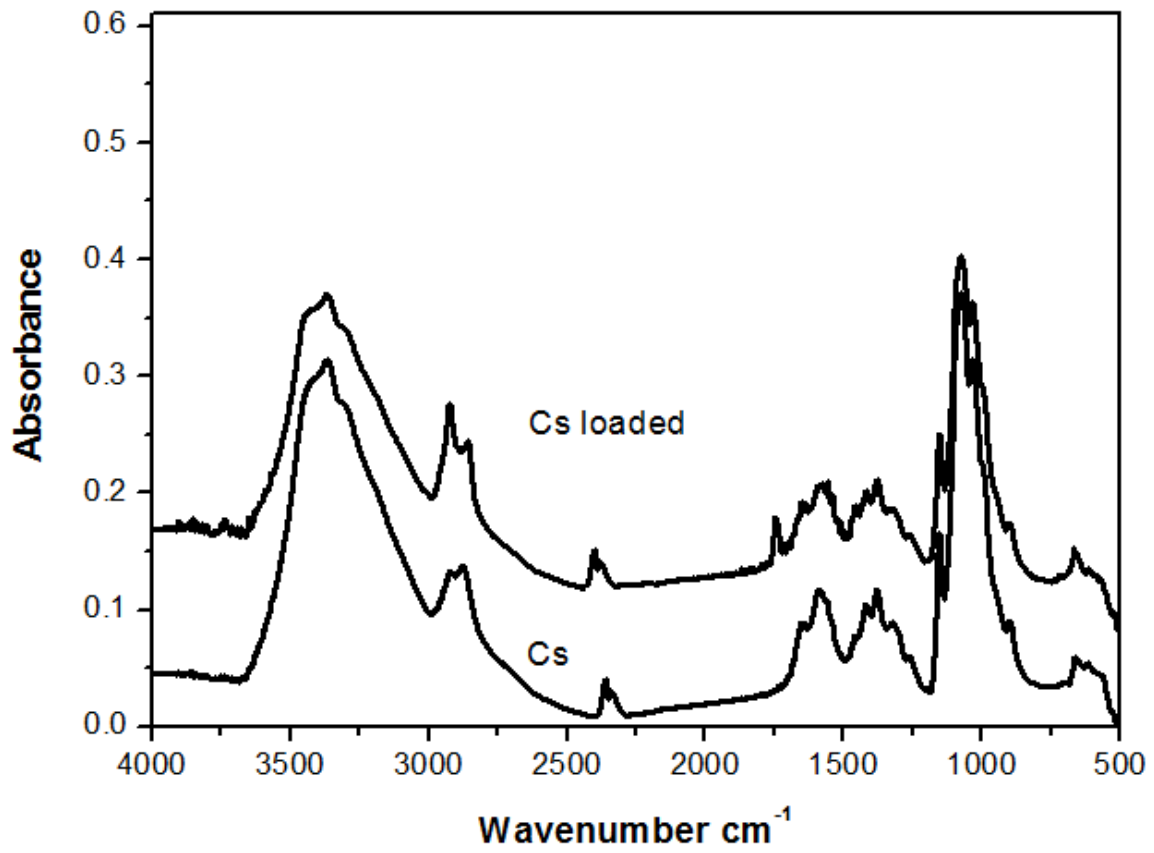
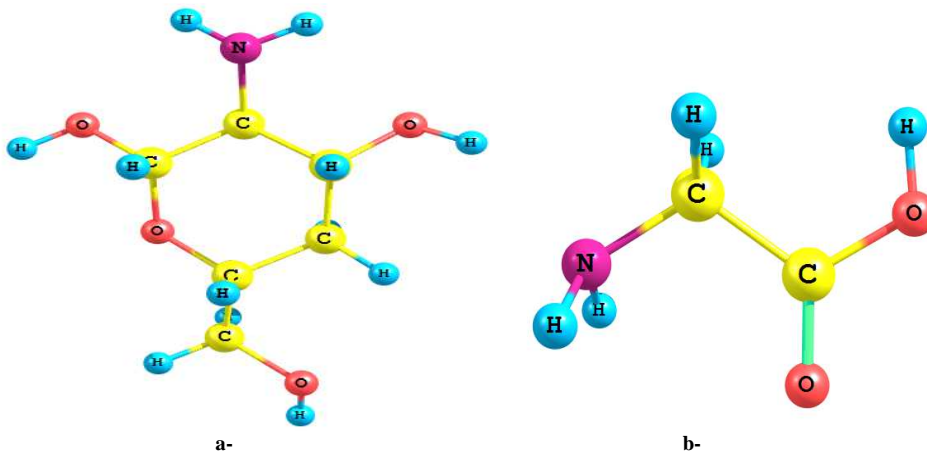


Figure1. FTIR absorption spectra of chitosan (Cs) and chitosan loaded with olive oil (Cs loaded)



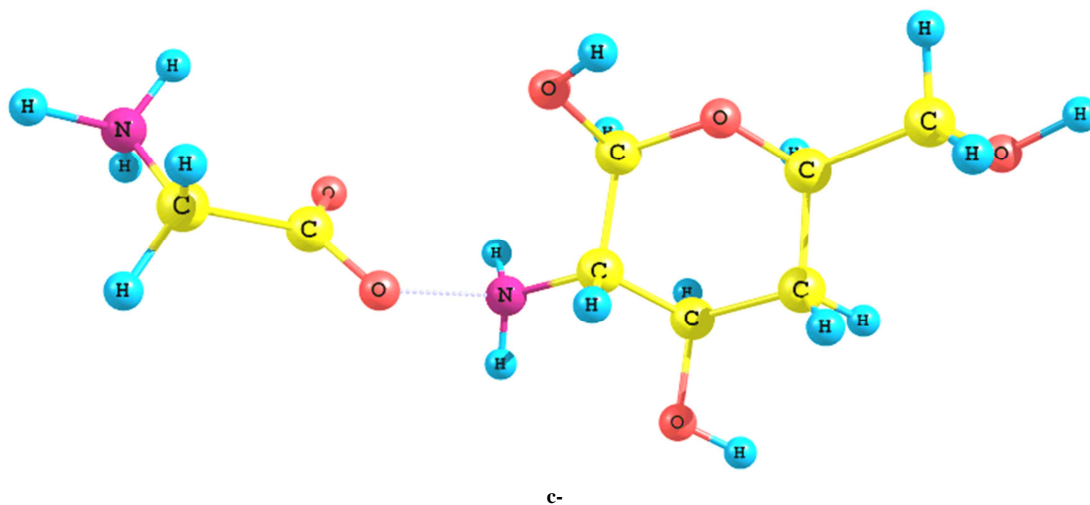


Figure 2. Optimized B3LYP/6-31g(d,p) model molecules for a- chitosan; b-the model molecule for olive oil (glycine) c-the interaction between chitosan and glycine through the NH₂ of chitosan

Table 1. B3LYP/6-31g(d,p) calculated total dipole moment (TDM) as Debye, SCF energy as A.U for chitosan, glycine and chitosan interacted with glycine

	TDM	Energy
Chitosan	3.49	-592.0814
Glycine	6.94	-284.8896
Chitosan/glycine	4.40	876.8348

REFERENCES

- [1] S Shojaee-Aliabadi; H Hosseini; MA; Mohammadifar; A Mohammadi; M Ghasemlou; SM Hosseini; R Khaksar. *Carbohydr Polym.* **2014**, 101, 582.
- [2] D Salarbashi; S Tajik; S Shojaee-Aliabadi; M Ghasemlou; H Moayyed; R Khaksar; MS Noghabi. *Food Chem.* **2014**, 146, 614.
- [3] E Almenar; R Catala; P Hernandez-Muñoz; R Gavara; *LWT-Food Sci Technol.* **2009**, 42, 587.
- [4] M Ghasemlou; N Aliheidari; R Fahmi; S Shojaee-Aliabadi; B Keshavarz; MJ Cran; R Khaksar. *Carbohydr Polym.* **2013**, 98, 1117.
- [5] M Rinaudo. *Prog Polym. Sci.* **2006**, 31, 603.
- [6] MN Ravi Kumar. *React Funct Polym.* **2000**, 46, 1.
- [7] P Dutta; S Tripathi; G Mehrotra. J Dutta. *Food Chem.*, **2009**, 114, 1173.
- [8] SF Hosseini; M Zandi; M Rezaei; F Farahmandghavi. *Carbohydr Polym.* **2013**, 95, 50.
- [9] KI Jang; HG Lee. *J Agric Food Chem.* **2008**, 56, 1936.
- [10] A Esmaeili; A Asgari. *Int J Biol Macromol.* **2015**, 81, **2015**, 283.
- [11] M Ibrahim; O Osman. **2009**, *J Comput Theor Nanosci.* 6, 1054.
- [12] M Ibrahim; A-A Mahmoud; O Osman; A Refaat; and ME El-Sayed. *Spectrochim. Acta A*, **2010**, 77, 802.
- [13] ME El-Sayed; A Omar; M Ibrahim; WI Abdel-Fattah. *J Comput Theor Nanosci.* **2009**, 6, 1663.
- [14] NS Ammar; H Elhaes; HS Ibrahim; W El-hotaby; MA Ibrahim. *Spectrochim. Acta A.* **2014**, 121C, 216.
- [15] H Elhaes; A-A Mahmoud; EM Ahmed; MS Abdel-Aal; O Osman; and M Ibrahim. *J Comput Theor Nanosci.* **2014**, 11, 1891.
- [16] Patents: G Rigby. USA Patent No. 2, 030, 880, (1936).
- [17] Gaussian 03, Revision B.05, MJ Frisch; GW Trucks; HB Schlegel; GE Scuseria; MA Robb; JR Cheeseman; JA Montgomery, Jr T Vreven; KN Kudin; JC Burant; JM Millam; SS Iyengar; J Tomasi; V Barone; B Mennucci; M Cossi; G Scalmani; N Rega; GA Petersson; H Nakatsuji; M Hada; M Ehara; K Toyota; R Fukuda; J Hasegawa; M Ishida; T Nakajima; Y Honda; O Kitao; H Nakai; M Klene; X Li; JE Knox; HP Hratchian; JB Cross; C Adamo; J Jaramillo; R Gomperts; RE Stratmann; O Yazyev; AJ Austin; R Cammi; C Pomelli; JW Ochterski; PY Ayala; K Morokuma; GA Voth; P Salvador; JJ Dannenberg; VG Zakrzewski; S Dapprich; AD Daniels; MC Strain; O Farkas; DK Malick; AD Rabuck; K Raghavachari; JB Foresman; JV Ortiz; Q Cui; AG Baboul; S Clifford; J Cioslowski; BB

Stefanov; G Liu; A Liashenko; P Piskorz; I Komaromi; RL Martin; DJ Fox; T Keith; MA Al-Laham; CY Peng; A Nanayakkara; M Challacombe; PMW Gill; B Johnson; W Chen; MW Wong; C Gonzalez; and JA Pople. Gaussian, Inc., Pittsburgh PA, **2003**.

[18] SH Vosko; L Wilk; M Nusair. *Can J Phys.* **1980**, 58, 1200.

[19] AD Becke. *Phys Rev A.* **1988**, 38, 3098.

[20] C Lee. *Phys Rev B.* **1988**, 37, 785.

[21] L You; F Lu; D Li; Z Qiao and Y Yin. *J Hazard Matter.* **2009**, 172, 38.