Effect of Gamma and CO_2 Laser Radiations on the Optical Properties of Pure Chitosan

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ABSTRACT

In this work, the effect of gamma and CO_2 laser radiations on the optical properties of 2% (wt/v) concentration of pure chitosan has been investigated. The optical properties (absorption, transmission, molar absorption coefficient and refractive index) of all prepared samples of chitosan solution, before and after gamma and CO_2 laser irradiated, were studied in the wavelength range (200-1100) nm for a gamma dose rate of 0.1 mR h^{-1}, and CO_2 laser power of 5W. The time of irradiation was five and ten days for gamma ray and 5s and 10s for laser. It has been found that there is an increase in the absorption of all samples irradiated with both types of radiation gamma and CO_2 laser. The transmission of all samples was decreased. The refractive index of all samples was decreased in the wavelength range (200-400) nm and then increased in the wavelength range (400-1100) nm for both types of radiations. It has also been found that the values of molar absorption coefficient for all irradiated samples were increased.

1. INTRODUCTION

Chitosan (CS) is the most abundant of the commonly studied biopolymers. Chitin,which is derived from live organisms such as shrimp, crabs, turtles, and insects is used to make CS, which is a hydrophilic, semi crystalline, linear polysaccharide [1], [2]. Furthermore, its non-toxicity, ionicity, antibacterial characteristics, and the capacity to form films all draw attention to biocompatible and biodegradable CS [2,4]. The thermal, optical, and structural properties of polymer films can all be affected by laser irradiation [5]. Radiation modification of polymers is a popular method for achieving unique physical and optical features. Ionization of the atoms and creation of a highly excited state occur when polymers are exposed to ionizing radiation [6], [7]. There are many studies on its optical properties that were close to the results obtained in our study, including; The CS-MgO nanocomposite film which was prepared by adding 10% weight to chitosan, then the absorbance and transmittance of the prepared samples were measured. The results showed an improvement in the values, while the refractive index showed an increase for the CS-MgO nanocomposite compared to the pure chitosan film as a result of

crystallization changes and the internal microstructure changes [8]. There are minor changes in the results of UV spectroscopy in the skeleton of chitosan after irradiation using 100 kGy of gamma rays [9]. Using the effects of a Nd:YAG (1064) nm laser on the optical properties of pure polymethyl (PMMA), the absorption and transmittance spectra were recorded in the wavelength range (190-890) nm using UV-visible spectroscopy, and the results showed that the absorbance, absorption coefficient, extinction coefficient and refraction index increase with increasing the number of laser pulses [10].

The aim of this work is to investigate the tuning of the optical constants of the samples after continuous irradiation using CO_2 laser 10.6 µm wavelength and gamma radiation at different time.

2. MATERIALS AND METHODS

2.1 Materials

Chitosan powder ($C_6nH_{11}nNO_4n$) (DD = 95 percent) was purchased from Shanghai Macklin Biochemical Company., Ltd, China, and (0.1M) acetic acid was purchased from Sigma-Aldrich.

2.2 Preparation of chitosan solution and irradiation

The chitosan solution was prepared by dissolving 0.2g of chitosan in 10 mL of acetic acid to achieve a 2% (wt/v) concentration, then the solution was stirred for 5 h until the chitosan was fully dissolved. The resulting solution was irradiated at ambient temperature by gamma-ray of ^{60}Co of activity 0.5 µci with a dose rate of 0.1 mR h^{-1} for 5 and 10 days, and by CO_2 laser beam of 5W for 5s and 10s.

2.3 UV-Visible spectrophotometer

A UV-VIS spectrophotometer (DRAWELL, DU-8200), which is a single beam spectrophotometer was used. It works in the wavelength range (190-1100) nm. In this work, the optical measurements were taken in the wavelengths range (200-1100) nm.

3. RESULTS AND DISCUSSION

3.1 Absorbance

In laser irradiation, absorption measurements were performed using the UV/visible spectrum (200-1100) nm range for all samples of chitosan solution (CS) prepared at 2% (wt/v) concentration. Fig. 1a shows the absorption curves as a function of wavelength in prepared chitosan solution samples. Through our observation of the Figure,

it was found that the behavior of the curves is the same for all models before and after irradiation, where a sudden increase was noted in the absorption values in wavelength range (250-400) nm and this might be due to a decrease in the absorption of the incident beam [11]. Then the curve begins to nearly stabilize after wavelengths higher than (400) nm. It is also visible in the Figure that the peak increases as the time of irradiation increases, but the peak does not shift in location, indicating that the application of the laser to the polymer does not affect the chemical structure of the material, but it does create new physical features [10].

As for gamma rays, the UV spectra versus non-irradiated and irradiated chitosan were studied to determine the differences in wavelength. It is observed that both non-irradiated and irradiated chitosan samples have nearly similar wavelength as shown in the Fig. 1b, where all samples show high absorption in the (200-400) nm region and then the curve starts to stabilize after wavelengths above 400 nm. A small peak approximately at 960 nm was visualized before and after irradiation, and the effect of gamma irradiation on chitosan samples was visualized by changes in chitosan color. These results agree with what was reported Previous studies[9,12].
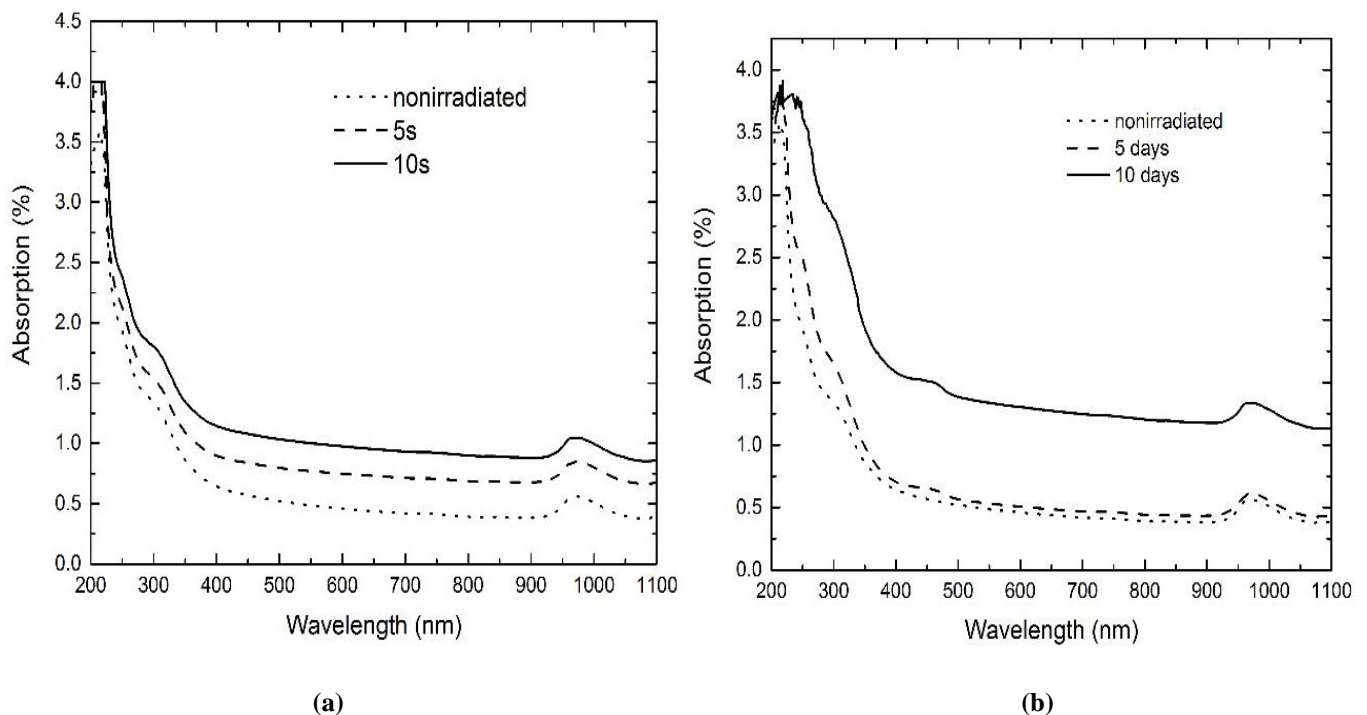

(a)   **(b)**

Fig. (1): The absorption spectrum as a function of wavelength of chitosan solution (a) irradiated by CO_2 laser 1064 nm wavelength for two different period time 5 sec and 10 sec. (b) irradiated by gamma ray for two different period time 5 days and 10 days

3.2 Transmittance

Figs. 2a and 2b, represent the change of the transmittance curve with the wavelength of the natural and irradiated chitosan. It is noted that the transmittance is an opposite case for the absorbance due to the logarithmic relationship that links the absorbance with the transmittance, as shown by the following relationship [13]:

$$A = log_{10}\left(\frac{1}{T}\right) \qquad (1)$$

Where, T is the transmittance. The transmittance curves behave in the same way in laser radiation and gamma as shown in Figs. 2a and 2b, where the transmittance of the prepared chitosan solutions after irradiation decreases in the wavelength range (200-400) nm and then starts almost steadily after wavelength (400) nm. From the Figures, we note that the longer the laser irradiation time, the lower the transmittance, and the same is the case in gamma radiation, the greater the number of days of irradiation, the lower the transmittance.

3.3 Refractive index

When investigating the optical properties of materials, determining the optical constants is one of the most difficult tasks because it requires complex equations and a lot of computation. To calculate the optical constants of materials, a variety of methods and procedures are used. The refractive index is calculated according to the following relationship [14]:

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \qquad (2)$$

The change in refractive index with wavelength is shown in Figs. 3a and 3b, and the refractive index curve is essentially identical to the nature of the reflectivity curve since refractive index is dependent on reflectivity.

Fig. 3a shows the change in refraction index for Chitosan before and after laser irradiation as a function of wavelength. Because the transmission of the longest wavelength is more, the refraction index drops at the longest wavelengths and increases at the irradiation time, these results agree with the results of ref. [10].

From Fig. 3b, it was noticed a decrease in the refractive index with respect to the position of the peaks, and this decrease in the refractive index occurs because of the degradation mechanism that occurs in irradiated chitosan samples. The curves then begin to rise, indicating that extending the irradiation time, the synthesis of chemically active free radicals while also supporting the formation of covalent connections between the different chains (cross-linking) and raising the refractive index, the obtained result is consistent with that previously reported by the researchers [12].

Moreover, the increase in the refractive index after gamma irradiation could be due to the breakdown of polymers, which leads to an increase in density, which raises the refractive index [15].

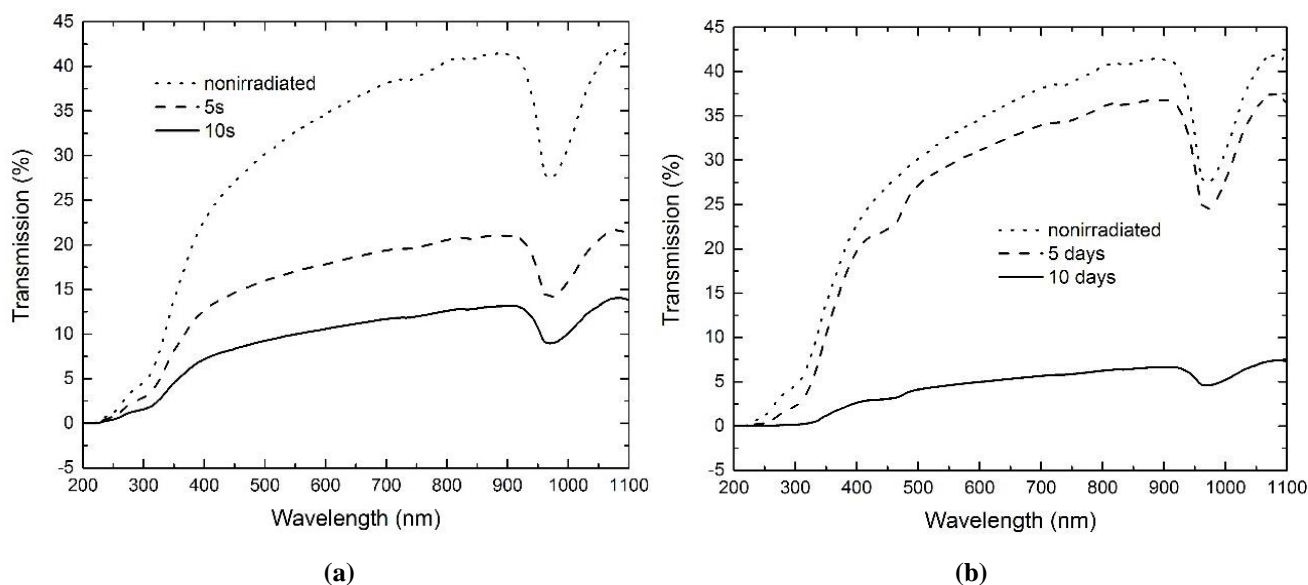**(a)**   **(b)**

Fig. (2): The transmission spectrum as a function of wavelength of chitosan solution (a) irradiated by CO₂ laser 1064 nm wavelength for two different period time 5 sec and 10 sec. (b) irradiated by gamma ray for two different period time 5 days and 10 days

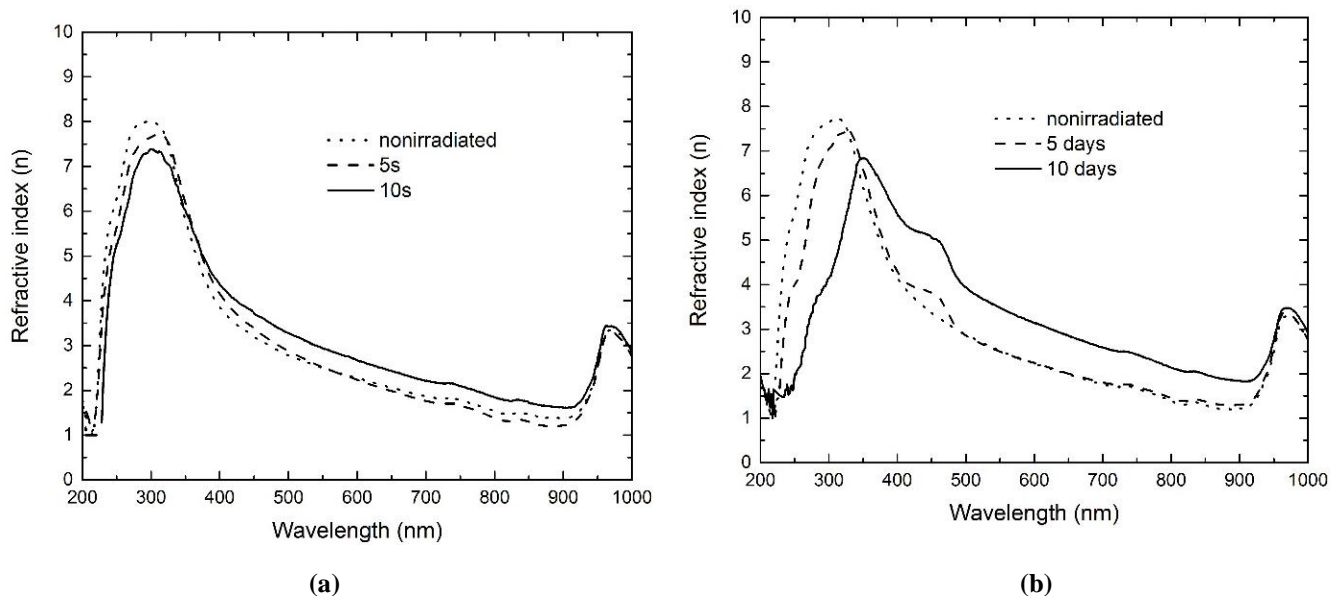**(a)**   **(b)**

Fig.(3): Refractive index (n) spectrum as a function of wavelength of chitosan solution (a) irradiated by CO₂ laser 1064 nm wavelength for two different period time 5 sec and 10 sec. (b) irradiated by gamma ray for two different period time 5 days and 10 days

3.4 Molar absorption coefficient

The molar absorption coefficient can be calculated using Beer-Lambert Law [16]:

$$A = \varepsilon l C \qquad (3)$$

Where ε is the molar absorption coefficient ($L.mol^{-1}cm^{-1}$), l is the path length (cm), and C is the chitosan concentration(M).

The molar absorption coefficient is an effective property of materials for absorbing light at a specific wavelength [17]. Due to the absence of research in determining the molar absorption coefficient of pure chitosan that has been published (to the best of the authors' knowledge), we decided to conduct an experiment to estimate the molar absorption coefficient of pure chitosan solution in the range 200-1100 nm. Figs. 4a and 4b show the molar absorption coefficient (ε) versus wavelength of chitosan solution irradiated with CO₂ laser of 1064 nm wavelength and gamma radiation. The graph demonstrates an increase in the molar absorption coefficient of chitosan solution for the two types of radiation, and this increase is particularly noticeable in the wavelength region between 400 and 1100 nm. Such an increase can be interrupted with the increment of the absorbance, since the molar absorption coefficient can be directly associated with the concentration of material.

Although the features of the molar absorption coefficient spectra did not change with increasing wavelength. For a solution irradiated with laser, the molar absorption coefficient values at UV wavelengths range from of 200 nm to 350 nm have increased from (65.67 $L.mol^{-1}.cm^{-1}$) for an un-irradiated sample to (83.255 $L.mol^{-1}.cm^{-1}$) for 5 sec and (102.77 $L.mol^{-1}.cm^{-1}$) for 10 sec. While the values for chitosan solution irradiated with gamma ray increased from (65.67 $L.mol^{-1}.cm^{-1}$) for the un-irradiated sample to (75.317$L.mol^{-1}.cm^{-1}$) and (147.72$L.mol^{-1}.cm^{-1}$) for 5 and 10 days of irradiation, respectively. Moreover, in the wavelength range 350 to 1100 nm, for samples irradiated with laser radiation, these values have dropped to be in the range of (65.67$L.mol^{-1}.cm^{-1}$) - (29.75 $L.mol^{-1}cm^{-1}$) and (51.44 $L.mol^{-1}.cm^{-1}$)- (65.62 $L.mol^{-1}.cm^{-1}$) for irradiated times 5s and 10 sec respectively (see Fig. 4a), and for samples irradiated with gamma radiation, these values have dropped to be in the range of (65.67$L.mol^{-1}.cm^{-1}$)- (29.75 $L.mol^{-1}cm^{-1}$) and (33.453 $L.mol^{-1}.cm^{-1}$)-(86.69 $L.mol^{-1}.cm^{-1}$) for 5 days and 10 days respectively (see Fig. 4b). The increasing of molar absorption coefficient spectra in the visible ranges for the pure chitosan solution samples reveals the role of laser and gamma radiations.

Finally, this study reveals that the gamma radiation has more effect on the increase of molar absorption coefficient of chitosan than the laser radiation especially in the visible range and also there is a shift of it spectra in the UV range towards the visible ranges.

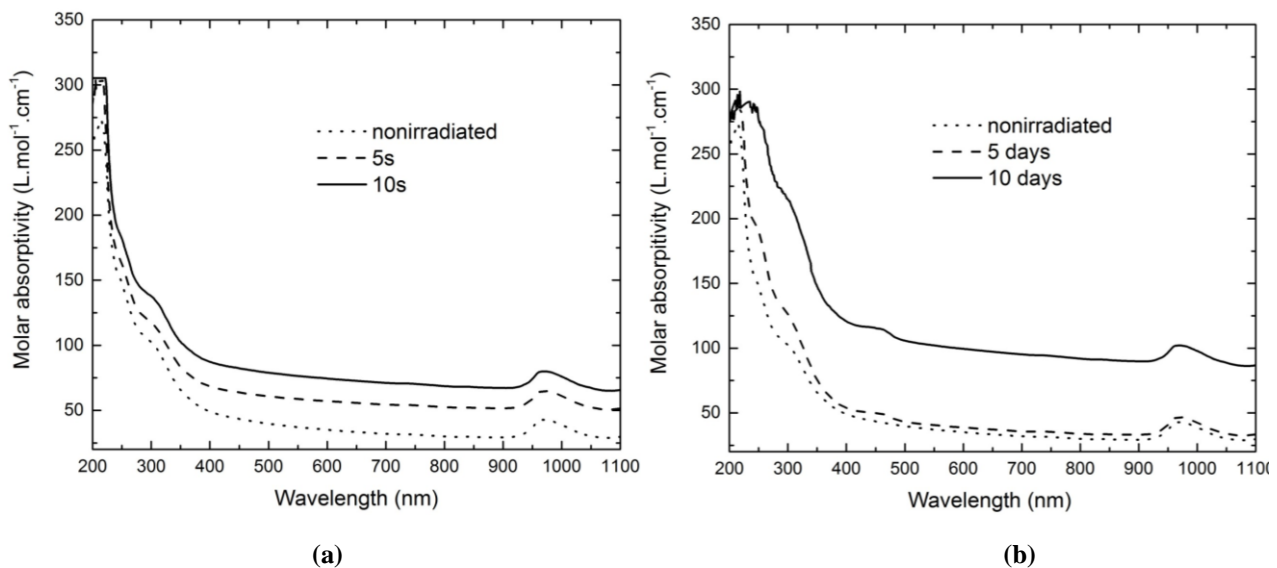**(a)**   **(b)**

Fig. (4): Molar absorption coefficient as a function of wavelength of chitosan solution (a) irradiated by CO₂ laser 1064 nm wavelength for two different period time 5 sec and 10 sec. (b) irradiated by gamma ray for two different period time 5 days and 10 days

4. CONCLUSIONS

Chitosan solution in a concentration of 2% (wt/v) have been prepared and then irradiated with gamma ray at a constant dose for 5 and 10 days and a continuous CO_2 laser beam of 10.6μm wavelength at constant energy for 5s and 10s. Then, a casting method technique was used to prepare films of irradiated solution. The UV-VIS spectrophotometer was used to study the optical properties. The absorption and molar absorption coefficient of prepared films were found to increase with the increase of irradiation time. The refractive index was noticed to increase at the longest wavelength, while, the transmission was observed to decrease with increasing the irradiation time for both types of radiation. These results indicate that, there is no change in the curves behavior of the optical properties of these samples and sensitive to gamma ray and CO2 radiation. Also, these results indicate that laser light can be used to modulate the optical properties of biopolymer.

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