

Study the effect of increasing Gamma ray doses on some physical properties of Carboxy methyl cellulose

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Abstract

In this study some of the physical properties of Carboxymethyl cellulose dissolves in distilled water with different concentration had been studied before and after irradiation by gamma ray of variable dose (5000rad, 7000rad, 9000rad). These properties are firstly the Rheological properties such as shear viscosity, relative viscosity specific viscosity and reduced viscosity are measured, secondly the mechanical properties such as ultrasonic velocity had been measured at frequency (40KHz). Other mechanical properties had been calculated such as absorption coefficient of ultrasonic waves, relaxation time, relaxation amplitude, specific acoustic impedance, bulk modulus and compressibility. The results show that all these properties are affected with variation in density and viscosity because of the intermolecular interactions Gamma radiation made degradation to polymer molecular chains that affect the physical properties as a result ultrasonic absorption increased and molecular weight decreased after irradiation.

Keywords: CMC solution, ultrasound technique, degradation, rheological properties, mechanical properties.

1. Introduction:

Carboxy methyl cellulose is an ionic linear polymer and used in more varied applications worldwide than any other water-soluble polymer known today. One of its important applications is using to increase petroleum production as (drilling fluid) from its original traps in our country. CMC solutions are pseudo plastic that is the

measured viscosity decreases with increasing shear rate and its also thixotropic [1,2] some times when solutions are subjected to high shear rate conditions ,then may be a time lag in the tendency of the apparent viscosity to increase again to its earlier (at rest), this time delay behavior is called thixotropy [2]. CMC is a cellulose derivative with carboxy methyl groups (-CH₂-COOH) bound to some of the hydroxyl groups of the glucopyranose monomers that make up the cellulose backbone [3] . It is often used as its sodium salt, sodium carboxy methyl cellulose (Gerhard Buchman -Germany). Irradiation process on polymer causes some changes in its physical and chemical properties such as increasing its softness and decreasing its solubility [4, 5].The polymer will suffer either degradation or cross-linking when it is interact with radiation. In case of degradation the mean molecular weight reduce and may be brittle or more flexible and its solubility either increase or decrease depending of the type of interactions with radiation [5]. The use of ultrasound as a tool in material science is increasing; the effect of ultrasound on organic synthesis, polymer reaction, electro plating, electro synthesis and electro polymerization has been exploited to good effect [6]. Ultrasonic technique is one of the basic International non-destructive methods for evaluation of materials and structures, a significant part of every ultrasonic inspection is the way in which the ultrasonic energy is transferred between the transducer and the tested object, different types of commercial liquids and gels are used as a coupling medium. Studies of ultrasonic irradiation show that it can be used for degradation of polymers, the breakage of chemical bonds is due to cavitations into the medium .Cavitations are the formation and violent collapse of small bubbles. This leads to shearing forces of sufficient magnitude to cause the rupture of chemical bonds Solvent effects might therefore be expected to influence the ultrasonic relation behavior, the absorption of ultrasonic in liquid polymer systems is governed by local modes of motion (segmental conformation change) and cooperative whole molecule movement (normal or Rouse modes), because of the existence of strong intermolecular interaction within the polymer. It should be possible to observe cooperative motion in the ultrasonic range [7]. Ultrasonic technique is good method for studying the structural changes associated with the information of mixture assist in the study of molecular interaction between two species [8, 9].

2. Experimental:

2.1 Preparation of Solutions:

CMC solutions were prepared by addition a known weight of CMC powder to affixed volume of distilled water then heating the mixture under reflux while agitating with magnetic stirrer to complete solubility of polymer. The solutions were then cooled to room temperature when a clear solution was obtained of concentration ranging (0.05 ,0.15 ,0.25 ,0.35 ,0.45 ,0.55, 0.65 and 0.75) gm/ml after that CMC irradiated by gamma ray with variable doses (5000, 7000 and 9000 rad) ,other solution of same concentrations were prepared after irradiation.

2.2 Density and Rheological measurements:

The density of the solution (ρ) was determined by the density bottle method and the viscosity measured before and after Radiation for all concentrations using Ostwald viscometer with accuracy of $\pm 1.05\%$, the method of measurement has been described elsewhere [10], different types of shear viscosity were determined before and after Radiation by the equations (1, 2, 3 and 4) [10]. The shear viscosity had been calculated by the following equation [11]:

$$\frac{\eta_s}{\eta_0} = \frac{t_s \rho_s}{t_0 \rho_0} \dots\dots\dots (1)$$

Where η_s, η_0 shear viscosity of solution and distilled water respectively.

ρ_s, ρ_0 are densities of solution and distilled water respectively.

Relative viscosity (η_{rel}) was calculated by the following equation

$$\eta_{rel} = \frac{t_s}{t_0} = \frac{\eta_s}{\eta_0} \dots\dots\dots (2)$$

t_s, t_0 are flow time of solution and distilled water respectively.

The specific viscosity (η_{sp}) and reduced viscosity (η_{red}) was calculated by the equations:

$$\eta_{sp} = \frac{(\eta_s - \eta_0)}{\eta_0} = \eta_{rel} - 1 \dots\dots\dots (3)$$

$$\eta_{\text{red}} = \frac{\eta_{\text{sp}}}{C} \dots\dots\dots (4)$$

Where (C) is the concentration. The intrinsic viscosity $[\eta]$ was measured by plotting a graph between reduced viscosities against the concentration when the extrapolation of the slope as (C) goes to zero represents the value of intrinsic viscosity as shown in fig (5). This value of intrinsic viscosity compared with that obtained theoretically by Arrhenius equation below: [10]

$$\ln \eta_{\text{rel}} = [\eta]C \dots\dots\dots (5)$$

And also was theoretically calculated by using Philip-off equation below: [10]

$$\eta_{\text{rel}} = \left[1 + [\eta] \frac{C}{8} \right]^8 \dots\dots\dots (6)$$

The viscosity average molecular weight (M_v) was calculated by using the following equation: [10]

$$[\eta] = KM_v^a \dots\dots\dots (7)$$

Where k, a are constant depends on the type of the polymer, for CMC the values of constants are (a=0.91, K=1.23*10⁻⁴ [12].

The effective molecular radius(r) was calculated by the following equations:[13, 14]

$$\eta_{\text{rel}} = 1 + 6.3 * 10^{24} r^3 C_m \dots\dots\dots (8)$$

$$\text{slope} = 6.3 \times 10^{24} r^3 \dots\dots\dots (9)$$

$$r = \sqrt[3]{\text{slope} / 6.3 \times 10^{24}} \dots\dots\dots (10)$$

Where slope equal to the value of slope plotted between relative viscosities against concentration

2.3 Ultrasonic measurements:

Ultrasonic measurements were made at constant frequency ($f=40$ kHz) using pulse technique of sender-receiver type (SV-DH-7A/SVX-7 velocity of sound instrument). The receiver quartz crystal mounted on a digital vernier scale of slow motion, the sender and receiver pulses (waves) were displaced on two traces of cathode ray oscilloscope, and the digital delay time of received pulses were recorded with respect to the distance. The pulses height on oscilloscope (CH1) represents incident ultrasonic wave's amplitude (A_0) and the pulses height on oscilloscope (CH2) represents the received ultrasonic wave's amplitude (A) after passing the solution.

2.4 Theoretical calculation:

The ultrasonic wave velocity (v) was calculated using the following equation [15]:

$$v = x / t \quad \dots\dots\dots (11)$$

Where (t) is the delay time of ultrasonic wave and (x) is the sample thickness or distance the wave passing through it.

The absorption coefficient (α) was calculated from Lambert – Beer law [14]:

$$A/A_0 = e^{(-\alpha x)} \quad \dots\dots\dots (12)$$

Where (A_0) is the initially amplitude of the ultrasonic waves, (A) is the wave amplitude after absorption.

Attenuation is generally proportional to the square of sound frequency so the relaxation amplitude (D) was calculated from the following equation [16]:

$$D = \alpha / f^2 \quad \dots\dots\dots (13)$$

Where (f) is the ultrasonic frequency of the instrument. Bulk modulus (K) of a solution is the substance's resistance to uniform compression; it was calculated by Laplace equation [16]:

$$K = \rho v^2 \quad \dots\dots\dots (14)$$

Where (ρ) is the density. Compressibility (B) was calculated by the following equation [16]:

$$B = (\rho v^2)^{-1} \quad \dots\dots\dots (15)$$

The acoustic impedance (Z) of a medium was calculated by equation [16]:

$$Z = \rho v \quad \dots\dots\dots (16)$$

3. Results and Discussion:

3.1 Rheological properties:

The values of density with concentration are shown in (Fig.1) this Fig shows the density is increasing with increase of the concentration, this behavior also shown by [13], Gamma radiation causes degradation to the polymer molecules chains which responsible for a lower values of density than before irradiation [6].

Shear Viscosity shown in (Fig .2) is increasing with concentration before and after Radiation, this attributed to the mechanism that hydrogen bonding of water attached to oxygen sites, this leads to salvation sheaths and increase the size of the molecules, Gamma radiations caused degradation to the polymer chains which are responsible for reduction values of viscosity than that before irradiation [12, 13]. Relative, specific and reduce viscosities show in (Fig.3), (Fig.4) and (Fig.5) respectively posses the same behaviors of shear viscosity because they derived from it as shown in equations (2,3 and 4). Intrinsic viscosity had been experimentally and theoretically obtained experimentally when the extrapolation of the slope to y axis of Fig.(5) when $(C=0)$ goes to zero represent intrinsic viscosity and theoretically obtained by using Phillip-off and Arrhenius equations no(5,6) respectively, the values of intrinsic viscosity experimentally and theoretically shown in table (1). This table shows that when increasing radiation doses by gamma, the value of intrinsic viscosity decreasing and the lowest value of intrinsic viscosity obtained at highest doses of radiation this attributed that intrinsic viscosity related to the size of polymer molecules, since radiation produced degradation then reduced the size of polymer molecular chains that lead to reduce intrinsic viscosity [17], and this table shows there are good agreement between experimental and theoretical values of Intrinsic viscosity. The viscosity average molecular weight was calculated by using equation (7). Results show that molecular weight after irradiation has lower values than that before which are show in table (1). This attributed to the fact that radiation made break as a result of degradation to molecular chains produced untie break chains which have reduction in repeat polymer chemical unit therefore reduced its molecular weight [12]. Effective molecular radius for High and Low concentration were decreased after Radiation as show in table (2), since radiation reduced the size of polymer chains because of degradation and this new chains randomly coiled in the solution they must have the smaller radius than that before irradiation [18].

3.2 Mechanical properties:

A useful method of studying mechanical properties of liquids is based on ultrasound. (Fig.6) shows that ultrasonic velocity is decreasing after irradiation and dose (9000) has the lowest value of velocity this attributed that radiation

breaks the bonds of polymer chains and there are small molecules in the solutions and since ultrasonic waves propagate as compression and rarefaction, so these small molecules followed and attenuated these waves and changing its density when passing through the medium (sample) so the velocity must decrease when radiation increased [19,20], so there are more attenuation by these molecules to sound wave and the absorption coefficient increasing after radiation as shown in (Fig.7).

The compressibility is decreasing with the increase of concentration as shown in (Fig.8) and attributed to the fact Laplace equation No (14) there are inverse proportionality between compressibility and ultrasonic velocity. Radiation Reduces the values of compressibility that make changes in structural relaxation which is responsible for reducing polymer compressibility [16] as shown in (Fig.8). Ultrasonic relaxation amplitude was calculated by using equation (13) and shown in (Fig.9) these values are increasing with concentration, this behavior is the same to that given by [6] for other polymers, and attributed to the fact that ultrasonic energy depends on viscosity, thermal conductivity, scattering and intermolecular processes. Thermal conductivity, scattering are known to be negligible, so viscosity is responsible for the increase of relaxation amplitude for this reason absorption coefficient commonly known as visco-absorption [7]. Specific acoustic impedance shown in (Fig.11) is decreasing with ultrasonic velocity. This behavior same to that given by [21] for other polymers and attributed that equation No.(16) has only one variable parameter which is velocity and density has very small variations with respect to the variation of velocity.

4. Conclusion

1-This study shows that intermolecular processes are responsible for the relaxation, and indicating decrease in the size of molecules in bath of ultrasonic waves as a result of gamma radiation.

2-Irradiation was increased the solubility of polymer in water it caused strong degradation to the polymer chains.

3-Irradiation decreased the molecular weight, so there were small and strong chains of molecules as a result of degradation and hydrogen bonds attached to the oxygen sites of polymer and decrease the size of the polymer chains.

4-By radiation can we obtain different molecular weight for this polymer means different industrial applications.

5-Irradiation enhances the absorption coefficient for CMC polymer so it can be applied as coated materials for objects that want be observed by sonar which used ultrasonic waves.

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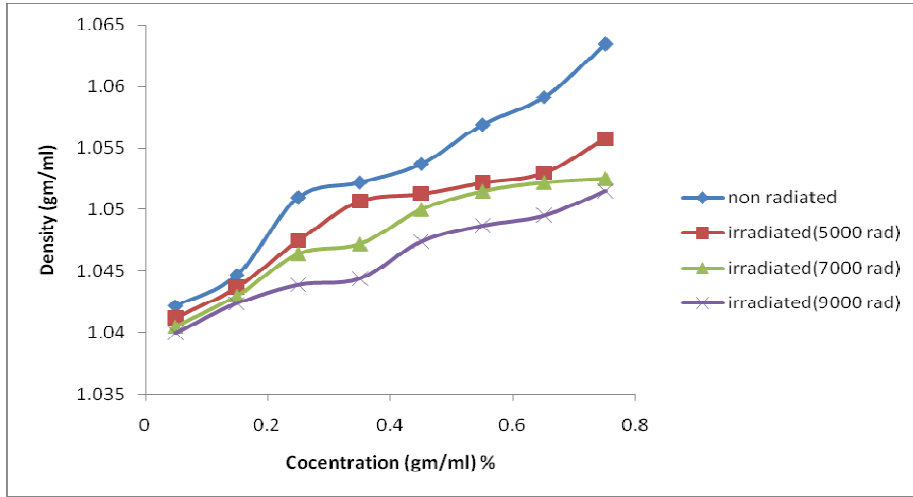
Table (1) comparison between experimental and theoretical results of intrinsic viscosity, Viscosity average Molecular

weight.

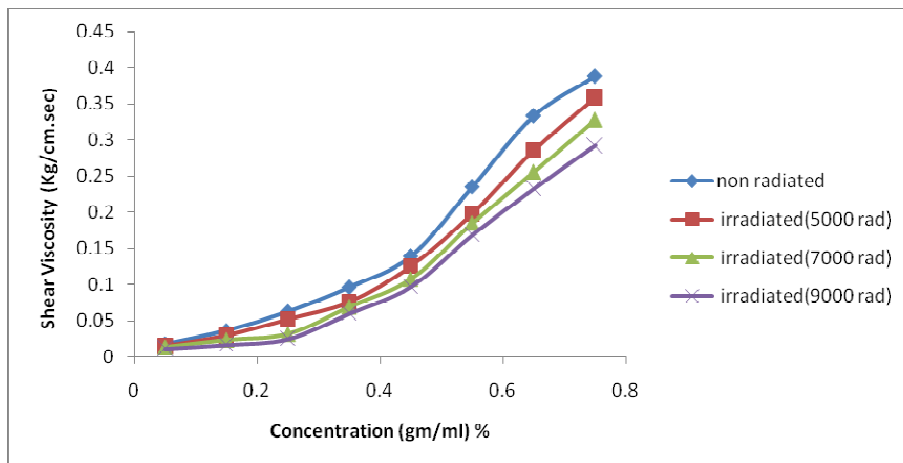
Polymer	Intrinsic Viscosity $[\eta]$ (dl/gm)		Exp.	Viscosity average weight (M_v)		Molecular weight (M_w)
	Arrhe.	Philip.		Arrhe.	Philip.	
CMC	Theor.		Exp.	Theor.		Exp.
	Arrhe.	Philip.		Arrhe.	Philip.	
Non.radiation	10.8	11.2	11	267906	278821	273358
Irr.(5000rad)	8.4	8.7	8	203302	211288	140505
Irr.(7000rad)	6	6.2	5.5	140505	145656	127703
Irr.(9000rad)	3.78	3.8	3	84599	58091	65639

Table (2) Comparison between effective radius for High and Low concentration

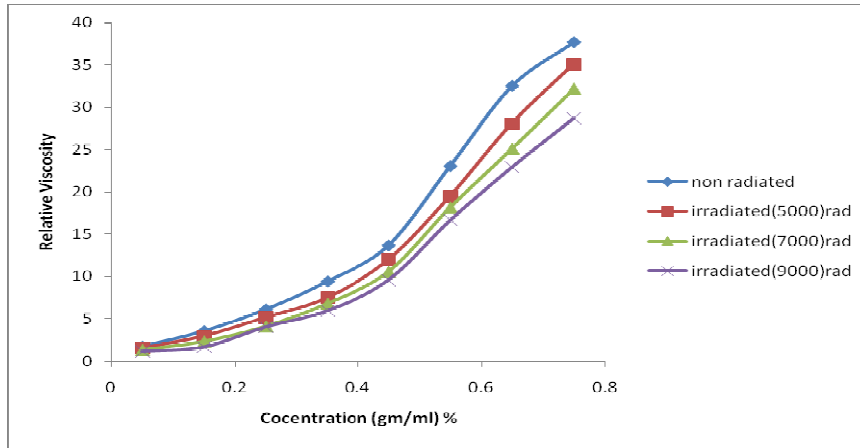
Effective radius (r) (cm)		
CMC polywer	High con.	Low con.
Non.radiation	2.467×10^{-8}	2.010×10^{-8}
Irr.(5000rad)	2.212×10^{-8}	1.828×10^{-8}
Irr.(7000rad)	2.082×10^{-8}	1.405×10^{-8}
Irr.(9000rad)	1.892×10^{-8}	1.054×10^{-8}



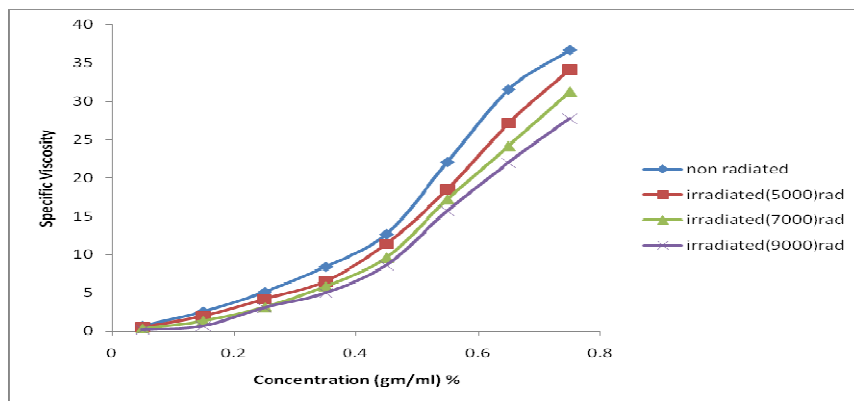
(Fig.1) Density vs. concentration



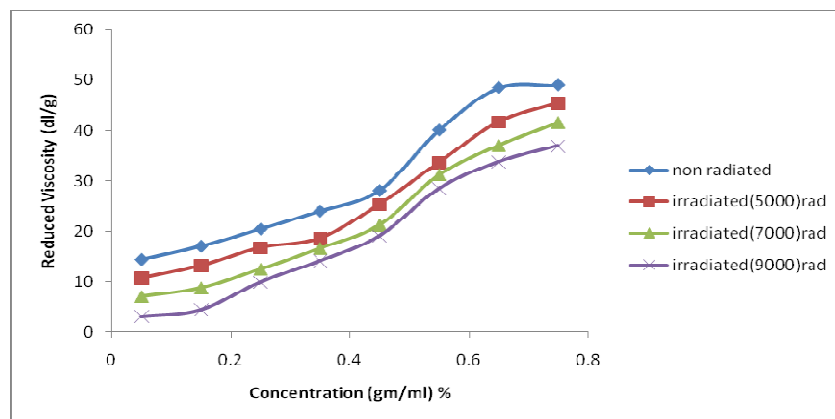
(Fig.2) Shear viscosity vs. concentration



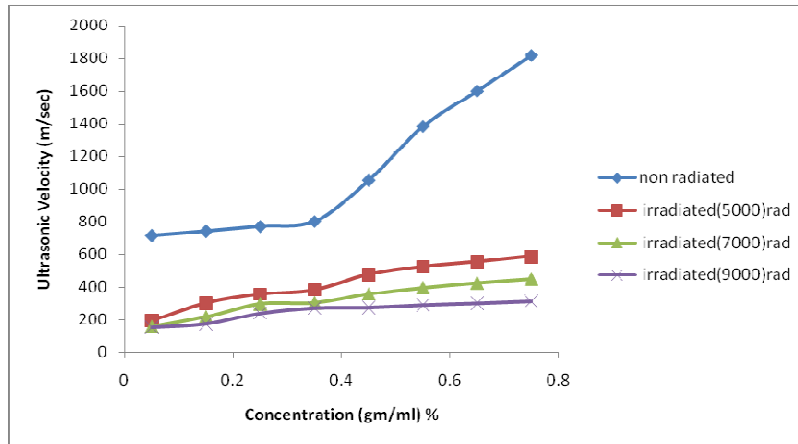
(Fig.3)Relative viscosity vs. concentration



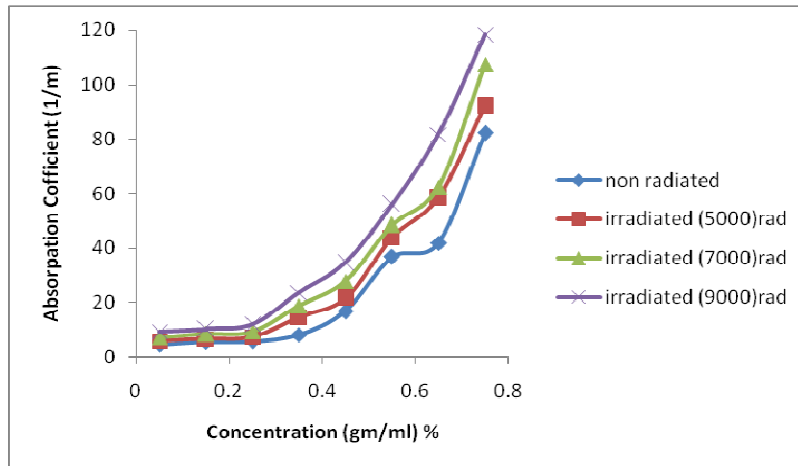
(Fig.4)Specific viscosity vs. concentration



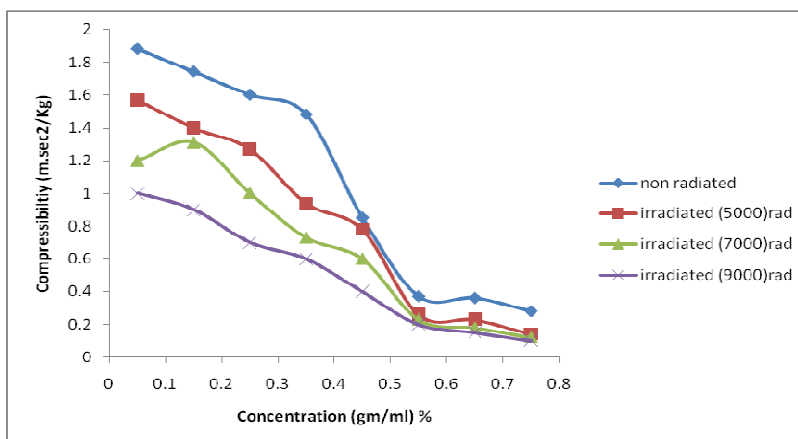
(Fig.5) Reduce viscosity vs. concentration



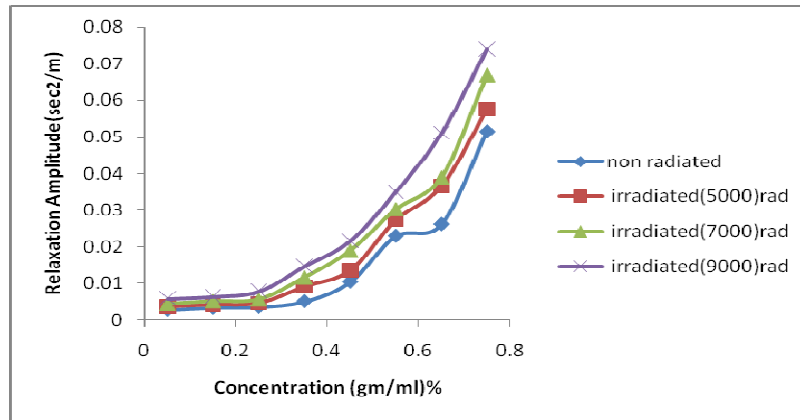
(Fig.6)Ultrasonic velocity vs. concentration



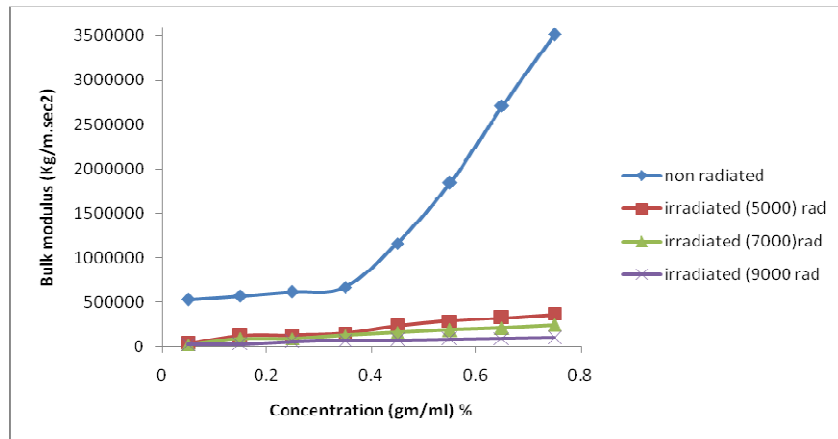
(Fig.7)Absorption coefficient vs. concentration



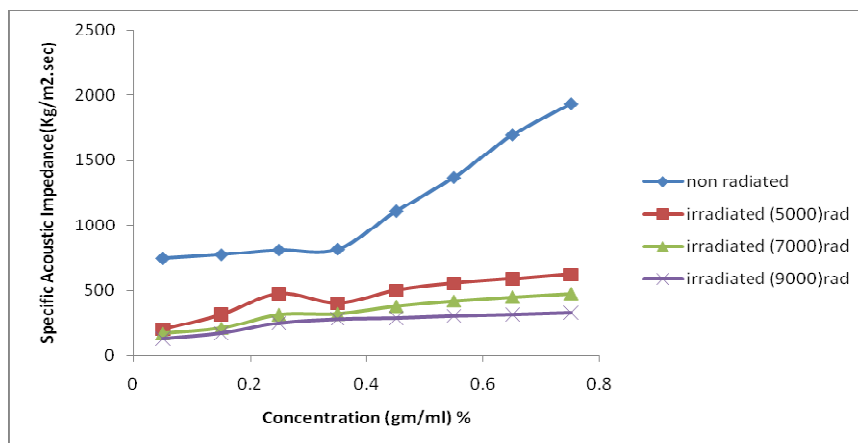
(Fig.8)Compressibility vs. concentration



(Fig.9)Relaxation amplitude vs. concentration



(Fig.10) Bulk modulus vs. concentration



(Fig.11) Acoustic impedance vs. concentration

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