The effect of Co^{60} source on some physical properties of polycarbonate in chloroform at room temperature

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Abstract

The aim of this work is to study the effect of GAMMA rays on some rheological and optical properties of Polycarbonate solution in chloroform at different concentrations before and after radiation with Co^{60} source for a rate of 508 (Rad/min) for 40 minutes.

Some types of viscosities, optical absorption , refractive index, average viscosity molecular weight, Effective molecular radius, Reflectivity, Coefficient of finesse, Specific reflectance .

The results show that most measured and calculated properties increase with concentration in solvent, but the values of density, shear viscosity, relative, specific, reduced, intrinsic and molecular weight increase with radiation and the values of absorbance, refractive index and coefficient of finesse decrease with radiation, this could attributed to degradation leads to gases product.

Introduction

The interesting and useful mechanical properties that are uniquely associated with polymeric materials are a consequence of their high molecular weight. Most important mechanical properties depend on and vary considerably with molecular weight [4].

Extremely large molecular weights are to be found in polymers with very long chains. During the polymerization process in which these large macromolecules are synthesized from smaller molecules, not all polymer chains will grow to the same length; this results in a distribution of chain lengths or molecular weights. Ordinarily, an average molecular weight is specified, which may be determined by the measurement of various physical properties such as viscosity and osmotic pressure. Molecular weights for high polymers may be in excess of a million. Since all molecules are not of the same size, there is a distribution of molecular weights Molecular weight is often expressed in terms of number and weight averages. Chain length may also be specified by degree of polymerization, the number of mer units per average molecule[5]. There are

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many ways, however, to calculate an average molecular weight. The type of property being studied will be determined the desired type of average molecular weight [6] Many primary or absolute techniques are based on colligative properties of the polymer such as melting point depression, vapor pressure and osmotic pressure. Other primary techniques use scattering and chemical analysis of end groups. None of the primary techniques are used on a routine basis as they all involve a significant effort and generally yield only one moment of molecular weight. .Intrinsic viscosity is theoretically a primary technique, in that for the theta solvation conditions secondary standards are not necessary. In usual practice, at non-theta conditions, intrinsic viscosity relies on knowledge of the Mark-Houwink coefficients for the thermal and solvent conditions of measurement [6]. The viscometer used to measure dilute solution viscosity is usually a capillary viscometer. This viscometer uses the Poiseuille equation for laminar pressure flow in a capillary tube[4].

The refractive index of a transparent material is a fundamental of that material and can be used to identify the material. The ratio of the velocity of light in vacuum to the velocity of light in a medium is referred to as the refractive index of the medium, n. When electromagnetic radiation, in the form of visible light, travels from one substance or medium into another, the light waves may undergo a phenomenon known as refraction, which is manifested by a bending or change in direction of the light. Refraction occurs as light passes from one medium to another only when there is a difference in the index of refraction between the two materials. The effects of refraction are responsible for a variety of familiar phenomena, such as the apparent bending of an object that is partially submerged in water and the mirages observed on a hot, sandy desert. The refraction of visible light is also an important characteristic of lenses that enables them to focus a beam of light onto a single point[7].

The characteristics of polycarbonate are quite like those of polymethyl methacrylate (PMMA, acrylic), but polycarbonate is stronger, usable in a wider temperature range but more expensive. This polymer is highly transparent to visible light and has better light transmission characteristics than many kinds of glass. Polycarbonate has a glass transition temperature of about 150 °C (302 °F), so it softens gradually above this point and flows above about 300 °C (572 °F). Tools must be held at high temperatures, generally above 80 °C (176 °F) to make strain- and stress-free products. Low molecular mass grades are easier to mould than higher grades, but their strength is lower as a result[8,9].

Effects induced by ionizing radiation (accelerated electrons, ion and protons, gamma and X rays) have been largely used to modify the chemical and physical properties of the polymers. Some of the changes have been atributed to the scissioning of the polymer chains, breaking of covalente bonds, promotion of

cross-linkages, formation of carbon clusters, liberation of volatile species and, in some cases, even formation of new chemical bonds [8,10].

The irradiation of polymeric materials with ionizing radiation (gamma rays, X rays, accelerated electrons, ion beams) leads to the formation of very reactive intermediates products (excited states, ions and free radicals), which result in rearrangements and/or formation of new bonds. The effects of these reactions are formation of oxidized products, grafts, scission of main chain (degradation) or cross-linking. Often the two processes (degradation - cross-linking) occur simultaneously, and the outcome of the process is determined by acompetition between the reactions.[10]

Radiation induced processes have many advantages over other conventional methods. In radiation processing of polymers no catalysts or additives are required to initiate the reaction. Absorption of radiation energy by the backbone polymer initiates generally a free radical process. The polymer, plastics and rubber industries have been the beneficiaries of the unique properties and advantages of ionizing radiation for several decades and there are already a number of very well established large scale applications of radiation processing in these industries.[11]

Experimental
1.Material:

Carbonate groups (-O-(C=O)-O-). Most polycarbonates of commercial interest are derived from rigid monomers. A balance of useful features including temperature resistance, impact resistance and optical properties position polycarbonates between commodity plastics and engineering plastics. The main polycarbonate material is produced by the reaction of bisphenol A and phosgene ($COCl_2$). The overall reaction can be written as follows: [12]
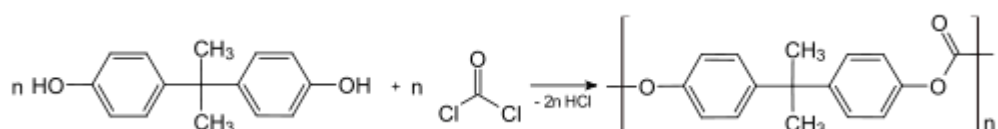
2. Samples preparation:

Using the Chloroform as a solvent, 9 different concentrations for each sample (non-radiated and irradiated) at room temperatures were prepared; the solutions were prepared by adding a known mass of the polymer to fixed mass of solvents, by using the equation:

$$conc.\% = \frac{m_p}{m_p + m_s} \times 100\% \qquad (1)$$

m_p: mass of polymer.
m_s: mass of solvent.

3. Density measurements:

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The densities of the solutions were determined using the density bottle &electrical sensitive balance with precision of ±0.0001%.

4. Viscosity measurements:

For determining the viscosities of the solutions we used OSTWLD viscometer at room temperature.

5. Irradiation method :

The main source of (γ) used in this work was Co^{60} with low dose rate irradiation, about 508 (rad/min) for 40 minutes on a disk shape samples with a thickness about 0.5 cm, where used in order to obtain dose uniformly during the irradiation. The distance between the source and the sample was 15 cm [13].

Theoretical calculation

1- Shear viscosity (η_s):

These values were calculated for all samples, using the following relation [14].

$$\frac{\eta_s}{\rho_s \cdot t_s} = \frac{\eta_w}{\rho_w \cdot t_w} \tag{1}$$

Were; η_s and t_s are shear viscosity & flow time for the samples& (η_w, t_w) are the same parameters for distilled water.(ρ_s, ρ_w) are the densities of each sample &water.

2- Relative, specific & reduced viscosity (η_{rel}, η_{sp}, η_{red}):

The above viscosities were calculated by using the following relations [15]:

$$\eta_{erl} = \eta_s / \eta_w = t_s / t_w \tag{3}$$
$$\eta_{sp} = \eta_{rel} - 1 \tag{4}$$
$$\eta_{red} = \eta_{sp} / C \tag{5}$$

Where: C is the sample's concentration.

3- Intrinsic viscosity $|\eta|$:

Plotting a graph for η_{re} against concentration of all samples had been drawn; the intercept with Y - axis of this graph is $|\eta|$ [4].

4- **Molecular weight (M_v):** An empirical equation is used to describe the intrinsic viscosity/molecular weight relationship, the Mark-Houwink equation,

$$|\eta| = KM_v^{\ a} \tag{6}$$

Where a and K are constants for specific polymer/solvent/temperature. The values of $|\eta|$ had been taken from table (1), and the constants (K, a) are depended on polymer type [13]. The value of the Mv of this polymer was calculated from following relation [16] $|\eta| = 1.12 \times 10^{-4} M_v^{\ 0.82}$ the calculated values are shown in table (2).

5- Molar absorption coefficient(α):

To calculate the optical absorption coefficient (α) of the samples, the following equation was used:

$$\log \frac{I_\circ}{I} = A = \alpha / C \qquad (5)$$

Where

I$_o$ the intensity of incident beam of light for special wavelength.

I   the absorbed intensity of the same beam.

A   the absorbance of the same beam.

If we plot A against C, and if we substitute L=1 cm. in equation (4) which represents the thickness of the test tube, therefore [17]

$$\alpha = A / C \qquad (6)$$

6- Effective molecular radius($r_{eff.}$):

Using the equation from ref.[18],the effective molecular radius for samples where calculated.

$$r_{eff.} = \sqrt{\frac{slope}{6.3 \times 10^{24}}}$$ where the slope is for graph plotted between $|\eta|$ and the molar concentration for all samples as shown in table (3) .

7- Reflectivity (Re)

The reflectivity can be calculated for all samples by using the following empirical equation[19]:

$$Re = \left(\frac{n-1}{n+1} \right)^2 \qquad (7)$$

Where n is the reflective index.

8-Cofficient of finesse (F)

The **coefficient of finesse.** It is a measure of the interference fringe sharpness and contrast. These values were calculated for all samples, using the following relation[20]:

$$F = \frac{4\,Re}{(1 - Re)^2} \qquad (8)$$

Where Re is the reflectivity.

9- Specific reflectance (Rs)

The following equation can be calculated the specific reflectance[20].

$$Rs = \frac{1}{\rho} \frac{(n^2 - 1)}{(n^2 + 2)} \qquad (9)$$

Where ρ is the density and n is the reflective index.

Results & Discussion

Most measured & calculated properties of samples at   different concentrations are increase linearly with polymer concentration in chloroform this accompanied by decrease in most of physical properties after radiation, except some of them as in tables(1-4) and figures(1-10).

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Considering viscosity as a relaxation phenomenon, the increases in the values of viscosity with increasing concentration could be attributed to the complex formation between molecules of this polymer in Chloroform[22].

The results showed little change in optical behavior of irradiated polycarbonate, in spite of the high decrease in the molecular weight of irradiated polycarbonate. The exposition to gamma radiation produces a more nouniform material[23].

The observed decrease in density was explained as being due to the radiation-induced branching inhibiting the process of crystallization and existing in the crystalline region as defects[24]

Also the results show that the value of viscosities determined in this work will decrease after irradiation by Co^{60} source because of penetration of ionizing radiation in the polymer yields main chain scissions, This lead to decrease in carbonyl groups with increase of radiation dose, and The major consequences are a decrease in the molecular weight and a yellowness of the polymer [24].

This scission yields an increase in melting temperature of this polymer and its solubility in Chloroform. An interaction causing association between two types of molecules forming the complex could come close to each other, leaving sufficient space around them, therefore these surrounding molecules could be compressed in this polymer, the motion of polymer macromolecules could be affected by interchain for macromolecules, may indirectly have an influence on other by way of mutual interactions with other molecules when these are solvent molecules, when polymer dissolved in solvent, the solution has a higher viscosity than for pure solvent [21].

The effect of gamma irradiation on the optical properties of polycarbonate solutions in chloroform is studied. The refractive index and Molar absorption Coefficient increased with irradiation, belong to the formation of permanent and transient color centers. The transient color centers (free radicals) "annealed" with time spectra shifted back to shorter wavelengths (blue shifts) 240nm, this result suggests that weak absorption exists in the region(280-700)nm., during the time period after irradiation. Since permanent centers are also formed, the spectra do not completely return to their pre-irradiation position[25].

Conclusion

1- Irradiation of polymers has established itself as one of the most acceptable approach to alter polymer properties significant .

2- The 508 (Rad/min) gamma dose irradiation decreases the Values of intrinsic viscosity and average viscosity molecular weight, in consequence, decrease Molar absorption Coefficient for polycarbonate in Chloroform as a solvent .

3- The irradiation of polymeric materials with ionizing radiation (gamma rays) leads to the formation of very reactive intermediates products (excited states,

ions and free radicals), which result in rearrangements and/or formation of new bonds.

4- Measurement of viscosity provides a good method for evaluation of polymer molecular weights, and for estimation of chain configuration in solution measurements.

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Table (1)

Values of intrinsic viscosity before and after irradiation for polycarbonate	
Intrinsic viscosity(di/gm)	**Polycarbonate**
0.3225	before irradiation
0.2057	after irradiation

Table (2)

Values of average viscosity molecular weight before and after irradiation for polycarbonate	
M$_v$ Average viscosity molecular weight	**polycarbonate**
16545.20347	before irradiation
9561.08128	After irradiation

Table (3)

The Values of Effective molecular radius for polycarbonate in Chloroform		
Effective molecular radius r$_{eff.}$(m)	**Slope** η_{sp}/ C	**Solvent**
1.5353x 10^{-13}	0.1485	Before irradiation
1.48217x 10^{-13}	0.1384	After irradiation

Table(4)

Molar absorption Coefficient for polycarbonate in Chloroform	
Molar absorption Coefficient	**Solvent**
0.0294	Before irradiation
0.0297	After irradiation
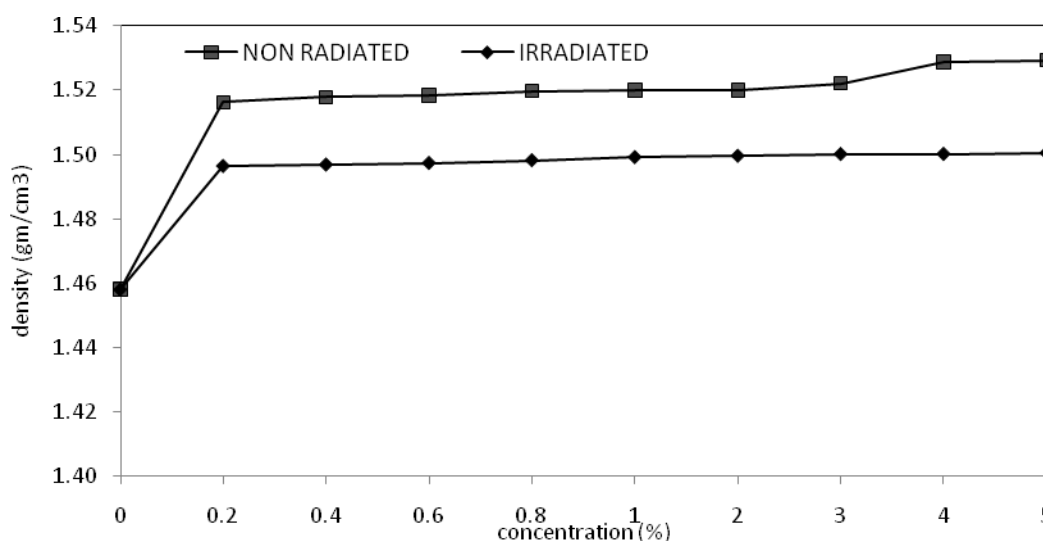
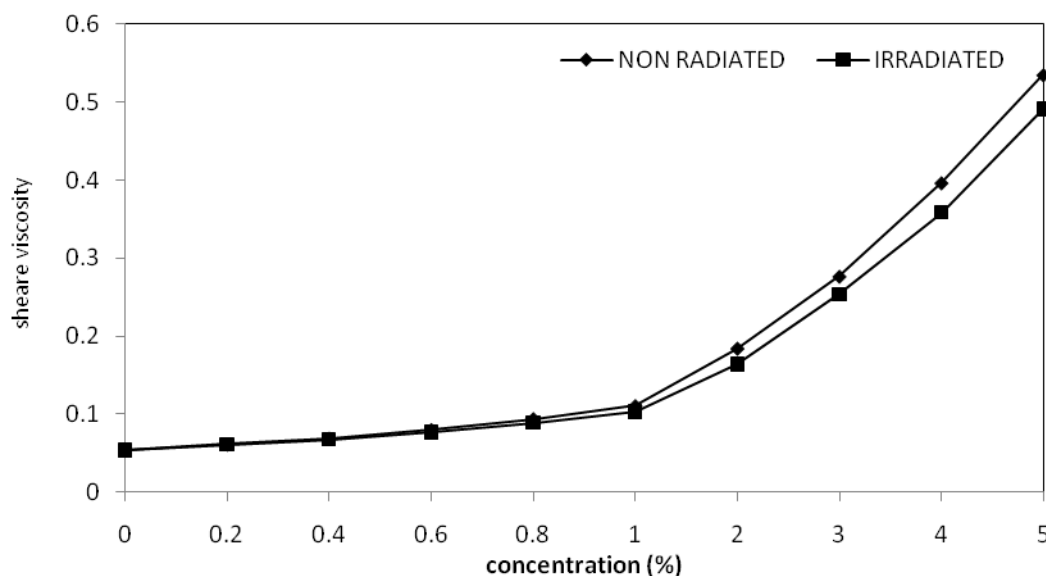Figure 1: Density changed with concentration.
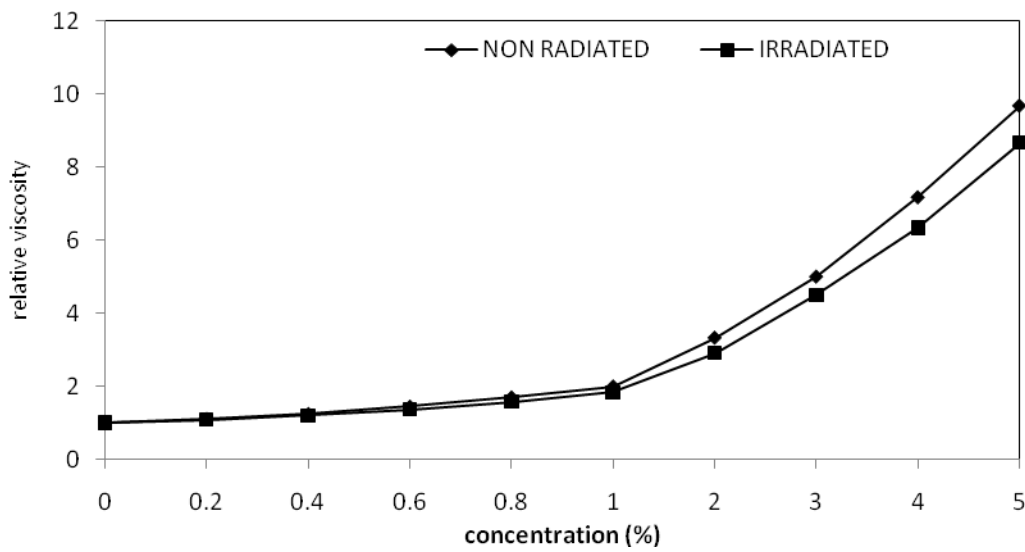

Figure 2: shear viscosity changed with concentration.

Figure 3: Relative viscosity changed with concentration.
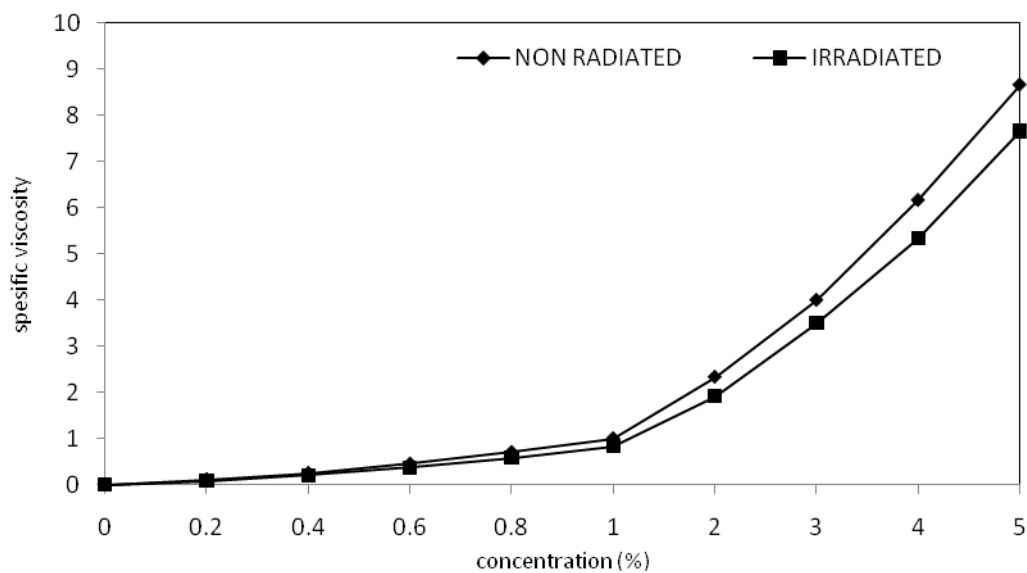
Figure 4: Specific viscosity changed with concentration.
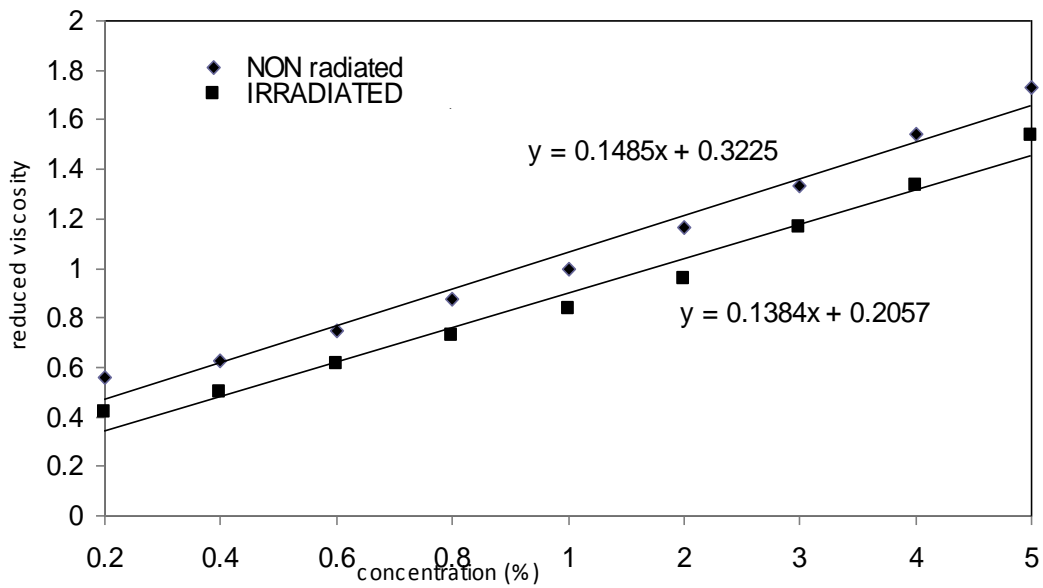
Figure 5: Reduced viscosity changed with concentration
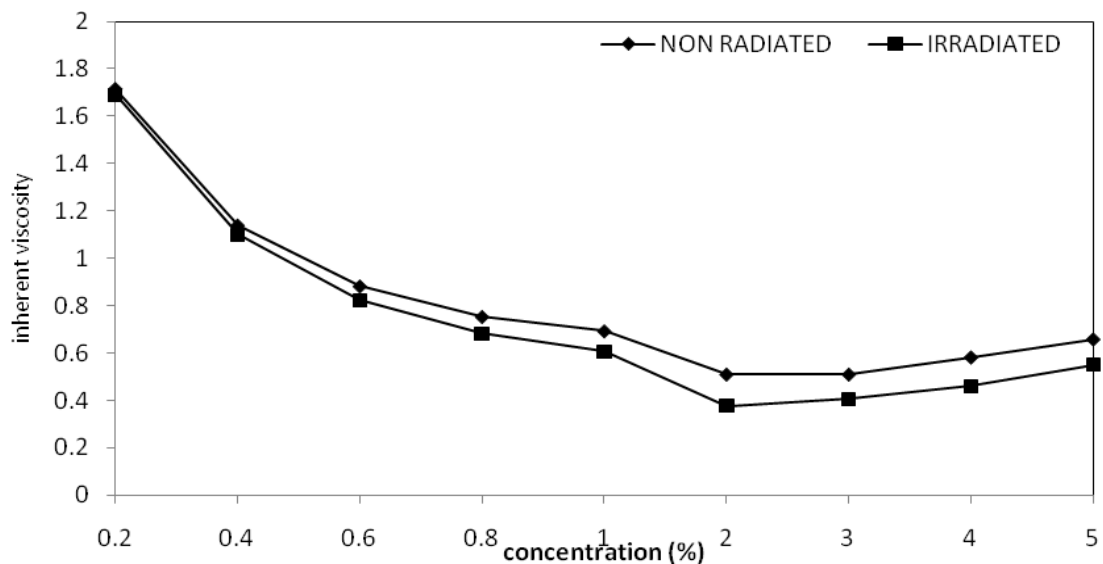
Figure 6: Inherent viscosity changed with concentration
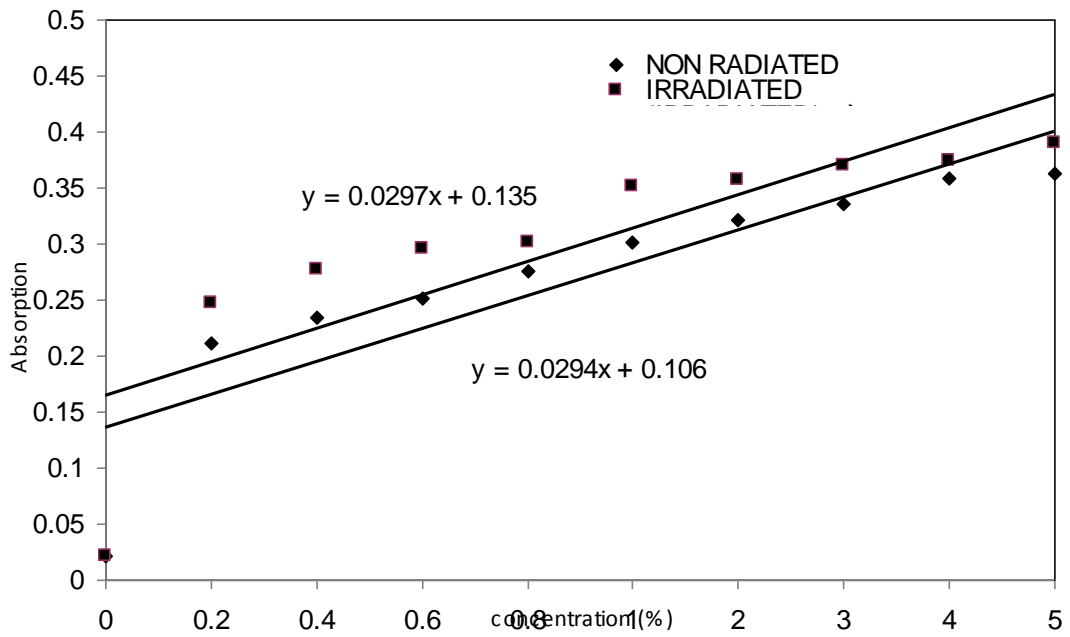
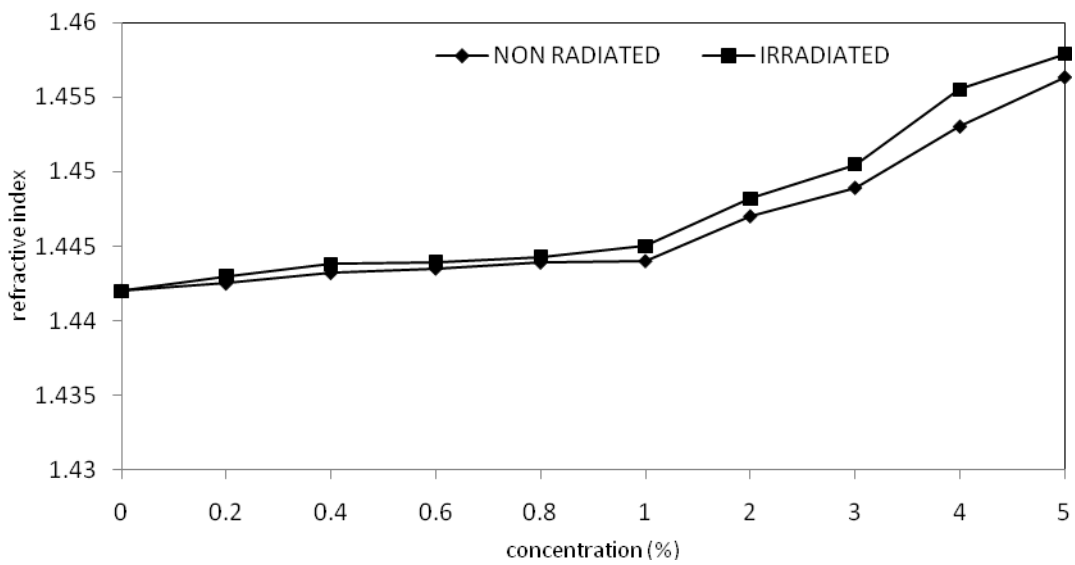Figure 7: Absorptive changed with concentration

Figure 8: Refractive index changed with concentration

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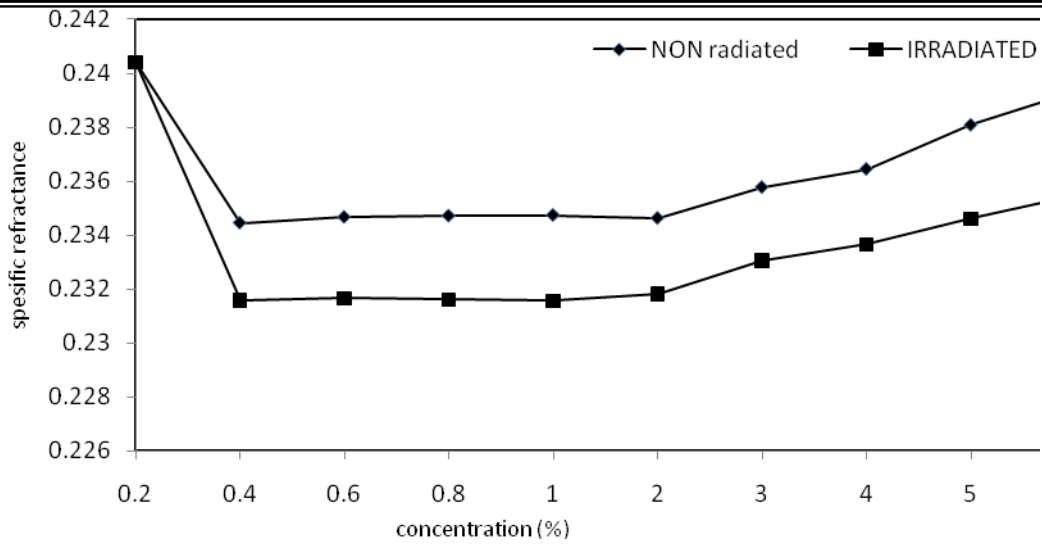Raouf Mahmood Rauof ,Hadi Ghali Attia , Hadeel Adeel Abd Algany

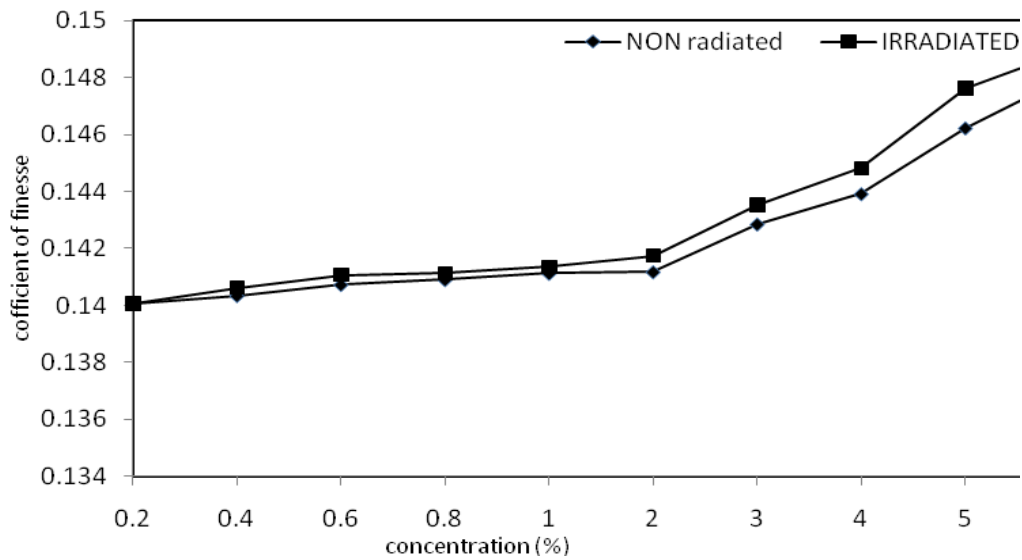Figure 9: Specific refractive changed with concentration

Figure 10: Coefficient of finesse changed with concentration

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الملخص

الهدف من البحث هو دراسة تأثير أشعة كاما على بعض الخصائص الريولوجية والبصرية لمحلول البولي كاربونيت المذاب في الكلوروفورم بدرجة حرارة الغرفة وبتراكيز مختلفة قبل وبعد تشعيعها بمصدر Co^{60} وبمعدل 508 راد لكل دقيقة ولمدة40 دقيقة..

تم تعيين قيم بعض أنواع اللزوجة، الامتصاصية الضوئية ،معامل الانكسار ، معدل الوزن الجزيئي اللزوجي ، نصف القطر الجزيئي الفعال، الانعكاسية، ، معامل الرقة و معامل الانكسار النوعي للمحلول البوليمري.

أظهرت النتائج أن اغلب الخصائص المقاسة والمحسوبة تزداد بزيادة تركيز البوليمر في المذيب,أما قيم كل من الكثافة، اللزوجة القصية ، اللزوجة النسبية، اللزوجة النوعية، اللزوجة المختزلة ،اللزوجة الأصيلة ،الوزن الجزيئي، تزداد بعد التشعيع و قيم كل من الامتصاصية، معامل الانكسار ومعامل الرقة تقل بعد التشعيع ،وقد يكون ذلك بسبب الانحلال الذي يؤدي إلى تحرر نواتج غازية.