

Effect of Gamma Radiation on Some Physical Properties of Polyvinyl Alcohol Dissolve in Dimethyl Sulfoxide

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Abstract

In this investigation the Rheological properties of *Polyvinyl Alcohol* (PVA) dissolves in Dimethyl Sulfoxide with different concentrations has been investigated before and after irradiation by gamma-ray Cobalt (Co^{60}) with different doses rate 50, 100 and 150 (Rad/min) for minutes. These properties are Density, shear viscosity, relative viscosity, specific viscosity and reduced viscosity have been measured. Also the average viscosity molecular weight and effective molecular radius have been calculated.

The results indicate that the properties increase with increasing of PVA concentration. Also the properties have been determined decreased after irradiation, for same concentration. This could be attributed to scission of PVA chains because of penetration gamma -rays in the polymer structure, may produce the dimer and the molecular weight decreased after irradiation.

Introduction

Gamma irradiation is a common method of sterilization which determines the free-radicals formation. Oxygen can diffuse into the polymer over time, reacting with the free-radicals from polymer matrix and it causes chain scission. This is accompanied by internal cross-linking or degradation reactions inducing changes in physical properties of the polymer [1].

The material is resistant to corrosion and abrasion, they have pores which absorb the humidity of the body and are recommended in hospitals. PVA is a hard and rigid polymer, with good mechanical properties, but it is not elastic, this fact indicates that the sterilization process may affect the film porosity. These high-energy treatments result in free radicals generation, main chains scission and crosslinking [3], and subsequently alter the distribution of the chains sizes in the bulk polymer.

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The Composition, microstructure, degree of porosity, or surface chemistry may influence the bacterial contamination of the materials. Through the methods of sterilization, the exposure to gamma rays is one of the most employed and common [2] techniques.

The combined action of ionizing radiation and of oxygen on the polymers may rapidly lead to a severe deterioration of their Properties . The radiation damage and the oxidative degradation cause chemical changes in the polymer structure with the build-up of a variety of new functional groups as carbonyls, carboxyls, esters, hydroxyls [1, 2].

The advantage of gamma irradiations is due to the fact that they are highly penetrating and economically feasible for a large-scale terminal sterilization of products in sealed packages. Ionizing radiation processing at low doses plays an important role in the microbial decontamination of pharmaceutical and medicinal products ,Ionizing events cause a shower of secondary electrons that activate numerous chemical reactions [3], many of which induce oxidative degradations in the presence of oxygen. The aromatic polymers are more resistant to high-energy radiation than aliphatic polymers [4]. The presence of impurities and additives may enhance degradation and/or crosslinking [5]. Any molecule is more stable to radiation in the solid state than in the liquid state [6]. PVA has a simple chemical structure with pendant hydroxyl groups.

A reference to the foregoing many application using PVA which exposure to low doses of radiation to prevent contamination. So that it is very important thing study the influence of gamma ray on properties of PAV where gamma ray is one of the common ray used for this purpose.

Radiation Modeling and Stimulation

The extent of the interaction of polymeric, organic compounds with ionizing radiation is related to the energy during the period of exposure to photon or particle flux. Fluence energy is absorbed as the particles of photon transfer energy to the bulk mass of the polymer through collision events (Compton Effect) or by energy transfer from the columbic field that accompanies the transient path of the particle or photon through the bulk material.

Interaction of radiation with the polymer begins at the atomic level and the associated absorption coefficients. The polymeric molecular formula, therefore, also influences the susceptibility of the polymer to incipient ionization based on the ionization potential of the composite elements[7].

The effect of the polymeric structural formula on degradation becomes important following the incipient ionization, Radiological

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studies of the bulk polymer provides insight into the chemistry of degradation and enable an improvement understanding of the structural feature that ensure radiation hardening. The test results thereby provide guidance in polymer application and in the synthetic design of novel polymers. The aim of this research to Study the effect of Gamma ray on rheological properties of the polymer, the range of low doses effect on chemical structural of polymer, and evaluate the Mean molecular weight and effective radius chain of polymer that exposes to low doses of gamma ray.

IN 2008 Yong Han Cho et.al investigated the effect of temperature dissolution on rheological properties of poly vinyl alcohol in Dimethyl sulfoxide over range between 70-130°C, the results indicated that the viscosity increased as dissolution temperature increased and the solid character got more prominent as dissolution temperature was increased. However, the relaxation time of the solutions was little dependent on dissolution temperature [8].

In 2009 Cristina Nechifor et.al were study the effects of gamma radiation on physical and chemical properties of PVA and PHU which were used as polymer membranes, They found that The gamma treatments of these membranes permit to obtain a stable surface in relation to the environmental conditions for small doses, but when the dose increases the gamma radiations induce changes in the chemical structure followed by degradation [1].

In 2010 Kariman studied PVA/chitosan, with different ratios, were exposed to gamma irradiation doses of 20, 30, 50 KGy, to evaluate the effect of irradiation dose on the physical properties of the blend. It was found that the gel fraction increases with increasing irradiation dose and PVA concentration in the blend.

Swelling percent increased as the composition of chitosan increased in the blend. The PVA/chitosan blend has a water content in the range between 40% and 60% and water absorption between 60% and 100%. The water vapor transmission rate value (WVRT) of the PVA/chitosan blend varies between 50% and 70%.

The examination of the microbe penetration shows that the prepared blend can be considered as a good barrier against microbes. Thus, the PVA/chitosan blend showed satisfactory properties for use as a wound dressing [9].

In 2010 Dong Wook Chae investigated The effects of molecular weight (MW) and concentration on the rheological properties of poly(vinyl alcohol)(PVA) solutions in dimethyl sulfoxide (DMSO) at 30 °C. They

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found The critical concentration (C^*), in which the entanglement and overlap of polymer molecules began to take place, decreased with increasing the MW of PVA and the PVA concentration increased, the dynamic viscosity was increased and the onset shear rate for pseudo plasticity was decreased [10].

In 2012 M.EL.KELANY studied the radiation sensitive indicators based on dyed poly(vinyl alcohol)(PVA) containing acid sensitive dye tetrabromophenolphthalein ethyl ester (TBPE) and trichloroacetamid (TCA) have been developed.

These plastic film dosimeters undergo color change from blue to green to pale green, indicating acid formation. These films can be used as dosimeters for food irradiation applications where the maximum of the useful dose ranges are between 15 kGy depending on (TCA) concentration in the film. The films have the advantage of negligible humidity effects on response in the intermediate range of relative humidity from 10 to 50 % and good stability before and after irradiation under different storage conditions [11].

EXPERIMENTALWORK

Materials:

1- Polymer:

Polyvinyl alcohol PVA were used in this work, PVA is obtained by the vinyl acetate polymerization in alcoholic solutions followed by partial hydrolysis. The PVA melting temperature is 230°C for 100% hydrolyzed polymer and 180–190°C for partial hydrolyzed polymer . The PVA density is 1, 26 g/cm³ for the amorphous phase at 25°C and it is 1, 35 g/cm³ for the crystalline phase at the same temperature [12].

2 -Solvent:

Dimethyl sulfoxide (DMSO) is a clear hygroscopic liquid; melting point 18 C; boiling point 189 C. It has little odor. It smells garlic like odor due to the impurity of dimethyl sulfide. It is miscible with water; readily soluble in almost all organic solvents such as alcohols, esters, ketones, chlorinated solvents and aromatic hydrocarbons.

Samples Preparation

Using Dimethylsulfoxide as solvent of polyvinylalcohol, five different concentrations ratios of each sample at room temperatures were prepared.

1-Density Determination of Liquids by Pycnometer:

Density determination by pycnometer is a. It uses precise method a working liquid with well-known density, such as water. We will use distilled water, for which temperature dependent values of density H₂O.

2-Viscosity determination of liquids by Viscometer:

To determine the shear viscosity of solution (PVA dissolved in DMSO) the Ostwald Viscometer as shown in figure (3-4) have been used

Dissolving Stage:

1- Preparing the Polymer:

Vacuum dry the polymer as usual repetitivemeasurements are needed to ensure that the polymer is really dry if it gets significantly heavier with time, you may need a new trap on the vacuum pump.

2- Nominally 1% Polymer Stock Solution (c_{max}):

Weigh 1 g into a 100-mL volumetric flask, using quantitative transfer techniques. chem. balances, but in a research measurement, one would use a good analytical balance. One would also calibrate the 100-mL volumetric, As usual, add only one-third of the required solvent (DMSO) until the polymer dissolves.

3-Dilutions:

Prepare solutions using glass pipets (e.g. 0.1, 0.2, 0.4 and 0.5 c_{max} but the exact matrix of solutions is non-critical). As always, try to minimize double-dipping (e.g., the 0.2 c_{max} solution should not be made from two uses of 10-mL pipets; it would be better to make an 0.25 c_{max} solution using a 20-mL pipet)

4- Dissolution Process:

The known mass of polymer (PVA) has been added to known volume of DMSO which placed in 100 ml glass bottles, the polymer has been dissolved in solvent by using water bath apparatus in which container of water heated to a given temperature, used for heating substances placed in smaller containers., the bottles of solution with different concentration were capped and stored in water bath container maintained at 40°C for 6 hour

Irradiation Method:

In polymer study most investigators prefer the use of nuclide source (^{60}Co) which has decays slowly to the ground state of ^{60}Ni through the β . The ^{60}Co is a long life isotope (- 5.26 years) that provides Gamma photons with energies of 1.17 MeV to 1.33 MeV. High energy ^{60}Co photons easily penetrate thick samples ensuring that the bulk mass of the target sample will receive a uniform dose [13].

Theoretical and Experimental Calculations:

Some of the empirical and theoretical information and equations have been used to determine the rheological properties and parameters which were given imagination about chemical structure of the polyvinyl

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alcohol. Then comparison between the Non radiation and irradiation samples properties.

1- Shear Viscosity (η)

The shear viscosity can be calculated from the folloing eguation

2-Relative, Specific & Reduced Viscosity ($\eta_r, \eta_{sp}, \eta_{red}$):

The viscosities have been calculated by using the following relations[13]:

$$\eta_r = \eta / \eta_s = t / t_s$$

$$\eta_{sp} = \eta_r - 1$$

$$\eta_r = \eta_{sp} / c$$

3-Molecular Weight (M_v):

The molecular weight of polymer must therefore be described as some average molecular weight calculated from the molecular weights of all chains in the sample. The molecular weight averages can be determined by using Viscosity model which depend on an empirical equation is used to describe the intrinsic viscosity/molecular weight relationship, the Mark- Houwink equation,

$$[\eta] = K M_v^a$$

where K is a constant of the unit of L/g, and is called a Mark-Houwink-Sakurada exponent. Note that K and a are different from polymer to polymer and can depend on the solvent as well.

t. We will obtain the formulas of $[\eta]$ for linear flexible chains in the theta solvent and the good solvent in the next section.

The values of $[\eta]$ had been taken from table (1), the constants (K, a) are depended on polymer and solvent type, for PVA dissolved in DMSO, $K = 1.6 \times 10^{-4}$, $a = 0.8$, then the value of the M_v has been calculated from following relation[14]

$$[\eta] = 1.6 \times 10^{-4} M_v^{0.80}$$

4-Effective Molecular Radius (r):

The effective molecular radius (r) for samples have been calculated [13]:

$$\eta_r = 6.3 \times 10^{24} \cdot r^3 \cdot c$$

$$\text{Slope} = 6.3 \times 10^{24} \cdot r^3$$

$$r = \sqrt[3]{\frac{\text{Slope}}{6.3 \times 10^{24}}}$$

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

RESULTS AND DISCUSSION

Results of Density:

The values of density against to concentration have been shown in Figure (1) which indicated that the density increase with increase of the

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concentration, Also the Gamma radiation causes degradation to the polymer molecules which is shown in same Figure[20].

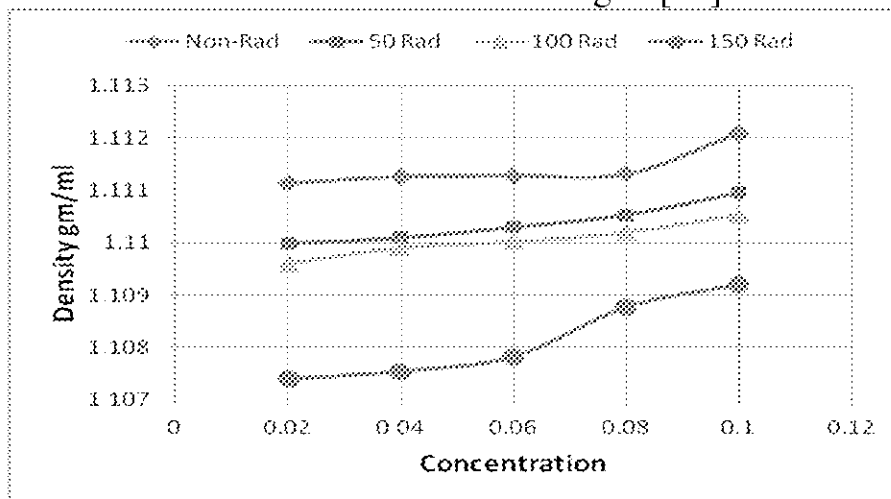


Fig.(1) Density Behavior with Different Concentration

Results of Rheological Properties:

The Values of Shear Viscosity are shown in Figure(2), Shear Viscosity increase with increase concentration before and after Radiation, Considering viscosity as a relaxation phenomenon, the increase in the values of viscosity with increase concentration could be attributed to the complex formation between molecules of this polymer dissolves in DMSO.

This attributed to the mechanism that hydrogen bonding attached to oxygen sites, this leads to salvation sheaths and increase the size of the molecules ,Gamma-ray has been caused degradation to the polymer chains which lead to decrease this property after irradiation [15].

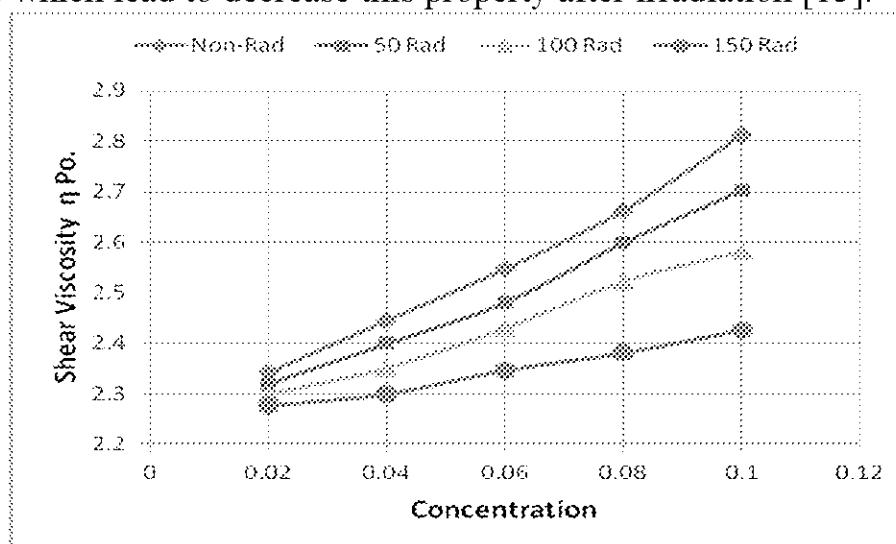


Fig. (2) Shear Viscosity Vs Concentration

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Also the results of Relative, specific and reduce viscosities show in Fig.(3), Fig.(4) and Fig.(5) respectively have the same behaviors of shear viscosity because of penetration of ionizing radiation in the polymer yields main chain scissions, This lead to decrease in carbonyl groups after irradiation dose, The major consequences are a decrease in the molecular weight and a yellowness of the polymer This scission yields an increase in melting temperature of this polymer and its solubility in DMSO. 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 inter chain 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 [16].

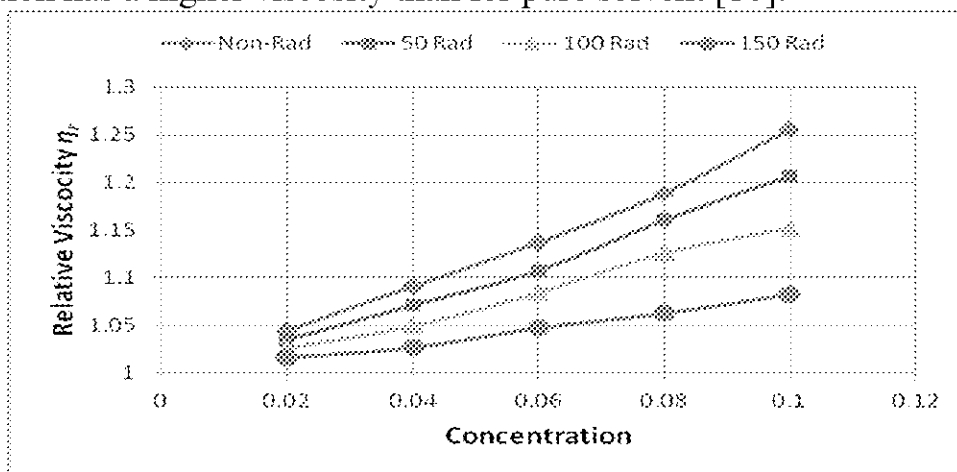


Fig.(3) Relation Between Relative Viscosity with Concentration.

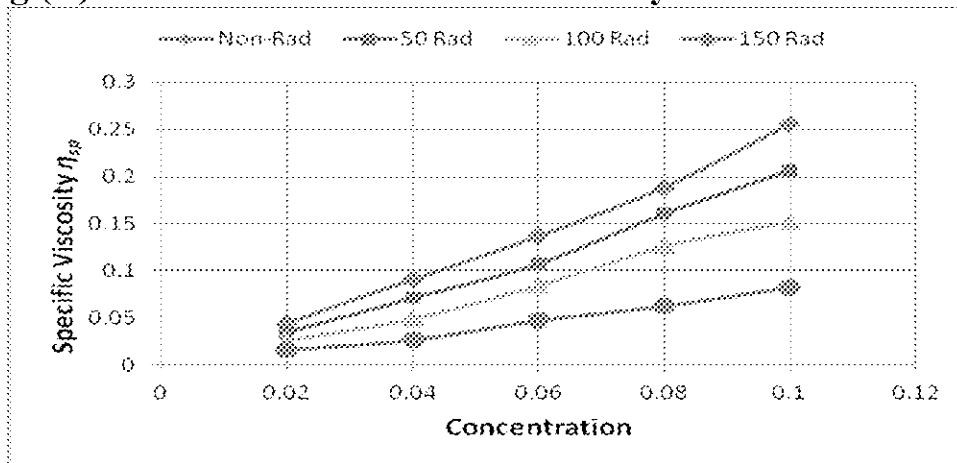


Fig.(4) Behavior of Specific Viscosity with Concentration.

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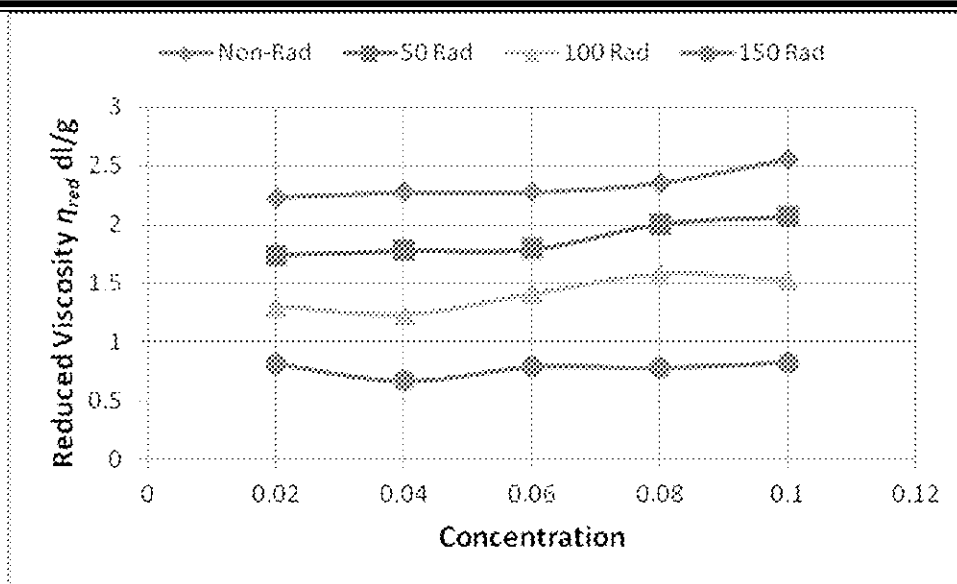


Fig. (5) Reduced Viscosity against Concentration.

Figure (6) shows Intrinsic viscosity which has been calculated experimentally before and after irradiation, the extrapolation of the slope to y-axis when (C = 0) of Figure (6).

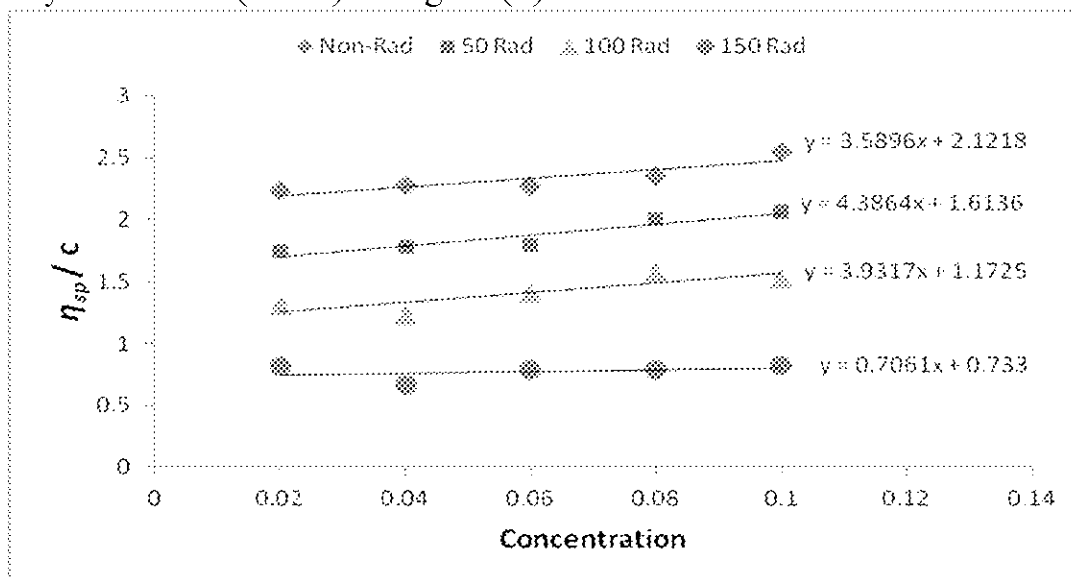


Fig. (6) Slope of Reduced Against Concentration.

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.

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Table (1) Values of Intrinsic Viscosity of Non and Irradiation Samples.

Polymer PVA	Intrinsic Viscosity [η] (dl/gm)
Non- Radiation	2.1218
Irradiation 50 Rad	1.6316
Irradiation 100 Rad	1.1725
Irradiation 150 Rad	0.733

Results of Mean Molecular Weight and Effective Radius:

Table (2) shows the viscosity average molecular weight, results show that molecular weight after irradiation has lower values than that before .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.

Table(2) Molecular weight of Non and Irradiation PVA.

Polymer PVA	Molecular Weight M_v
Non- Radiation	80879.5
Irradiation 50 Rad	59158.3
Irradiation 100 Rad	39919.2
Irradiation 150 Rad	22819.9

Table (3) shows the value of effective molecular radius before and after irradiation where the effective molecular radius decrease after irradiation, 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.

Table (3) Comparison between Effective Radius of Non and Irradiation Samples.

Polymer PVA	Effective Radius cm
Non- Radiation	7.437×10^{-9}
Irradiation 50 Rad	7.005×10^{-9}
Irradiation 100 Rad	6.395×10^{-9}
Irradiation 150 Rad	5.116×10^{-9}

CONCLUSION

The results of investigation indicated to the following conclusions:

- 1- The Gamma radiation significant effect on rheological properties of the Solution.
- 2- Irradiation was increased the solubility of polymer in solvent it cased 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.

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تأثير أشعة كاما على بعض الخواص الريولوجية لبولي فنل

الكحول المذاب في داي مصل سلفو اوكسايد

د. نهييب نوري

سلوى عصمت

الخلاصة

في هذا البحث تم حساب الخواص الريولوجية لبولي فنل الكحول المذاب في داي مصل سلفو اوكسايد مع نسب مختلفة قبل وبعد التعرض لاشعة كاما مع معدلات مختلفة (50، 100، 150) راد / دقيقة . ومن الخواص التي تم دراستها وقياسها الكثافة ، لزوجة القص ، اللزوجة النسبية ، اللزوجة النوعية واللزوجة المختزلة . وكذلك حساب معدل الوزن الجزيئي المعتمد على اللزوجة مع حساب نصف قطر الجريئة الفعال .

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النتائج تشير إلى أن الخواص تزداد مع زيادة تركيز بول فنل الكحول إضافة إلى ذلك أن الخواص تقل بعد الإشعاع لنفس التراكيز وهذا النقصان يعزى إلى انفصال حلقات البوليمر بسبب نفاذ الأشعة في تركيب البوليمر والذي يؤدي بذلك إلى تقليل الوزن الجزيئي بعد الإشعاع