Structural Study Of Rheological And Mechanical Properties Of Polyvinyl Alcohol By Ultrasonic

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Abstract:

Some of physical properties of polyvinyl alcohol dissolves in distilled water had been studied. These properties are classified of two kinds, first Rheological properties such as shear viscosity, relative viscosity, reduced viscosity, intrinsic viscosity, average viscosity molecular weight, effective molecular radius and density . Second mechanical properties, such as ultrasonic velocity had been measured by ultrasonic waves system of frequency   21 KHz, other properties had been calculated such as absorption coefficient of ultrasonic waves, relaxation time, relaxation amplitude, specific acoustic impedance, compressibility and bulk modules .The results show that all these properties are increasing with the increase of the polymer concentration except velocity is decreasing with increase the concentration since adding more PVA lead to solvation sheeths, and increase the size of molecules then reduces velocity. Results also show that there is good agreement between experimental and theoretical values.

الخلاصة:

تم دراسة بعض الخواص الفيزيائية لبولي فانيل الكحول المذاب في الماء المقطر وهذه الخواص تصنف إلى نوعين النوع الأول الخواص الريولوجية مثل اللزوجة القصية واللزوجة النسبية واللزوجة النوعية واللزوجة المختزلة واللزوجة الذاتية ومعدل الوزن الجزيئي اللزوجي ونصف قطر الجريئة الفعالة والكثافة. النوع الثاني من الخواص هو الميكانيكية ومنها سرعة الموجات الفوق السمعية حيث تم قياسها باستخدام منظومة الموجات الفوق السمعية بتردد ثابت مقداره KHz ٢١   ومن ثم تم حساب الخواص التالية مثل معامل امتصاص الموجات الفوق السمعية وزمن الاسترخاء وسعة الاسترخاء والممانعة النوعية والانضغاطية ومعامل المرونة . أوضحت النتائج أن جميع هذه الخواص تزداد مع زيادة تركيز البوليمر ماعدا سرعة الموجات الفوق السمعية تتناقص مع زيادة التركيز السبب هو عند إضافة تركيز أكثر من بوليمر   PVA يؤديَّ إلى انتفاخ سلاسل جزيئات البوليمر والذي بدوره يؤدي إلى زيادة حجم الجزيئات وهو السبب الذي يؤدي الى نقصان السرعة. وأيضا أوضحت النتائج هناك توافق جيد بالقيم النظرية والمقاسة عملياً.

Introduction:

Polyvinyl alcohol is water – soluble synthetic polymer, its solubility in water depends on its degree of polymerization and degree of hydrolysis of the precursor. Unlike many vinyl polymers, PVA is not prepared by polymerization of the corresponding monomer. The monomer, vinyl alcohol, almost exclusively exists as the tautomeric form, acetaldehyde. PVA instead is prepared by partial or complete hydrolysis of polyvinyl acetate to remove acetate groups.(Bin et. al.,2006) . PVA resistant to oil, grease and solvent. It has high tensile strength and flexibility, as well as high oxygen and aroma barrier properties. However these properties are depend on humidity, in other words, with higher humidity more water is absorbed. The water, which acts as a plasticizers, will then reduce its tensile strength, but increase its elongation and tear strength. PVA is fully degradable and is a quick dissolver.(Fromageau, et.al.,2003), (Hassina , 2009) .

There are many industrial applications of poly (vinyl alcohol) are all based on and limited by the use of water solutions. The polymer is not considered thermoplastic as the degradation temperature is below the melting point.

Poly(vinyl alcohol) is commercially available in granular and powdered form. Grades include both fully hydrolyzed and partially hydrolyzed products. A wide variety of molecular weight and hydrolysis is commercially available.(Guohua,et.al.,2006) (Bhajantri,et.al., 2006)

Major end uses include textile sizing, adhesives, protective colloid for emulsion polymerization, paper coating, cement and mortar additive, poly(vinyl butyral), fibers, and films (Abd El-Kader,et.al.,2008).The mechanical properties were studies using ultrasonic pulse technique. Acoustic relaxation measurements on other polymers have been reported by several workers(Hassun and Isa,1989) and (Tomasz, 2010). The a caustic relaxation has been ascribed to the conformation changes of the polymers back bore and the breadth of the relaxation has been

explained in term of a number of specific conformational transformation (Hassun and Rahman,1990)(Khalida, 2004)

The aim of this research is to find different properties of this polymer and determine its different industrial a applications according to these properties.

Experimental Part

1- Preparation of Solutions

The PVA solution were prepared by soluble the PVA in distilled water with many different concentrations (0.2%,0.4%,0.6%,0.8% and 1%),the solubility is made by addition of a known weight of the polymer to affixed volume of water and then heating this mixture under reflux whilst agitating with magnetic stirrer for about 20 min. Until a clear solutions were obtained (Yonedaa and Ichihara 2005).

2- Measurements and Rheological calculations

The density of the solution was determined and their viscosities measured using an Ostwald viscometer, with accuracy of ± 1.05%, the method of measurement has been described, elsewhere(Hassun,1990),(Al-Bermany,2004) shear viscosity and its different types, viscosity average molecular weight and effective molecular radius were determined by the following equations (Illiger,et.al.,2008) (Yonedaa and Ichihara,2005)

The Shear viscosity had been calculated by the following equation:

$$\frac{\eta_s}{\eta_o} = \frac{t_s \rho_s}{t_o \rho_o} \quad \text{---------------------- (1)}$$

Where ρ_s and η_s are the solution density and viscosity respectively, ρ_o and η_o are density and viscosity of distilled water respectively. Relative viscosity η_{rel} was calculated by the following equation.

$$\eta_{rel} = \frac{t_s}{t_o} = \frac{\eta_s}{\eta_o} \quad \text{------------------------ (2)}$$

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

$$\eta_{sp} = \frac{(\eta_s - \eta_o)}{\eta_o} = \eta_{rel} - 1 \quad \text{---------------- (3)}$$

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

Where C the concentration. The intrinsic viscosity $[\eta]$ was measured by plotting a graph between reduced viscosity against the concentration when the extrapolation of the slope as (C) goes to zero represents the value of intrinsic viscosity $[\eta]$ as shown in fig(5)

This value compared with that obtained theoretically by Arrhenius equation below (Harold ,1991).

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

And also was theoretically calculated by using philipoff equation below:

$$\eta_{rel} = (1 + [\eta] \frac{C}{8})8 \quad \text{------------------------------------- (6)}$$

The viscosity average molecular weight (Mv) was calculated by using the following equation:

$$[\eta] = K M_v^a \quad \text{--- (7)}$$

the values of constants are (a=0.67, K=1.59*10-4)(Crompto,2006),The effective molecular radius r was calculated by using the following equation:

$$r = \sqrt[3]{slop/6.3*10^{24}}$$ ---------------------------- (8)

and subtract the slop of striate line which relate the relative viscosity with concentration in equation above .

3-Measurements and Mechanical Calculations

The Ultrasonic velocity (V) was measured using the pulse ultrasonic technique of sender-receiver type SV-DH-7A, SVX-7 with (0-50 kHz) variable frequency at frequency 21 KHz, the metal vibrator was coated with oil and kept in contact with the wall of the glass tank containing the test sample the receiver quartz crystal was mounted on a digital vernier of slow motion. The receiver crystal could be displaced parallel to the sender through 10 cm. The sender and receiver pulses were displaced on two traces of cathode ray oscillograph

Theoretical values such as absorption coefficient α of ultrasonic waves, relaxation time τ, relaxation amplitude D, compressibility β, specific acoustic impedance Z and bulk modules K for the polymer solutions have been calculated using the following equations(Blitz,1967) (Hassun,1990).

The absorption coefficient had been calculated by the following equation:

$$\alpha = \frac{8*\pi^2 f^2 \eta}{3\rho V^3}$$ ---------------------------------- (9)

where f the frequency of ultrasonic waves, η is the viscosity of solution, ρ isthe density, and v is velocity of ultrasonic waves .

The relaxation time τ had been calculated by the following equation:

$$\tau = \frac{4\eta}{3\rho V^3}$$ ------------------------------- (10)

The relaxation amplitude had been calculated by the following equation:

$$D = \alpha/f^2$$ ---------------------------------- (11)

The specific acoustic impedance had been calculated by the following equation:

$$Z = \rho V$$ ------------------------------------ (12)

The compressibility β had been calculated by the following equation:

$$\beta = (\rho V^2)^{-1}$$ -------------------------------- (13)

The bulk modules K had been calculated by the following equation:

$$K = \beta^{-1} = \rho V^2$$ ----------------------------- (14)

Results and Discussion

1- Rheological properties:

The density is increasing with the increase of polymer concentration as shown in figure (1) since the density is as mass divided by volume and we adding different weight of polymer to fixed volume of solvent so there are linear increment for density.

Viscosity shear is increasing with concentration as shown in figure (2) this attributed to the mechanism that hydrogen bonding of water attached to oxygen sites, this leads to solvation sheeths and increase in the size of the molecules, so its viscosity (Illiger, et.al., 2008) furthermore water act as plasticizer will reduce tensile strength and increase its chains elongation

(Fromagean, et. al., 2003). Relative and specific viscosities shown in figure (3,4) posses the same behaviors of sheer viscosity because they derived from it as shown in equations (2,3).

Intrinsic viscosity had been experimentally and theoretically obtained experimentally when the extrapolation of the slop to y axis of figure(5) when C=0 goes to zero gives intrinsic viscosity and theoretically obtained by using Phillip off and Arrhenius equations no(5,6)respectively and the values of intrinsic viscosity experimentally and theoretically are shown in table (1).This table shows there are good agreement between experimental and theoretical values of Intrinsic viscosity .The viscosity average molecule weight was calculated by using equation (7). And the constant (a) equal to (0.67) and k= (5.9×10^{-4}) also there are good agreement between experimental and theoretical values of molecular weight in the same table.

the effective radius is calculated also by using equation (8) shown in that table .
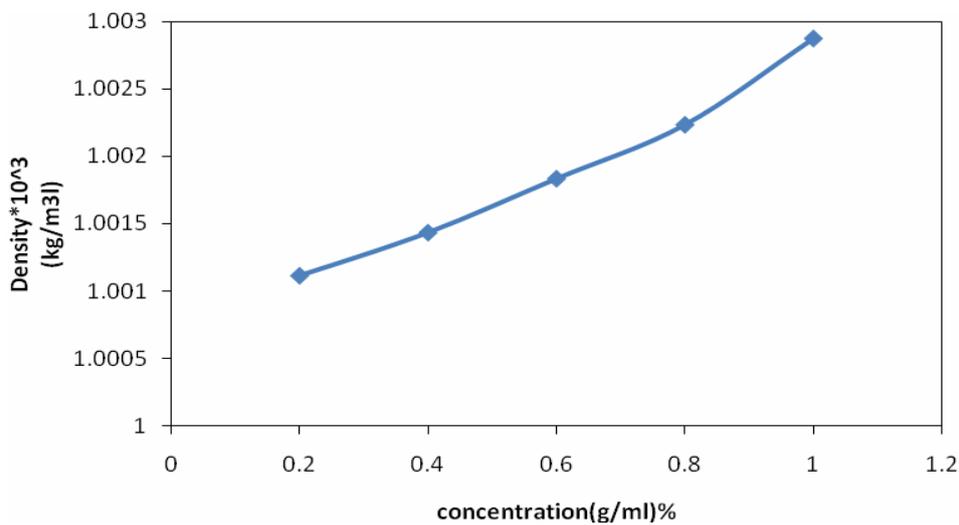
Fig.1 The variation of density Vs concentration of polyvinyl alcohol
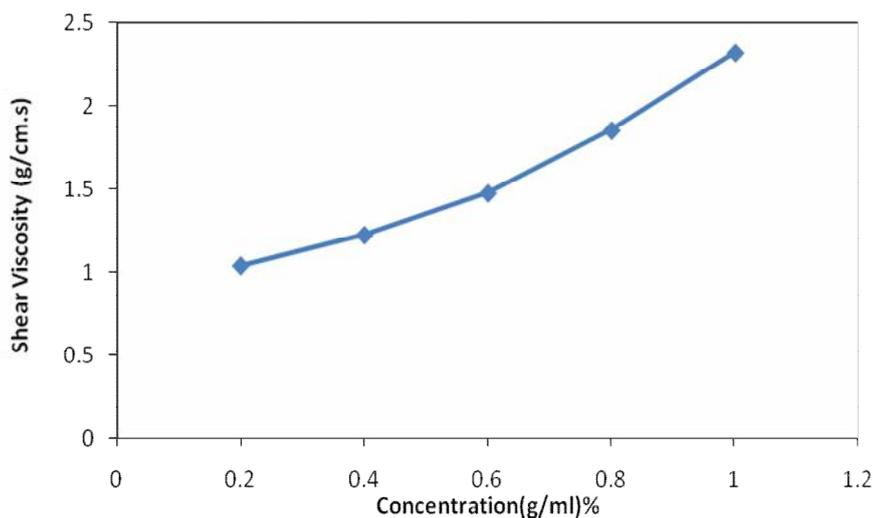
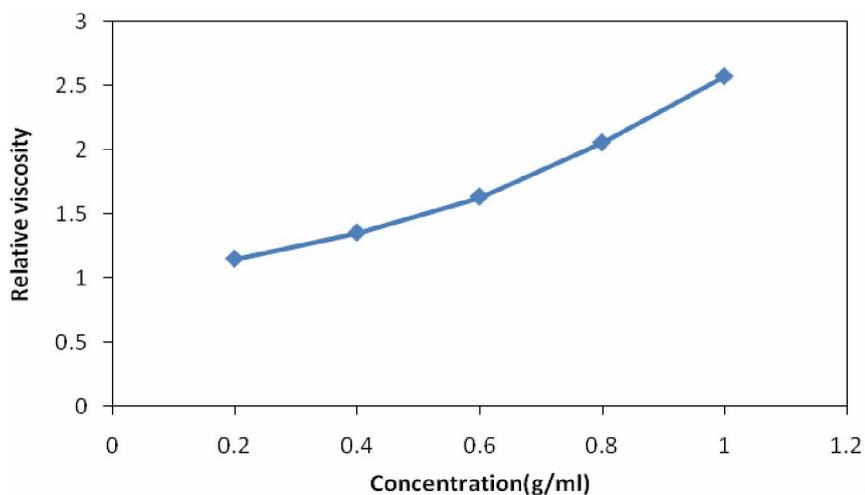Fig.2 the variation of shear viscosity Vs concentration of polyvinyl alcohol

Fig.3 the variation of relative viscosity Vs concentration of polyvinyl alcohol
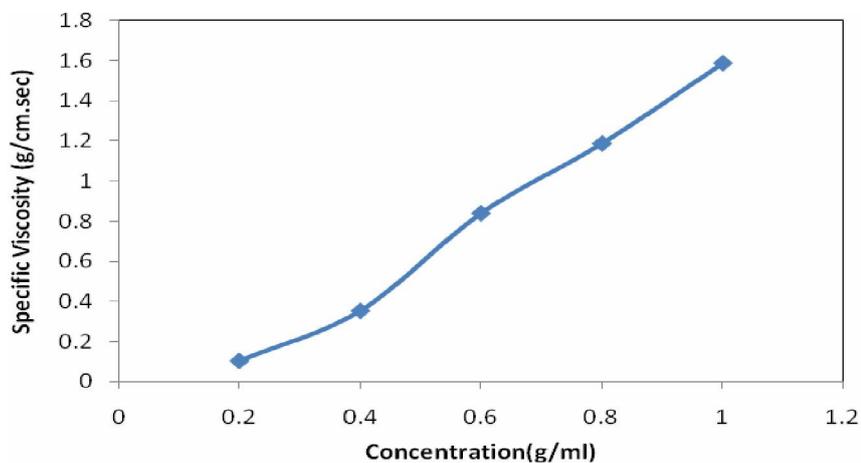

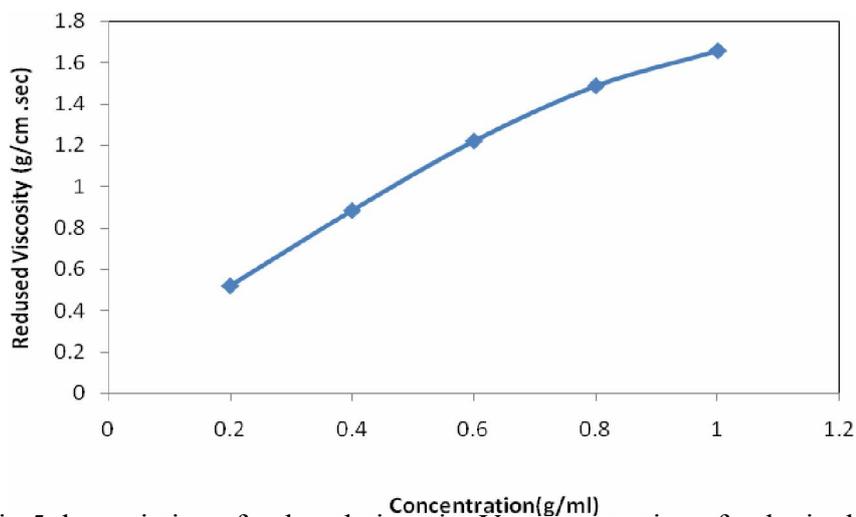Fig.4 the variation of specific viscosity Vs concentration of polyvinyl alcohol

Fig.5 the variation of reduced viscosity Vs concentration of polyvinyl alcohol

Table (1) comparison between experimental and theoretical results of Itrinsic viscosity, molecular weight and the effective radius.

	Intrinsic viscosity (dl/gm)		Viscosity average molecule weight(M_v)		Effective Molecular radius (cm)	
Theoretical	Arrh.eq.	Philip.eq.	Arrh.eq.	Philip.eq.	Arrh.eq.	Philip.eq.
	0.705178	0.71143	46550.3	46963.4	6.01E-09	6.4594E-09
Experimental	0.7000		46208.5		5.47941E-09	

2-Mechanical properties:

Ultrasonic velocity with concentration are shown in figure (6) this shows that as concentration increase the velocity decreases , because structural or volume relaxation it occurs in associated liquids such as polymers

A liquid when at rest has a lattice structure similar to that possessed by solid   when waves are propagated through it. The resultant periodic changes of wave pressure causes molecules to flow into vacancies in the lattice during compression phase and to return to their original positions in the lattice during rarefaction so when concentration increases the velocity will be decrease, because there is more attenuation of polymer molecules to ultrasound waves. (Formageau,et. al.,2003). Absorption coefficient was calculated by using equation no.(9) the figure (7) shows that absorption coefficient is increasing with concentration this attributed to the fact that when polymer concentration increase their will be more molecules in solution this lead to more attenuation against wave   propagation. This behavior same to that give by (Al-Bermany,2004)(Hassun,1990) for other polymers. Ultrasonic relaxation time was calculated by using equation no.(10) and shown in figure (8),so relaxation amplitude was calculated by using equation no.(11) and shown in figure (9). their values are increasing with concentration, this behavior same to that give by (Najin and Hassan 2005) for other polymers and attributed to the fact that ultrasonic energy depends on viscosity thermal conductivity, scattering and intermolecular processes , thermal conductivity and scattering effects are known to be negligible (Blitz,1967),(Hassun,1990) so viscosity is responsible for the increase of relaxation amplitude for this reason absorption coefficient commonly known as visco –absorption.

Specific a acoustic impedance shown in figure (10) is decreasing with concentrations. This behavior same to that given by (Najin and Hassan 2005) for other polymers and attributed to the equation no. (12) has only one variable parameter which is velocity and density has very small variations with respect to that of velocity. The compressibility is increasing with the increase of concentration figure(11) and attributed to the fact that in Laplace equation no. (13) there are

inverse proportionality between compressibility and ultrasonic velocity and the bulk modulus is decreasing with concentration figure(12).
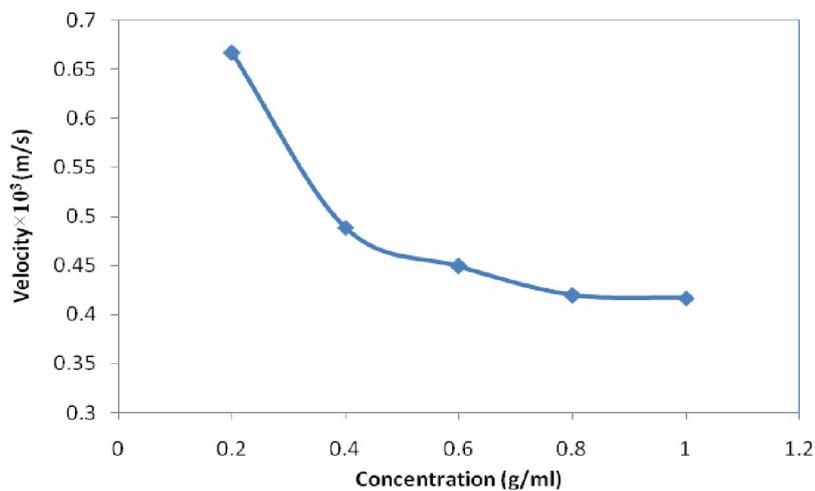

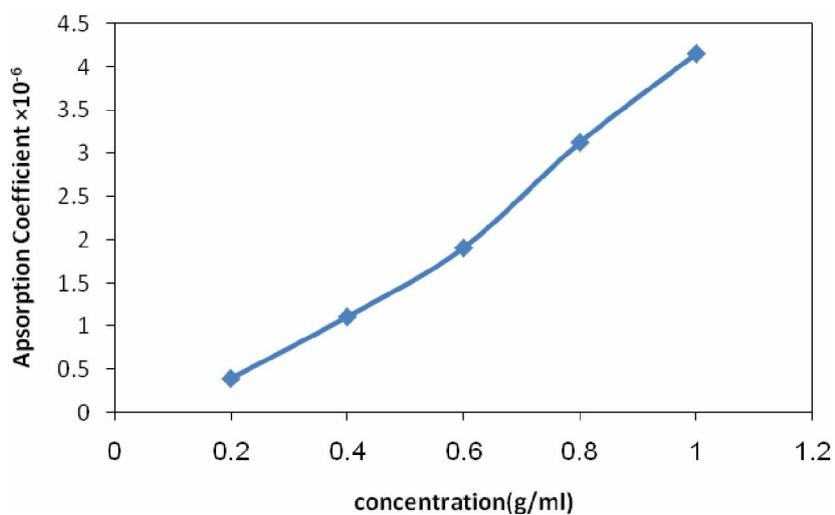Fig.6 the variation of ultrasonic velocity Vs concentration of polyvinyl alcohol

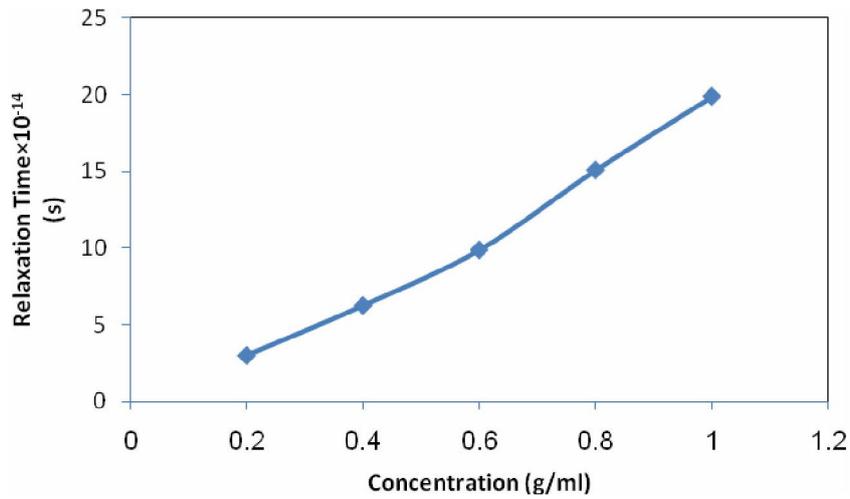Fig.7 the variation of absorption coefficient Vs concentration of polyvinyl alcohol

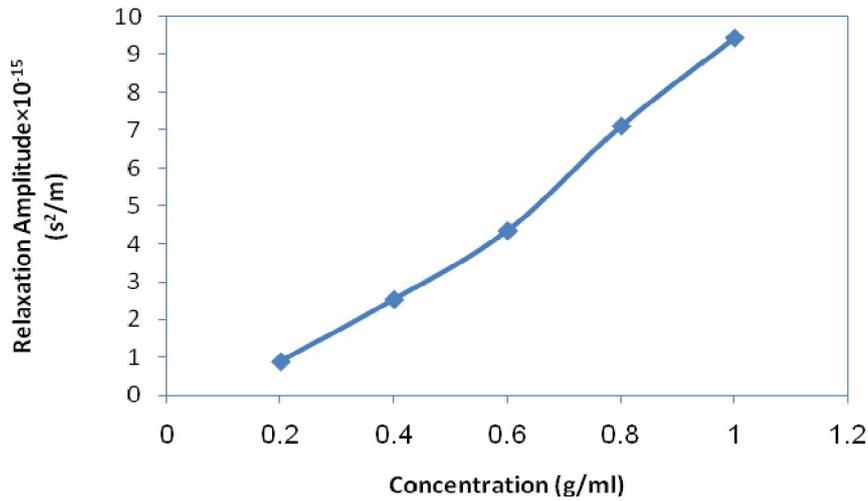Fig.8 the variation of relaxation time Vs concentration of polyvinyl alcohol

Fig.9 the variation of relaxation amplitude Vs concentration of polyvinyl alcohol
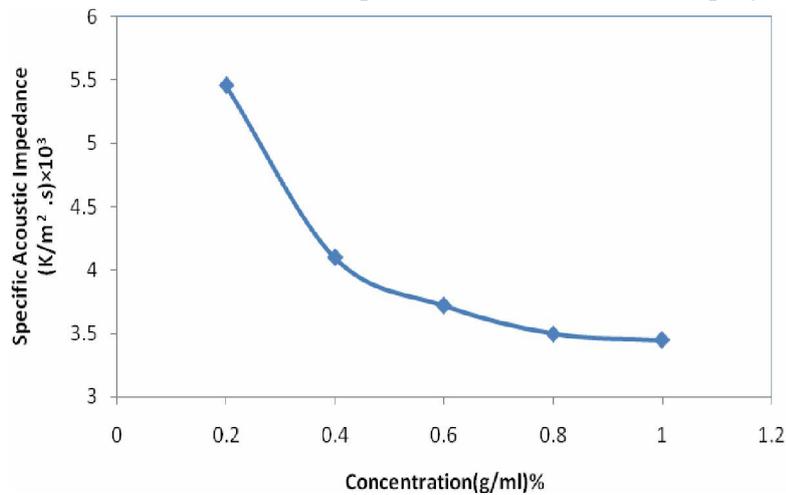

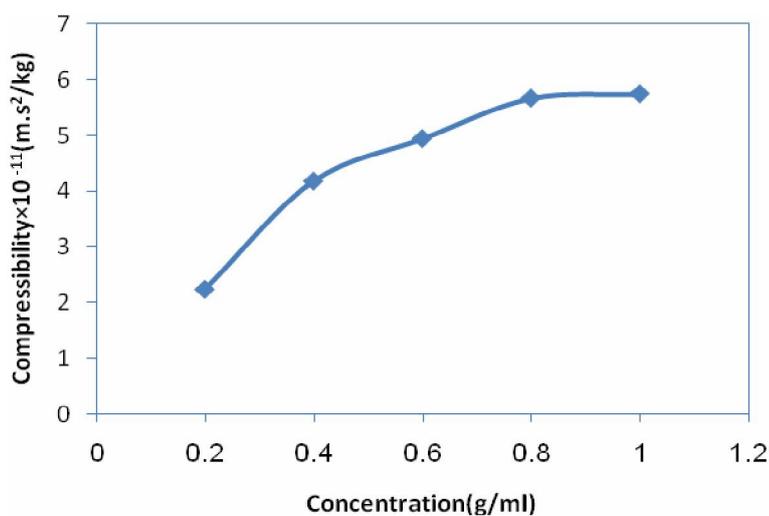Fig.10 the variation of specific acoustic impedances concentration of polyvinyl

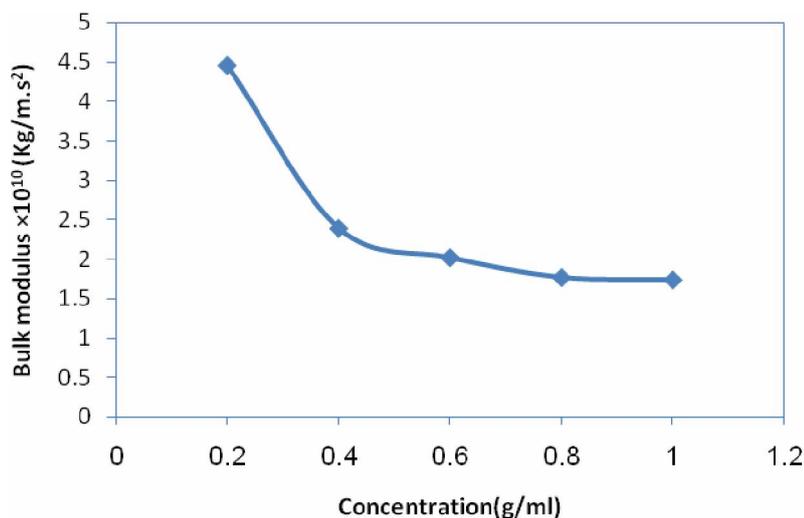Fig 11 the variation of compressibility Vs concentration of polyvinyl alcohol

Fig .12 the variation of bulk modulus Vs concentration of polyvinyl alcohol

Conclusion:
1-   This study shows that intermolecular processes are responsible for the relaxation, and indicating increase in the size of molecules in bath of ultrasonic waves

2- When concentration increase the velocity decreases there will be complexes molecules were formed in the solution by the effect of peroxide and roots as a results of degradation of the polymer chains. By ultrasonic waves.

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