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Ultrasonic study of HEC/ ZnO and HEC/ TiO2 film composites prepared by casting method

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Abstract:
The HEC/ZnO and HEC/TiO_2 composite membranes were prepared by a sol-gel casting method. In order to evaluate some physical properties of HEC/TiO_2 and HEC/ZnO composites the ultrasonic measurements were performed for the samples at room temperature (298.15 K.) with frequency (35KHz), these properties are ultrasonic velocity, compressibility, bulk modulus, absorption coefficient, relaxation amplitude, transmittance, relaxation time and viscosity. It was found that there is significant relationship between ultrasonic velocity and material properties also results show that adding ZnO and TiO_2 effect on densities which were responsible for the ultrasonic wave's absorption inside the composites which effected also on the transmittance and reduce velocity.
Keywords: HEC composite; ZnO; TiO2; Ultrasound technique; physical properties

Introduction:

The sol-gel casting method is widely used in the preparation processes for inorganic/organic composites. The advantages of the sol-gel method are that the synthesis process is done at room temperature and organic polymer can be introduced at the initial stage in which the particles of solution kept in the homogeneous dispersed state [1]. Composites have good potential for various industrial fields because of their excellent properties such as high hardness, high melting point, low density, low coefficient of thermal expansion, high thermal conductivity, good chemical stability and improved mechanical properties such as higher specific strength, better wear resistance and specific modulus [2]. The addition of inorganic particles into polymer matrices arises a new composite material has unexpected properties, which greatly differ from that of conventional materials [1]. HEC is a water-soluble synthetic polymer, due to the characteristics of easy preparation, good biodegradability, excellent chemical resistance and good mechanical properties; HEC has been used on many biomaterial applications [3]. 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 [4]. The manner in which the propagation of the ultrasonic wave is affected by the structure of the material results in parameters that can lead to the characterization of the material. [5], the absorption of ultrasound in polymer systems is governed by local modes of motion and cooperative because of the existence of strong intermolecular interaction within the polymer. Ultrasonic attenuation measurements are a standard method used to assess the effects of material degradation [6]. 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 [7].

Experimental:

Materials

Table (1) the material under study (The materials were used as received without further purification.)

Material	Assay	M.W. (g/mol)	Density (g/cm^3)	Company	Country
HEC	99.9%	___	1.3	Panreac	Spain
TiO_2	99.8%	79.866	4.23	Fluke	USA
ZnO	99.7%	81.408	5.606	Merck	Germany

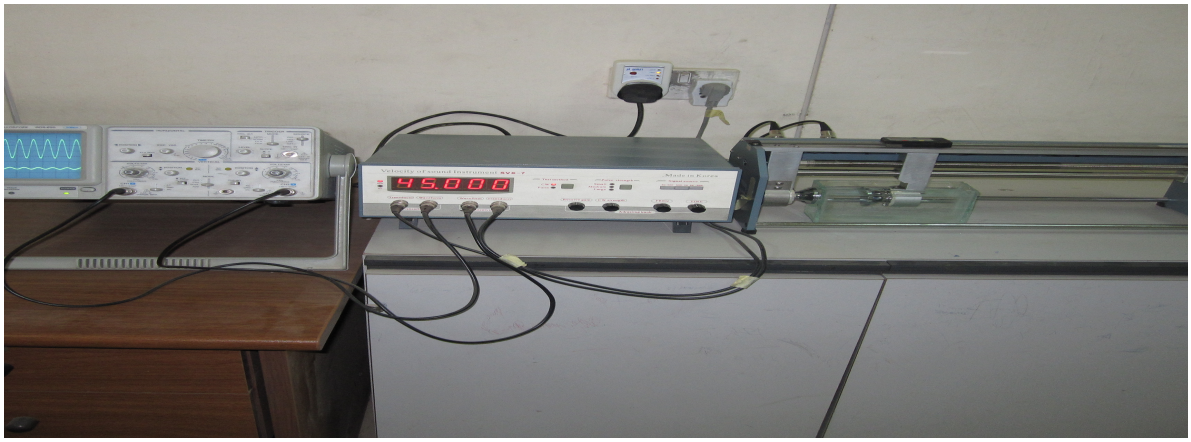
Preparation of Samples

The HEC/ZnO and HEC/TiO_2 composite membranes were prepared by casting method, the appropriate weight of HEC was dissolved in (25ml) of distilled water under stirring and heat (70◦C) for (30min) then the ZnO and TiO_2 were added for each sample, the resulting solution was stirred continuously until the solution mixture became a homogeneous viscous appearance at room temperature (298.15 K.) for (30 min.). The composite membranes are obtained by leaving the mixture solutions in a petre dish at room temperature (298.15 K. – 300.15 K.) for 4 weeks. The densities of the samples were measured by the weight method.

* We will refer to the HEC/ZnO as S1 and HEC/TiO_2 as S2 in this study.

Measurements

Ultrasonic measurements were made by pulse technique of sender-receiver type (SV-DH-7A/SVX-7 velocity of sound instrument – Korea), as shown in Fig. below the measurements were made at fixed frequency (f = 35KHz), the receiver quartz crystal mounted on a digital variable scale of slow motion, the receiver crystal could be displaced parallel to the sender and the samples were put between sender and receiver. The sender and receiver pulses (waves) were displaced as two traces of cathode ray oscilloscope, and the digital delay time (t) of receiver pulses were recorded with respect to the thickness of the samples (x). The pulses height on oscilloscope (CH1) represents incident ultrasonic wave's amplitude (A_o) and the pulses height on oscilloscope (CH2) represents the receiver ultrasonic wave's amplitude (A).



Theoretical calculation

The ultrasound wave velocity (V) was calculated using the following equation [8]:

$$V = X / t \qquad \ldots\ldots (1)$$

Compressibility (β) is a measure of the relative volume change of a fluid or solid as a response to a pressure (or mean stress) change, it was calculated by the following Laplace equation where (ρ) is the density [9]:

$$\beta = (\rho v^2)^{-1} \qquad \ldots\ldots\ldots (2)$$

Bulk modulus (B) of a composite is the substance's resistance to uniform compression, it is defined as the pressure increase needed to decrease the volume; it was calculated by [10, 11]:

$$B = \rho v^2 \qquad \ldots\ldots\ldots (3)$$

The acoustic impedance of a medium (Z) was calculated by equation [12]:

$$Z = \rho v \qquad \ldots\ldots\ldots (4)$$

Absorption coefficient (α) was calculated from Lambert – Beer law [13]:

$$A/A_o = e^{(-\alpha x)} \quad \ldots\ldots (5)$$

Attenuation is generally proportional to the square of sound frequency (f) so the relaxation amplitude (D) was calculated from the following equation [14]:

$$D = \alpha / f^2 \quad \ldots\ldots\ldots (6)$$

Transmittance (T) is the fraction of incident wave at a specified wavelength that passes through a sample was calculated from the following equation [15]:

$$T = I / I_o \quad \ldots\ldots (7)$$

Where (Io) is the initially intensity of the sound waves and (I) is the received intensity. The wavelength (λ) is the distance that sound (of a particular frequency) travels during one period (during one oscillation), and it changes only when the speed of the wave changes inside the samples we can calculate it by the equation [16]:

$$\lambda = v / f \quad \ldots\ldots \quad . (8)$$

On the basis that all solids flow to a small extent in response to small shear stress, some researchers have contended that substances known as amorphous solids, such as glass and many polymers may be considered to have viscosity. This has led some to the view that solids are simply "liquids" with a very high viscosity; the viscosity of the samples was measured by knowing absorption coefficient using the equation: [5]

$$\eta_{shear} = 3 \alpha \rho v^3 / 8 \pi^2 F^2 \ldots\ldots\ldots (9)$$

The relaxation time (τ) was calculated from the equation: [11, 17]

$$\tau = 4 \eta_{shear} / 3\rho v^2 \quad \ldots\ldots\ldots (10)$$

Results and discussions

The composite membranes density were measured by the weight method at room temperature (298.15 K.), figure (1) shows that the density of the membrane increase for S1 and S2 because its molecules which are heavier than HEC molecules occupied the vacancies between polymer macromolecules displaying HEC molecules from their position and because density is mass per unit volume so increasing the density with increasing the concentration, the S1 membranes have higher densities than S2 and this is attributed to the density and molecular weight of each as listed in table (1), the density values effected in other properties under study.

The ultrasonic velocity technique has several advantages over standard techniques where it can be applied; these include ease of use sample size and independence of the size of the tested particles. It does depend on an initial calibration to a direct strength measurement technique [18], as shown in figure (2) the ultrasonic velocity was calculated for different concentrations for S1 and S2, the ultrasound velocity are decreasing with the increasing the filler concentration; since the filler molecules filled the vacancies of the polymer chains that randomly coiled and give composite good tensile strength that increasing the impedance against velocity so reducing the later slightly, the velocity in S2 is higher than in S1 depending on the densities.

Compressibility of S1 and S2 were calculated using Laplace equation no. (2), figure (3) shows that the compressibility are decreasing with increasing concentration this could be attributed that ultrasonic waves propagation made polymer chains that randomly coiled to be each close together, this change confirmation and configuration of these molecules, so there are more compression happen of these molecules through ultrasound wave propagation [19,9] this compression fills the vacancies between polymer molecules and restricted the movement of these molecules this lead to reduce the elasticity of the composite as shown in figure (3).

The bulk modules are increasing with concentration a shown in figure (4), this could be attributed to the amount of contraction is governed by the compressibility, which is dependent on the intermolecular forces and because of the compressibility is inversely related to the bulk modulus by means of equations (2 and 3) so there are increasing in bulk modulus with increasing concentration , figure (4) also shows from (0.08-0.1 gm/ml) concentration the bulk modulus values for S1 and S2 are clear rise and descent in the modulus values this may be because of the molecules make entanglement interaction to the polymer chains and network formation [20].

The specific acoustic impedance are decreasing with concentration increasing as shown in figure (4); this attributed when the concentration increasing there are rearrangements of the polymer network by breaking chains bonds [21].

The transmittance are increasing with increasing S1 and S2 concentration as shown in figure (5) this attributed that the molecules fills the vacancies between polymer chains and restricted these chains in fixed volume so when ultrasonic passes through composite it faces strong resistance to follow, the S1 is absorbed the ultrasound wave better than S2 as shown in figure (5), the transmittance depend on the density, concentration and the filler type in the HEC matrixes. [22]
The absorption coefficient is decreasing as shown in figure (6) this could be attributed to the changes in the particle size distribution function of the three types of molecules that formed the composite; the intermolecular processes were assumed to be responsible for reducing acoustic attenuation then reducing the relaxation time for the composite molecules to be stated in their positions as shown in figure (6) [23]

The relaxation amplitude are decreasing with concentration as shown in figure (7) since it depend on the absorption coefficient as related in equation no.(5) and this could be attributed to the polymer molecules are swelling water and increase its size and these molecules restricted and the free radicals obtained as a result of degradation by ultrasonic [24].

The output wavelength gradually decreases with concentration as shown in figure (8), since there are increasing in concentration so the molecules come close together and there are more compressibility and rarefaction of more propagation against these molecules [25].

Share viscosity is decreasing with the increase of filler concentrations as shown in (fig.10) this is attributed to the changes in the particle size distribution function, the mechanism of hydrogen bonding of water attached to oxygen sites, this lead to salvation sheaths and increase the size of molecules [26], the viscosity in S2 is more than that in S1 this caused by network polymer chain formation [19] and the density listed in table (1) for both filler types.

Relaxation time is decreasing with increasing concentration as shown in (Fig.4), when the filler molecules attached to the polymer molecules and filled the vacancies, so there will be network formations in the composite which reduces the elasticity then reduce the relaxation time of excited molecules. [21]

Conclusion:

1-This study shows that adding ZnO and TiO_2 as fillers increase the density of the composites
2-The new densities for S1 and S2 are responsible for decrease the absorption coefficient, relaxation amplitude and transmittance
3- The intermolecular processes indicating increase in the size of molecules in bath of ultrasonic waves then reducing the velocity when concentration increases the velocity decreases there will be more molecules,
4-The molecules reducing absorption of sound waves according to Lambert-Beer Law velocity
5- From above this composites are good mediums for transfer sounds can be used in sonic instruments

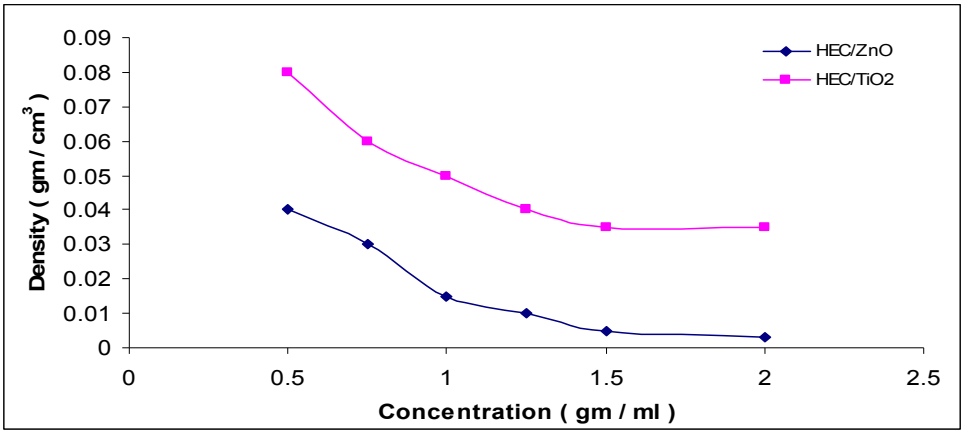


Fig.(1) The density vs.concentration

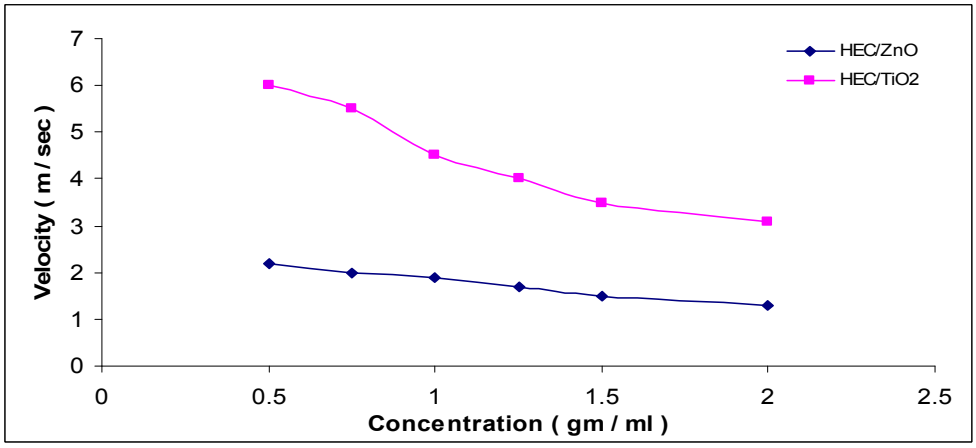


Fig (2) velocity vs.concentration

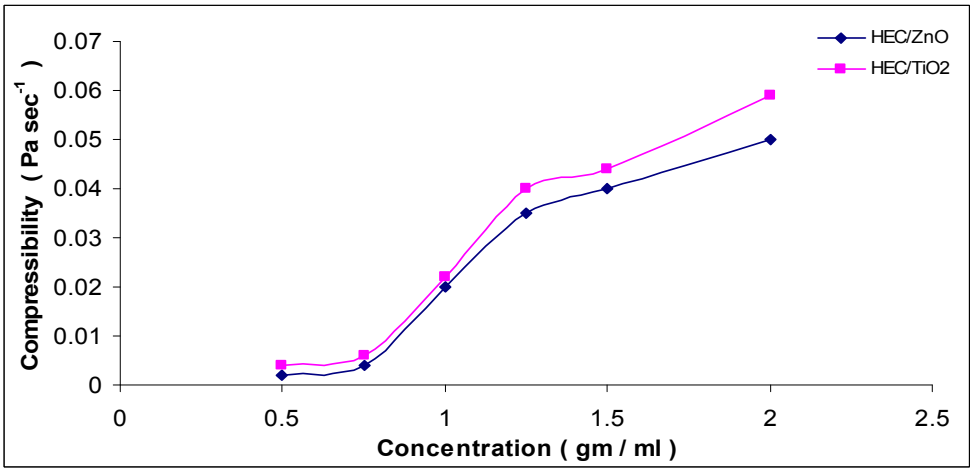


Fig.(3) Compressibility vs.Concentration

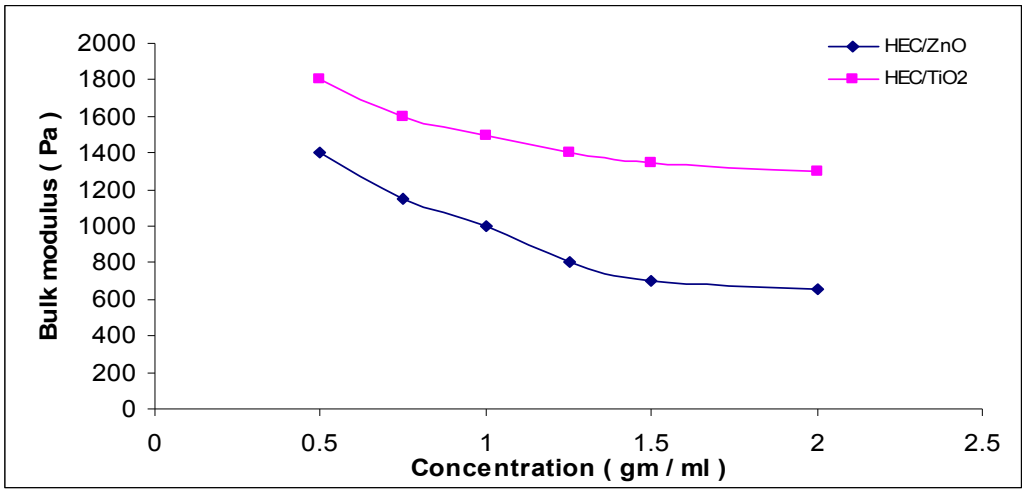


Fig.(4) The bulk modulus vs.concentration

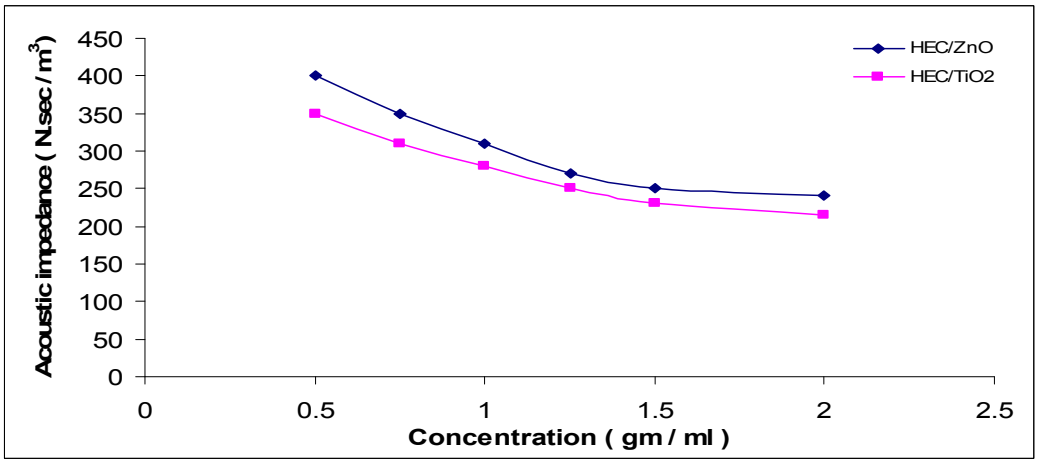


Fig.(5) The acoustic impedance vs.concentration

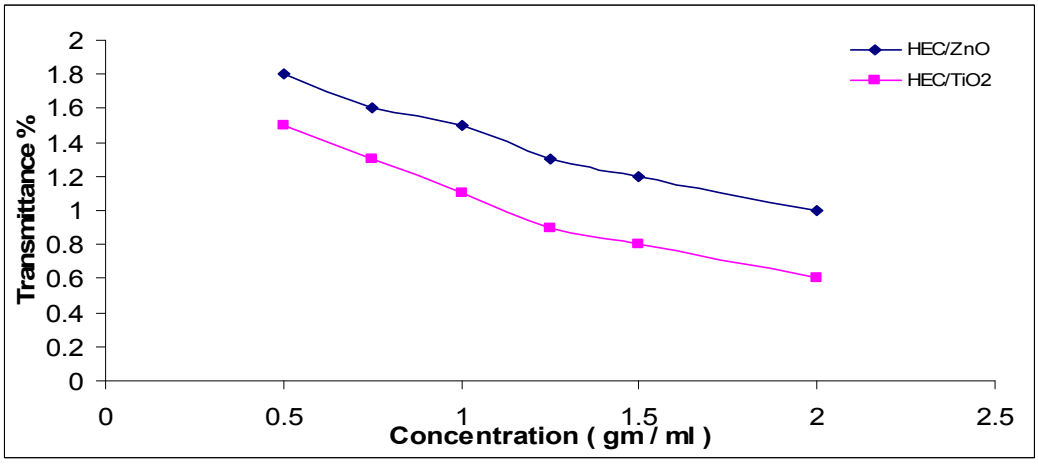


Fig.(6) The transmittance vs.concentration

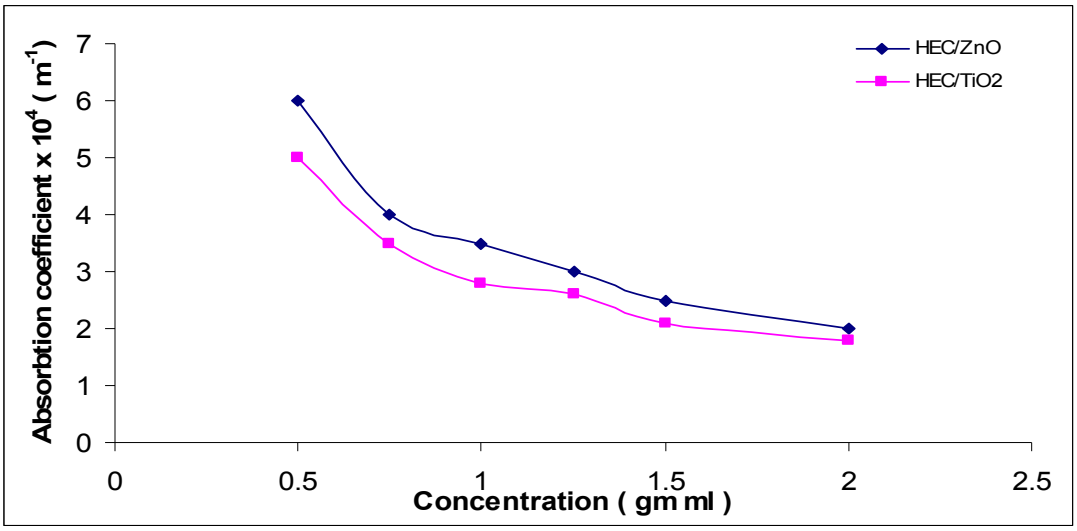


Fig.(7) The absorption coeffiecent vs.concentration

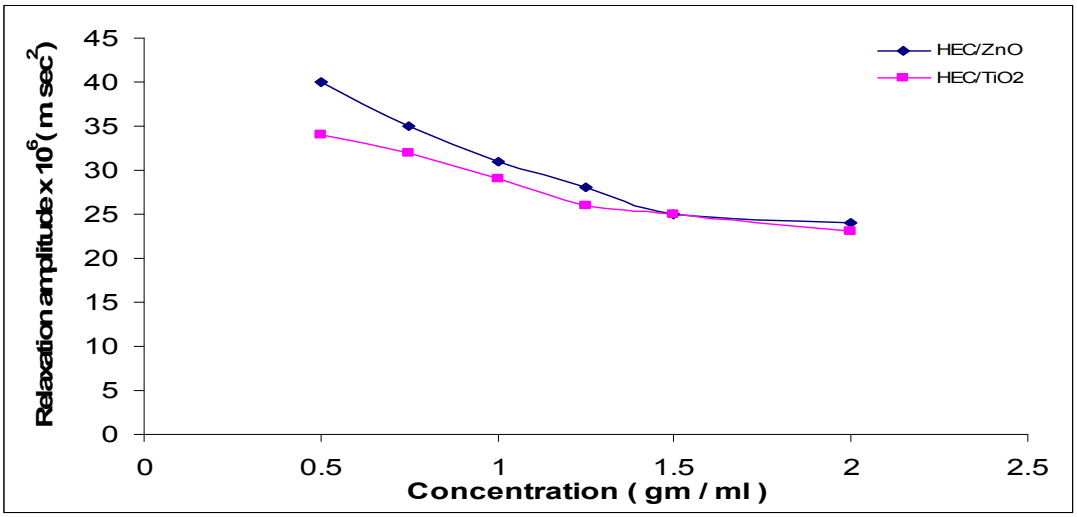


Fig.(8) The relaxation amplitude vs.concentration

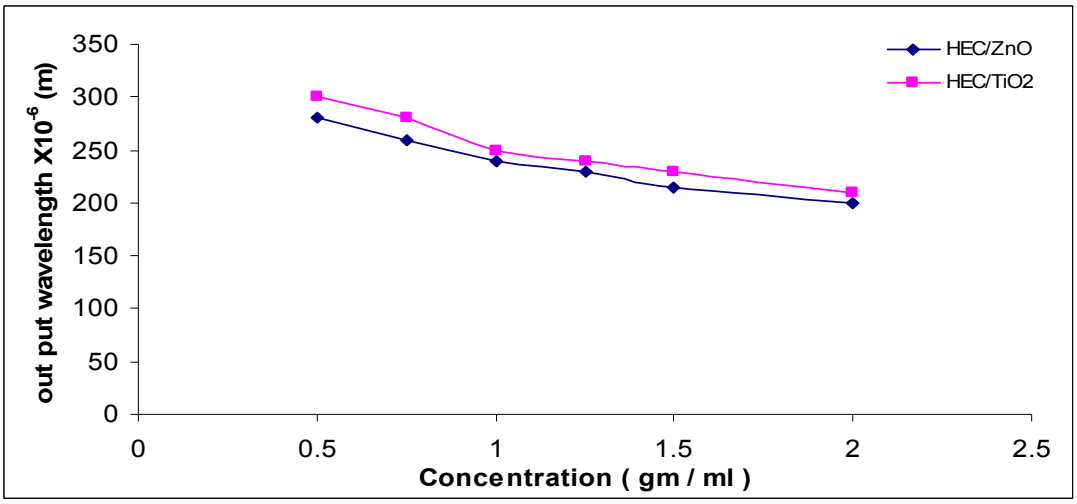


Fig.(9) The output wavelength vs.concentration

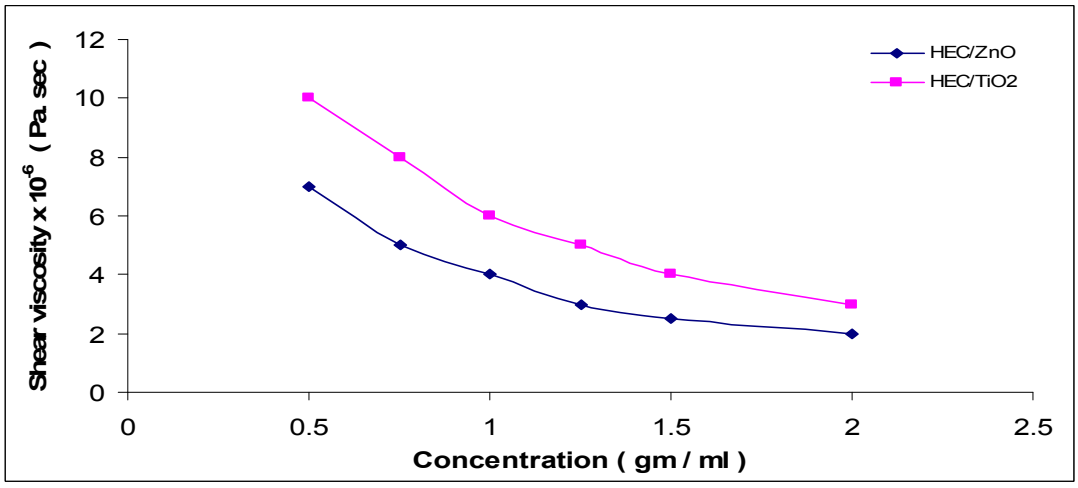


Fig.(10) The shear viscosity vs.concentration

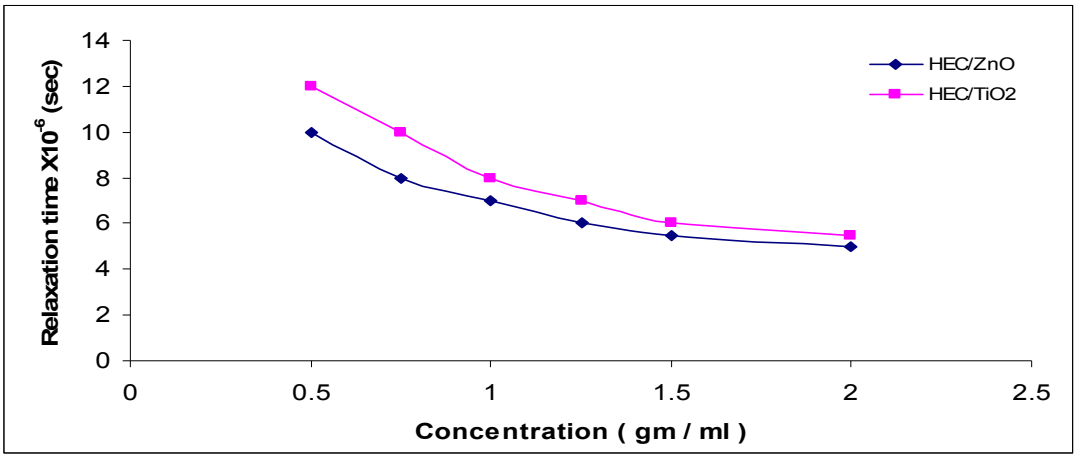


Fig.(11) The relaxation time vs.concentration

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