Studying the Ultrasonic Properties, DC Conductivity and Coefficient of Thermal Conductivity of PVA-Egg Shells Composites

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Abstract
The polymer composite used in the present study were made of polyvinyl alcohol (PVA) as a matrix and *Iraqi egg shells as filler*. Polymer composites were fabricated by mixing PVA with (5, 10, 15, 20, 25, 30, 40 and 50) wt.% of egg shells powder by using a magnetic stirrer at temperature 90°C for 4hr to obtain homogeneous solution then samples were prepared by casting techniques. The ultrasonic measurements (transmittance, absorption coefficient and relaxation amplitude, acoustic impedance, compressibility and compressibility) of composites were carried out by using ultrasound technique. Measurement of DC conductivity and coefficient of thermal conductivity were done as a function to wt. % of egg shells. It was found that the samples contain additives of eggshells 5%, 10%, 20% and 30%, the attenuation decreased by increasing frequency up to 40 KHZ and then increased after this frequency; while the sample contains 15% of the eggshells, the attenuation not alter significantly with increasing frequency. Sample with 50 % egg shell has two peaks at 20 and 30 kHz. As can be seen that the samples which contain a proportion of eggshells 5, 10, 20, 25, 30 and 40%, the transmittance coefficient increases with increasing frequency up to 40 kHz and then decreases and relaxation amplitude decreases with increasing frequency from 5 to 50 KHZ. Generally observed acoustic impedance decreases with increasing eggshells except percentage 20%, where the highest value for the impedance. Compressibility generally increases with increasing of eggshells up to 40 % and then decreases. The electrical conductivity increase as concentrations of egg shells increase up to 30 % then conductivity decreases at 40 % then increases slightly at 50 %. It was found that coefficient of thermal conductivity increases with increasing of egg shells up to 40 % then decreases.

Keywords: PVA, egg shells, ultrasonic properties, dc conductivity, coefficient of thermal conductivity.

1. Introduction
Egg shell (ES) is a biomaterial containing 95 % by weight of calcium carbonate in the form of calcites and 5 % by weight of organic materials, such as (Al₂O₃, SiO₂, S, Cl, P, Cr₂O₃, MnO) (Hussein et al. 2011). Many studies have proved that chicken egg shell is an agriculture by product that has been listed worldwide as one of the worst environmental problems, especially in those countries where the egg product industry is well developed. In the U.S. alone, about 150,000 tons of this material is disposed in landfills (Shuhadah et al. 2008). The generalized egg shell structure, which varies widely among species, is a protein lined with mineral crystals, usually of a calcium compound such as calcium carbonate; these characteristics qualify ES as a good candidate for bulk quantity, inexpensive, lightweight and low load-bearing composite applications, such as the automotive industry, trucks, homes, offices, and factories (Hassan et al. 2012). Polyvinyl alcohol is commercially available in dry granular or powdered form; it is a water-soluble and fully biodegradable polymer (Chen et al. 2002). PVA is having planar zigzag structure like polyethylene (Horii et al. 1992). All PVA grades are readily soluble in water. As a hydrophilic polymer, PVA exhibits excellent water retention properties. Conditions for dissolution are governed primarily by degree of hydrolysis, but they are influenced by other factors such as molecular weight, particle size distribution and particle crystalline (Peppas & Merrill 1977). In addition to its solubility, PVA is also appreciated for its good mechanical properties in the dry state, resistance to common solvents, barrier effect in dry atmospheres, possibility of food contact for suitable grades, biodegradability. The use of organic or inorganic filler has become ubiquitous in polymeric systems. Polymer composites are manufactured commercially for many diverse applications such as sporting goods, aerospace components, automobiles, etc. (Hussain et al. 2006). Composite materials have successfully substituted the conventional materials in several applications like light weight and high strength. The reasons why composites are selected for such applications are mainly due to their high strength-to-weight ratio, high tensile strength at elevated temperatures, high creep resistance and high toughness (Indicula & Boudenne 2006). For example when silica particles are added into a polymer matrix to form a composite, they play an important role in improving electrical, mechanical and thermal properties of the composites (Peters 1998). Abdullah et al. (2012) investigated the dielectric behavior and alternating electrical conductivity of polyvinyl alcohol doped with varying concentration of kaolin. Hussien (2011) studied the effect of alumina additive on the D.C and A.C electrical properties of poly-methyl methacrylate composite, his results showed that the D.C electrical conductivity increased with increasing the
alumina concentrations and temperature. Hashim (2012) found that the electrical conductivity of composites (polyvinyl alcohol and silver carbonate, cobalt nitrite) increases with increase the cobalt nitrite and silver carbonate concentrations and temperature. Many studies have been achieved to investigate thermal conductivity, Nayak et al. (2010) studied thermal conductivity of pine wood dust filled epoxy composites. Kumar et al. (2012) developed an analytic model to estimate the effective thermal conductivity of two phase materials. Devendra & Rangaswamy (2012) determined the thermal conductivity, thermal expansion coefficient, time to ignition and flame propagation rate of E-Glass fiber reinforced epoxy composites with filling varying concentration of aluminum oxide (Al₂O₃), magnesium hydroxide (Mg(OH)₂), silicon carbide (SiC), and hematite powder and their results showed that Al₂O₃ and Mg(OH)₂ filled composites exhibited low thermal conductivities while composites filled by SiC particles exhibited low thermal expansion coefficient when compared with other filled composites. Many studies have demonstrated good relationship between the velocity of sound and mechanical properties of composites for example (Rashid & Kadem 2011) used the ultrasonic technique to study physical properties of palm fiber /PVA composite polymer. Ultrasonic transmission technique was used to investigate the water-saturated aluminum foams with an open network of interconnected ligaments (Zhang et al. 2011). Also a technique was developed for measurement of bubble, droplet and particle-size distributions in multiphase systems, based on the propagation speed and attenuation of ultrasound in multiphase systems (Cents et al. 2004). Furthermore the transmission ultrasonic technique was used to estimate the phase velocity dispersion of the bulk waves in a highly attenuating planar PVDF plastic sample (Raisutis et al. 2008). The present work is undertaken to investigate experimentally the ultrasonic measurements (including transmittance, absorption coefficient, relaxation amplitude, acoustic impedance, bulk modulus and compressibility), thermal conductivity and electrical conductivity of PVA- egg shells composite.

2. Experimental work

2.1 Sample preparation:

The solid composite used in the present study is made of PVA polymer as a matrix and Iraqi egg shells as filler. Iraqi egg shell have been collected and washed carefully and dried, the milling process was achieved by using electrical ball mall for 3 hr, and then the powder of egg shell was passed through sieve with diameter of 125 micrometer and used as filler. A magnetic stirrer was used for 3 hr to make the solution highly homogeneous. Each solution was placed in a Petri dish and then placed in a dust free chamber to evaporate the solvent slowly in air at room temperature for seven days to make cast samples.

2.2 Ultrasonic measurements:

Ultrasonic measurements were performed by using ultrasound technique (velocity of sound instrument type SV-DH-7A/SVX-7) to calculate the following properties (transmittance, absorption coefficient, relaxation amplitude) of a range of sound frequencies from 5 to 50 KHz by setting the instrument test mode to the continuous wave while acoustic impedance, compressibility and compressibility were measured by determine velocity of wave by setting test mode to the pulse wave. The above properties were calculated by using the following equations:

2.2.1 Transmittance

The transmittance ($T$) is the fraction of incident wave at a specified wavelength that passes through a sample as follows (Basu 2001):

$$T = I/I_o$$

2.2.2 Attenuation coefficient

The amplitude change of a decaying plane wave can be expressed by (Opielinski et al. 2010):

$$a = -\frac{L}{\pi} \ln \left( \frac{A_o}{A} \right) \ (m^{-1})$$

Where $A_o$ is the initially amplitude of the ultrasonic wave. The amplitude $A$ is the reduced amplitude after the wave has travelled a distance $x$ from that initial location. In this expression, $a$ is an attenuation coefficient.

2.2.3 Relaxation amplitude

Relaxation amplitude was calculated from the following equation (Wu & Liu 2011):

$$D = a / f^2 \ (m. sec^{-1})$$

Where ($f$) is the ultrasonic frequency.

2.2.4 Velocity of sound wave

Pulse velocity is the distance travelled during a unit of time by a sound wave propagating through an elastic
medium as expressed by (Turgut 2004):
\[ v = \frac{x}{t} \quad (m/sec) \]  
(4)

Where \( x \) is the sample thickness, \( t \) is the time of passage the sound wave through the material.

### 2.2.5 Acoustic impedance

The acoustic impedance, \( z \), is the product of the density, \( \rho \), of a material and the speed that sound will travel through it, \( v \), as follows (Gasni 2012):
\[ Z = v \rho \quad (kg.m^{-2} . s^{-1}) \]
(5)

### 2.2.6 Bulk modulus

Bulk modulus can be expressed by the equation (Gasni 2012):
\[ B = \rho v^2 \quad (kg.m^{-1}.sec^{-2}) \]
(6)

### 2.2.7 Compressibility

Compressibility is the inverse of bulk modulus (Gasni 2012):
\[ \beta = (\rho v^2)^{-1} \quad (kg^{-1}.m.sec^{-2}) \]
(7)

### 2.3 Electrical conductivity:

Keithly electrometer (2400) was used to calculate DC conductivity of PVA-egg shell samples, all measurement were performed at room temperature by using the equation:
\[ \sigma = \frac{L}{RA} \quad \text{(ohm.m)} \]

Where:
\( A \) = the electrodes area: \( A = \pi r^2 \) where \( r = 0.5 \) cm.
\( R \) = volume resistance (Ohm).
\( L \) = average thickness of sample (m)

### 2.4 Coefficient thermal conductivity:

Thermal coefficient meter YBF-3 was used to measure coefficient of thermal conductivity of samples and the measurements were achieved at 60°C by steady state method, each measurement took time of 40 minutes. Measurements have been done in accordance with the instructions of the device.

### 3. Result and discussion

Figure 1 shows the behavior of attenuation with increasing of frequency for samples of PVA-egg shells. From the figure it is found that the samples contain additives of eggshells 5, 10, 20 and 30%, the attenuation decreases by increasing frequency up to 40 KHz and then increases after this frequency. Skinner et al. (2006) found similar behavior up to 7000 Hz. Whereas the sample contains 15% of the eggshells, the attenuation not alter significantly with increasing frequency with note the greatest absorption at the frequency of 10 KHz and 40 KHz. Zhang et al. (2011) found that the changing of attenuation with frequency is less obvious and exhibits no increasing attenuation level within the main frequency band from 0.7 to 1.3 MHz due to scattering. Figure as well shows that the sample containing 40% of eggshells the attenuation coefficient increases up to 20 KHz then decreases until 40 KHz and then increases. Sample with 50% egg shell has two peaks at 20 and 30 kHz. Generally according to Figure 1 it can be seen that increasing the proportion of eggshells up to 40% leads to an increase in the attenuation coefficient but increase the proportion of egg shells up to 50% reduces the attenuation coefficient. The interaction between the polymer and filler influences also the attenuation in composites through scattering, antiphase vibrations, and interfacial friction (State et al. 2010). Strong effects, due to the resonance of particles with a certain size, are damped due to the presence of particles with a different diameter, which have a different resonance frequency (Cents et al. 2004). The pulsation and oscillation of a particle in the presence of an ultrasonic wave causes the generation of secondary ultrasonic waves by the particle, thus some of the ultrasonic energy associated with the incident wave is redirected into different directions, and an increase in the attenuation coefficient may be detected (McClements 1997). For this reason some absorption peaks appear in some samples. Niemi et al. (2005) also found several attenuation peaks between 5 and 10 MHz. Figure 2 shows the behavior of the transmittance coefficient with wave frequency. As can be seen that the samples which contain a proportion of eggshells 5%, 10, 20, 25, 30 and 40%, the transmittance coefficient increases with increasing frequency up to 40 kHz and then decreases; while the sample containing 15%, the transmittance not change significantly with frequency with appearance of maximum transmittance at 35 KHz. The same behavior was observed for sample containing 50% egg shells with the greatest transmittance at the frequency of 25 kHz. When an ultrasound wave
is incident at the interface between two different materials, some sound is reflected and the rest is transmitted across the interface. The relative amplitude and phases of these waves depend upon the change in acoustic impedance across the boundary. As the magnitude of the change in acoustic impedance increases, a greater proportion of the incident energy is reflected and hence less is transmitted across the boundary (Smith 2001). Therefore, increasing the proportion of eggshells resulted in an increase in the amount of acoustic impedance, leading to more reflection of the waves and therefore decreased transmittance as in sample with 50% of egg shell. The presence of the greatest value to the transmittance of some samples resulting from these samples has the lowest value of the attenuation coefficient (as shown in the figure 1), which means less interaction between the waves and the polymer and therefore the waves penetrate the material. Figure 3 illustrates that relaxation amplitude decreases with increasing frequency from 5 to 50 KHz. The relaxation amplitude significantly decreases up to 30 KHz after that change is almost stable. At low frequencies the molecules have time to respond to the applied stress while at high frequency no molecular relaxation take place (the stiffness of polymer is more) (Anderson et al. 2011). Figure 4 shows the behavior of the acoustic impedance of the samples with the increase in the proportion of eggshells. Generally acoustic impedance decreases with increasing eggshells except percentage 20%, where the highest value for the impedance. A measurement of the material’s ability to transmit ultrasound is known as the acoustic impedance, which is a useful concept in ultrasound (Skinner et al. 2006). Also specific acoustic impedance is a quantity which depends on the molecular packing of the systems (Yasmin & Gupta 2012). Therefore the lower concentration of egg shells has higher values of acoustic impedance, because there are more vacancies in the membrane that decreasing elasticity and impedance, but at high concentration these vacancies filled with egg shells that make membrane to be good medium to transfer ultrasound waves.

Figure 5 shows that the speed of sound change with the ratio of egg shells added where this attributed that as concentration increases there must be more degradation by ultrasonic increasing the broken chains that give composite more elasticity which reduced the velocity, so lower concentration have higher velocity (Foled et al. 1988) this behavior same to that obtained for other polymers (Rashid & Kadem 2011). The speed of sound is a property of the medium, because sound travels through different media at different speeds, propagation of sound wave occurs due to the elastic forces between constituent particles. Elastic forces depend on the host material; it takes less or more time to transmit the wave (Gasni 2012). The fillers particles dispersed into the polymer are acting as network nodes impeding hence chain mobility (McClements 1997). So eggshells can be considered obstacles to the sound track. Sound waves are made up of kinetic energy, it takes more energy to make large molecules vibrate than it does to make smaller molecules vibrate. Thus, sound will travel at a slower rate in the more dense object. Figure 6 shows that the bulk modulus, except the proportion 20%, decreases with increasing of additives of egg shells up to additives of 40% and then increases. The bulk modulus describes volumetric elasticity, or the tendency of an object to deform in all directions when uniformly loaded in all directions; it is defined as volumetric stress over volumetric strain, and is the inverse of compressibility. Generally, the modulus of composites increases with increasing particle volume fraction when the particles are stiffer than the matrix (Rohatgi et al. 2009). Since the velocities of waves are decreased due to the lower modulus of polymer (Kim et al. 2004) therefore by observing figure 3 and 4 it can be seen that the modulus of elasticity decreases with decreasing wave velocity which in turn results from increasing the proportion of egg shells. Figure 7 represents the variation of compressibility with additives of egg shells. Generally, compressibility measures the change in volume with respect to pressure also compressibility is a measure of the relative volume change of a fluid or solid as a response to a pressure (or mean stress) change (Bennethum 2006). It can be seen from figure 7 that compressibility generally increases with increasing eggshells up to 40% and then decreases. Since compressibility is inverted of bulk modulus, so it is clear that at a ratio of 40 to be the largest compression (figure 7) corresponding the lowest value for bulk modulus (figure 6). Rashid (2011) found the same behavior by using TiO2 filler to PVA. Figure 8 shows the behavior of conductivity according the additives of egg shells. The dependence of the electrical conductivity of PVA filled with egg shells on the filler content volume fraction is shown in figure 8. The electrical conductivity increase as concentrations of egg shells increase up to 30% then conductivity decreases at 40% then increases slightly at 50%. The electrical conductivity imparted by the filler to the polymer does not increase continuously with increased electroconductive filler content, i.e., the relationship is nonlinear (Lux 1993). It is noticed that a higher concentration of recycled copper is needed to create a conductive path throughout the entire composite. A dramatically increase in electrical conductivity was observed around a particular concentration of the filler. This concentration is generally called percolation concentration (Novak et al. 2003), i.e. the filler concentration at which the step change in conductivity occurs, it is seen that the percolation concentration was around 30% of egg shell. The egg shells powder contain trace elements of dioxide (Mn, Fe, Al, Cr, Ca, Mg, Na, Zn, Cu) leads to promote the conductivity of the composites (Ghani et al. 2012). In this case, infinite cluster of particles is formed within a polymeric matrix. This cluster penetrates throughout the sample and represents a conductive way for movement of ions throughout the sample. Figure 9 represents the behavior of coefficient of thermal conductivity with additives of egg shells. It was found that coefficient of...
thermal conductivity increases with increasing of egg shells up to 40% then decreases. It should be noticed that thermal conductivities of polymers depend on many factors, such as chemical constituents, strength of bonding, structure type, molecular weight of side groups, molecular density distribution, type and strength of defects or structural faults, size of intermediate range order, processing conditions and temperature (Han & Fina 2011). It can be seen from Figure 9 that increases of additives of egg shells up to 30% represents the first stage, in which most particles dispersed separately, so the thermal conductivity increases slowly with content of egg shells The abrupt increase of conductivity of the second stage indicates the formation of the continuous pathway. After that, further increase of the egg sells content has reverse effect leading to decrease of thermal conductivity.

4. Conclusions
Increasing the proportion of eggshells up to 40% leads to an increase in the attenuation coefficient but increase the proportion of egg shells up to 50% reduces the attenuation coefficient. Samples contain additives of egg shells 5%, 10%, 20% and 30%, the attenuation decreases by increasing frequency up to 40 KHz and then increases after this frequency. Also the sample contains 15% of the eggshells, the attenuation not alter significantly with increasing frequency with note the greatest absorption at the frequency of 10 KHz and 40 KHz. The samples contain a proportion of egg shells 5, 10, 20, 25, 30 and 40%, the transmittance coefficient increases with increasing frequency up to 40 KHz and then decreases. While the sample containing 15%, the transmittance not change significantly with frequency with appearance of maximum transmittance at 35 KHz. Acoustic impedance and bulk modulus, except the proportion 20%, decrease with increasing of additives of egg shells up to additives of 40% and then increases. Compressibility generally increases with increasing egg shells up to 40% and then decreases. The electrical conductivity increase as egg shell concentrations increases up to 30%; while coefficient of thermal conductivity increases with increasing of egg shells up to 40% then decreases.

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Figure 1. Relationship between Attenuation Coefficient and Frequency for PVA Samples Contain Different Additives of Egg Shells

Figure 2. Relationship between Transmittance and Frequency for PVA Samples Contain Different Additives of Egg Shells

Figure 3. Relationship between Relaxation Amplitude and Frequency for PVA Samples Contain Different Additives of Egg Shells
Figure 4. Relationship between Acoustic Impedance and Additives of Egg Shells

Figure 5. Relationship between Velocity of Sound and Additives of Egg Shells

Figure 6. Relationship between Bulk Modulus and Additives of Egg Shells
Figure 7. Relationship between Compressibility and Additives of Egg Shells

Figure 8. Relationship between DC Conductivity and Additives of Egg Shells

Figure 9. Relationship between Coefficient of Thermal Conductivity and Additives of Egg Shells
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