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Influence of ZnO on the ultrasonic velocity and elastic moduli of soda lime silicate glasses

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The effects of ZnO on longitudinal and transverse ultrasonic wave velocities of soda lime silicate (SLS) glasses have been measured using the pulse-echo method at 5 MHz frequency at room temperature. The elastic properties: Longitudinal modulus, shear modulus, Young's modulus, bulk modulus, Poisson's ratio, and Debye temperature are found to be rather sensitive to the glass composition. Experiments showed that these parameters depend upon the ZnO-modifier content.

Key words: Glasses, annealing, ultrasonic measurements, elastic properties.

INTRODUCTION

Soda lime silica (SLS) glass is the most common commercial product, which constitutes about 90% of the glass produced today. However, after use, waste disposal is a problem of immense magnitude, so new products utilizing recycled waste SLS glass are needed to use this waste and encourage further glass recycling. Current efforts to solve the ecological problem of waste and to recycle large quantities of SLS glass typically involve sorting the glass containers by color and type, then removing all the foreign materials such as labels, metals caps and strips, and finally remelting the bottles. Most SLS glasses are composed of soda (Na_2O), lime (CaO), and silica composition. The study of SLS glasses becomes more popular because these glasses are cheap, with low melting temperature ($\sim 700^\circ\text{C}$), are chemically durable, and relatively easy to melt and form. SLS glasses containing other oxides have previously attracted some interests. Lu et al. (1988) studied the structural change of soda-lime glass with minor P_2O_5 addition and heat treatment. They found that with the increasing P_2O_5 content or altering the heat treatment conditions of SLS glass, resulted in structural changes as evidenced in the Raman, IR, and ESR spectra. The content of phosphate tetrahedral double bonds in the

glass is observed to be maximum with increase of about 2% P_2O_5 . During heat treatment, there appear changes in the structure of phosphate and silicate tetrahedral and in the distribution of sodium cations.

McCauley et al. (1981) studied the impact resistance in SLS glasses through zinc oxide substitutions and found that 8.52 wt. % increases in ZnO reduced the Young's modulus by 9.0% and increased the impact resistance of the SLS glass by 4.1%. Lusvardi et al. (2007) carried out research on the combined experiment and computational approach to $(\text{Na}_2\text{O})_{1-x}\text{-CaO-(ZnO)}_x\text{-2SiO}_2$ glasses characterization. The result shows that Zn acts as a weak tetrahedral network former, independent of the glass Na content and the density of glasses increases linearly with the zinc concentration. Qian et al. (2008), studied the structure of soda silica glasses containing ZnO and concluded that ZnO could act both as network former and as a network modifier, the former in the form of ZnO_4 tetrahedral structure connected to neighboring SiO_4 by bridging oxygen (Si, O, Zn bonds), while the latter with ZnO_6 octahedral structure, resting with the availability of network modifying cations for charge compensation. Besides that, ZnO also improves chemical resistance, lowers thermal expansion, and adds elasticity, properties which make it useful in certain types of laboratory glass. Makishima and Mackenzie (1973, 1975) proposed a theoretical model to calculate the elastic moduli of oxide glasses in terms of the packing density of chemical compositions and the dissociation energy of oxide

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constituents per unit volume. Watanabe et al. (2001) had investigated the relationship between elastic moduli and temperature for seven commercial silicate glasses and found that for low expansion glasses, the elastic moduli increase with increasing of temperature. It can be concluded that moduli increases for low-expansion materials and decreases for high-expansion materials (Ono et al., 2009). Hwa et al. (2003) investigated the elastic moduli of low-silica calcium alumino-silicate (LSCAS) glasses at room temperature by ultrasonic pulse-echo technique. They found that the longitudinal and transverse velocities of these glasses are composition-dependent.

Many studies of the elastic properties of glass-forming materials have been carried out in order to understand the behavior of glass and glass ceramics. Modulus of elasticity is an indication of the magnitude of bond strength in material (Matori et al., 2006; Varshneya, 2006; Ojovan et al., 2007). From the term of elastic properties such as Young's, bulk, shear, and longitudinal moduli, we will know how much tensile stresses can be applied before materials deform or fracture (Lambson, 1984). It is important to know the strength of glass in order to determine the durability of glass and glass ceramics (Sinton and Lacourse, 2001; Lee et al., 2006; Juoi et al., 2008) for special application.

The prime goal of the present work is to complete the study that was done on the mechanical properties of glasses from SLS glasses and ZnO using pulse-echo method.

EXPERIMENTAL

A series of glasses were prepared by mixing together specified weights of zinc oxide, (ZnO) (99.99%, Aldrich) and SLS glass waste. The SLS was ground to < 200 μm using a mortar and pestle. Chemical compositions of the SLS were determined by inductively coupled plasma emission spectroscopy (ICP). In order to reduce tendency to volatilization, the mixture was kept at 400°C for a period of 1 h. The crucible was then transferred to an electric furnace at 1300°C for 2 h to ensure completion of homogeneous melting. The melt was poured onto stainless steel plate and annealed for 1 h at 400°C, which is below their glass transition temperature. In order to measure the ultrasonic velocity, each glass specimen must have a pair of end faces that are flat and mutually parallel. Details of glass sample preparation are available elsewhere (Afifi and Marzouk, 2003). The glasses produced were transparent, clear, and free from defects. The glassy state of the samples was confirmed using XRD technique.

The density of each annealed glass was measured at room temperature by means of Archimedes technique with acetone as the reference liquid. The sensitivity of the digital weighing machine used was ± 0.001 g. The ultrasonic wave velocities V (in ms^{-1}) propagated in the glasses were obtained at room temperature, using pulse-echo technique, by measuring the elapsed time between the initiation and the receipt of the pulse appearing on the screen of MATEC Model MBS8000 DSP (ultrasonic digital signal processing) system with 5 MHz resonating frequency. Burnt honey was used as bonding material between X-cut and Y-cut transducers (for generating and detecting the longitudinal and shear ultrasonic waves, respectively), and glass sample.

The pulser section generates electrical pulses that are converted into ultrasonic signals using matched transducers. The ultrasonic pulse travels through the specimen bonded to the transducer and an echo is registered each time and returns to the transducer. The amplitude of the successive echoes decrease exponentially due to attenuation in the sample and multiple echoes are observed on the screen. The ultrasonic wave velocity can be calculated using the following equation (El-Mallawany et al., 2006):

$$V = \frac{2X}{\Delta t} \quad (1)$$

where X is the sample thickness and Δt is the time interval. The measurements were repeated three times to check the reproducibility of the data. The estimated accuracy of the velocity measurement is about 0.04%.

RESULTS

Five series of glasses were melted successfully and formed into a glass from SLS glass and ZnO. All the glasses were transparent, bubble-free, and homogeneous. After melting and quenching, each composition was chemically analyzed by ICP and the chemical compositions are given in Table 1.

The X-ray diffraction patterns of the studied glasses show no discrete or continuous sharp peaks, but the characteristic halo of the amorphous solids.

The density (ρ) and longitudinal (V_l) and transverse (V_s) ultrasonic velocity of all glasses studied are reported in Table 2. Figure 1 shows the variation of ultrasonic velocity for the glasses as a function of ZnO content (wt. %). From Table 2, it can be seen that the density increases gradually as the weight fraction of ZnO increases from 5 to 40 wt. %. The densities of these glasses are generally high and ranged from 2.60 to 3.31 g/cm^3 . The increase of density is due to the heavier zinc atomic mass and the low zinc coordination number with respect to sodium. The atomic mass and ionic radius of Si atom are 28.09 g and 1.32 Å, respectively, which are less than that of Zn atoms, which has atomic mass 65.37 g and ionic radius 0.74 Å. Therefore, it results in the increasing of densities.

The increase in density is also attributed to the formation of new linkages with the addition of ZnO that contribute to a volume contraction (Behera and Acharya 2008). The densities of SLS glasses are greater than vitreous silica due to the filling of interstices in network (Houerou et al., 2003). The Zn^{2+} tends to occupy interstitial sites within the highly open glass network. Therefore, a greater mass exists in just a slightly increased molar volume, and hence the density increases.

DISCUSSION

Figure 1 shows longitudinal velocity V_l and shear velocity V_s of glasses revealing that the longitudinal and shear velocity decreased with increasing ZnO content. Due to

Table 1. Chemical composition of all glasses in weight (%).

Designation	Composition (wt. %)		SiO ₂	CaO	Na ₂ O	Al ₂ O ₃	K ₂ O	MgO	ZnO	Others
	SLS	ZnO								
S1	95	5	65.7	10.7	11.6	2.7	1.4	2.1	5.2	0.6
S2	90	10	63.1	10.2	11.0	2.4	1.3	1.9	9.6	0.5
S3	80	20	55.4	9.1	10.2	2.1	1.1	1.7	19.7	0.7
S4	70	30	45.9	7.9	8.4	1.8	0.9	1.4	29.6	4.1
S5	60	40	39.2	7.6	7.4	1.4	0.6	1.2	38.9	3.7

Table 2. Measured density (ρ), longitudinal ultrasonic velocity (V_l), and shear ultrasonic velocity (V_s) of glasses.

Sample	ρ (g/cm ³)	V_l (m/s)	V_s (m/s)
S1	2.600	4836	3115
S2	2.679	4667	3048
S3	2.870	4640	2667
S4	3.099	4084	2013
S5	3.313	3541	1704

the atomic radius of atom Zn being larger than atom Si, the addition of Zn²⁺ ions will space out the bonding of SLS glass, therefore, causing the splitting of Si-O-Si bond and hence, the bridging oxygen (BOs) is converted into non bridging oxygen (NBOs). The formation of NBOs will decrease the connectivity of the glass (Marzouk and Gaafar, 2007). Their structure is weakened as a result of increases of NBOs bonds with the increase of composition of ZnO. There are more and more ions being opened up in the network as the addition of Zn²⁺ into the glass interstices. The Zn²⁺ ions occupy the interstices in the network, reducing the unoccupied free volume of the structure. The atoms in glass absorb the energy of travel during wave propagation. The reduction in energy per unit volume causes the amplitude of the wave to decrease with increasing displacement.

The velocity of sound wave becomes slower as the displacement of the atom becomes larger due to the vibration of atoms. The reduction of velocity can be explained according to the damping effect (Kai and Wenrui, 2001). If the structure has a high damping, the vibration is dissipated quickly and cannot travel very fast. Thus, it causes weakening of the glass structure and reduction in the rigidity of the network. Hence, the glass network becomes less favorable for the propagation of ultrasound as evidenced in the decrease in both (longitudinal and shear) waves velocity. From the result obtained, it can be said that the hardness of the glasses decrease as the content of ZnO is increased. Although the glasses become softer, it is denser as the density increase in value.

For an isotropic solid, the stress-strain relation can be written in terms of two constants λ and μ (Lame'

constants). The values of λ and μ are obtained from the longitudinal and shear ultrasonic velocities as follows:

$$V_l = \left[\frac{\lambda + 2\mu}{\rho} \right]^{1/2} \quad (2)$$

$$V_s = \left[\frac{\mu}{\rho} \right]^{1/2} \quad (3)$$

where ρ is the density of the glass.

Figure 2 shows the relation between these constants and weight percent content of ZnO. It is quite clear from these figures that Lamé' constants decreased with increased in ZnO. The decrease in Lamé' constants indicate the decrease in the rigidity of these glasses (Sidkey and Gaafar, 2004) as a consequence of the replacement of SLS by ZnO.

Table 3 presents the experimental values of the elastic moduli; Young's modulus (E), shear modulus (S), bulk modulus (K), micro-hardness (H), which determines the stress required to eliminate the free volume (deformation of the glass network), and Poisson's ratio (σ) as calculated from the following equations:

$$E = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu} \quad (4)$$

$$S = \mu \quad (5)$$

$$K = \lambda + \frac{2}{3}\mu \quad (6)$$

$$H = \frac{(1-2\sigma)E}{6(1+\sigma)} \quad (7)$$

$$\sigma = \frac{\lambda}{2(\lambda + \mu)} \quad (8)$$

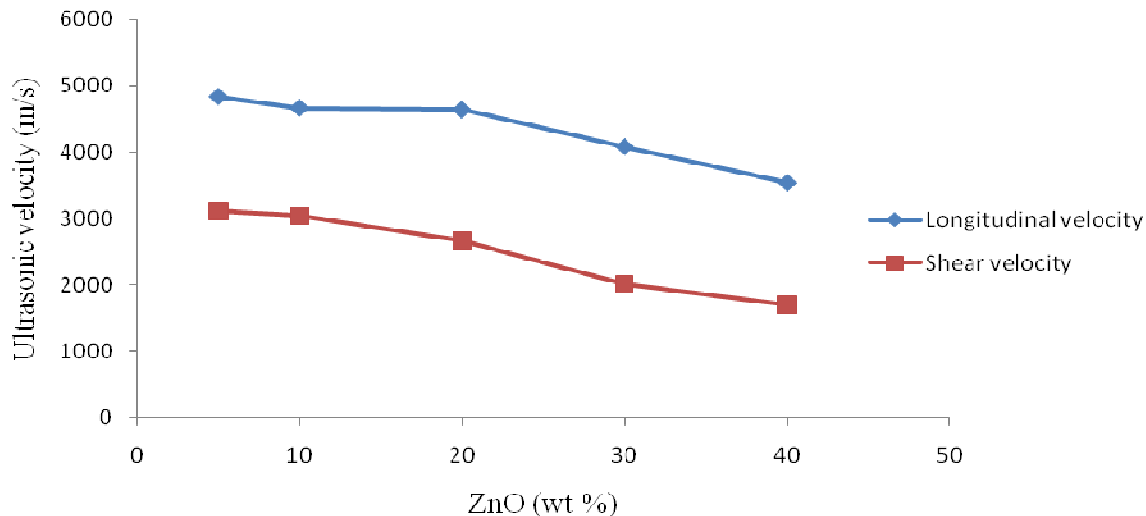


Figure 1. Ultrasonic velocity vs. weight (%) of ZnO in glasses.

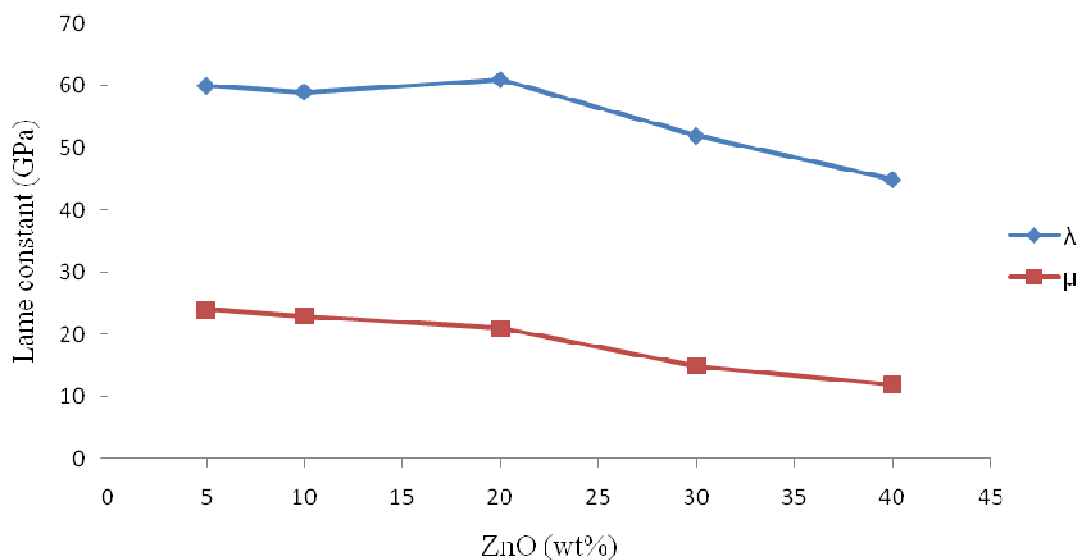


Figure 2. Variation of Lamé's constant (λ and μ) of glasses with ZnO (wt. %) content.

As seen, from Table 3, all the elastic moduli values decreased with increasing ZnO. All the elastic moduli variations with glass composition are similar to the variation of ultrasonic velocity with composition, but the Poisson's ratio is opposite, that is, Poisson's ratio increased with the increasing ZnO concentration. Poisson's ratio is defined as the ratio between lateral and longitudinal strain produced when tensile force is applied. For tensile stresses applied parallel to the chains, the produced longitudinal strain will be the same and is unaffected by the crosslink density, while lateral strain is greatly decreased with the crosslink density. This will lead to a decrease in glass rigidity. Theoretically,

Poisson's ratio for oxide glasses generally lies between 20 to 30 wt. % so that our ZnO-SLS glass is in the range of oxide glass.

Young's modulus represented the stiffness of materials, which is related to the bonding strength between the atoms in a material, hence, the greater the modulus, the stiffer is the material. The modulus is influenced by the dimensionality and connectivity of the structure (Veeranna and Anavekar, 2004). Table 3 shows that Young's modulus of glasses that decreases with the increasing of ZnO could be due to the presence of NBOs in the glass structure. NBOs decrease the connectivity of the glass network. Thus, the structure of the glass

Table 3. Experimental values of Young's modulus (E), shear modulus (S), bulk modulus (K), micro-hardness (H), and Poisson's ratio (σ).

Sample	E (GPa)	S (GPa)	K (GPa)	H (GPa)	σ
S1	57.79	25.22	27.16	5.96	0.14
S2	56.15	24.88	25.16	6.17	0.12
S3	51.17	20.41	34.57	3.35	0.25
S4	33.64	12.55	34.94	1.34	0.33
S5	25.96	9.61	28.71	0.96	0.34

become less rigid and less stiff, which Young's modulus decreases with the increasing of ZnO from 57.80 to 25.96 GPa. McCauley et al. (1981) stated that lowering Young's modulus in SLS glass induced an impacting mass that becomes more slowly decelerated and produces a smaller stress in the glass. Young's modulus also indicates how much the material can withstand strain when a certain amount of stress acted upon it. From the result, it can be seen that the glasses still can tolerate strains due to smaller stress acting on it even though the glasses are less stiff.

Conclusion

Elastic properties studies on $(ZnO)_x(SLS)_{1-x}$ glass system have been investigated to ascertain the effect of Zn^{2+} ion in these glasses. The densities show an increasing trend due an increase in ZnO content and also due to the heavier Zn atoms. An increase in the density of the glasses accompanying the addition of ZnO probably results in a change in crosslink density. The sound velocity v_L and v_s , elastic properties such as Young's modulus, bulk modulus, shear modulus, and longitudinal modulus decreased, while Poisson's ratio increased with ZnO content. The increase in Poisson's ratio suggests that the rigidity of the glasses has decreased.

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