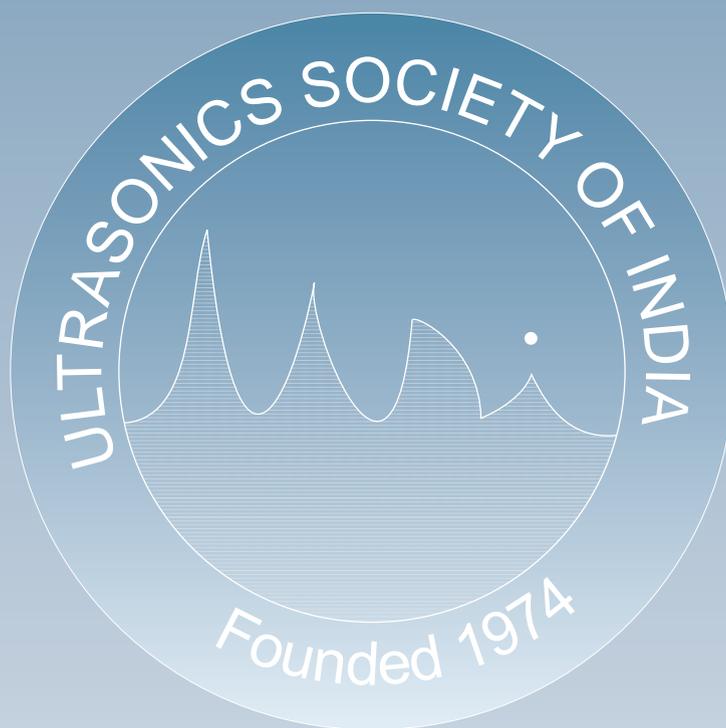


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Journal of Pure and Applied *Ultrasonics*

No. 4 **Volume 36** **October - Dec. 2014**

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Journal of Pure and Applied Ultrasonics

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Ultrasonic attenuation measurement and its applications

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The work has been carried out at CSIR-National Physical Laboratory (NPL) on development of method for measurement of absolute attenuation. The paper reports techniques of measurement and the work carried out at NPL referring to the work carried out by earlier workers on attenuation measurement. The beam diffraction correction has either been ignored or taken from a reference graph by earlier workers. Present method developed involves beam diffraction correction and requires no reference values. The method is useful to evaluate attenuation values at different frequencies within 6dB band width of transducer. No need to use different transducers of different frequencies. In the present method a broad band ultrasonic transducer is used in the immersion testing set up. Ultrasonic spectrum analysis technique, using fast Fourier Transform, is used to evaluate various echo amplitudes of the received signals with respect to corresponding frequencies. Measurements were taken on aluminum and steel alloy sample blocks. Technique uses single longitudinal wave normal beam transducer to measure both longitudinal and transverse wave attenuation in materials employing isotropic rod sample at different frequencies.

Keywords: Ultrasonic attenuation, diffraction correction, L-wave pulse-echo method.

Introduction

Ultrasonic attenuation values are very helpful in the characterization and nondestructive evaluation (NDE) of material. Attenuation has important role in ultrasonic NDE such as in defining the limit of frequencies over which a material may be tested. Higher frequency is preferred for better resolution but it attenuates much faster. An optimum frequency has to be selected keeping in view of the attenuation and resolution. Attenuation in material must be known for sizing the defect using DGS or AAC diagrams and for better estimation of equivalent flat bottom hole (FBH) diameter. Ultrasonic attenuation estimation is an essential feature most commonly used in medical ultrasound for quantitative tissue characterization. Ultrasound attenuation is also an important factor affecting spatial resolution of ultrasound images since the higher ultrasonic frequencies are attenuated more than the lower ones. Knowing the attenuation as a function of frequency and depth would allow estimation of the depth-dependent 1-dimensional point spread function component caused by attenuation. Knowledge of this component can be used to improve the spatial resolution of the ultrasonic image¹.

However, natural properties and loading condition can be related to attenuation. Attenuation often serves as a measurement tool that leads to the formation theories to explain physical or chemical phenomena. Ultrasonic attenuation studies have been made in different type of solids earlier *viz.* dielectric, semiconducting and metallic substances at room temperature as well as at higher temperatures²⁻¹⁶.

Ultrasonic attenuation can be defined in two forms apparent or relative attenuation and absolute or true attenuation^{5,7}. Usually measured attenuation is an apparent attenuation and is measure of energy loss of sound propagation in media. It is reduction of ultrasound beam as a function of distance through the medium, and is well used for comparison of materials. The apparent attenuation needs beam diffraction correction for estimating the absolute attenuation values. Absolute attenuation is the combined effect of absorption and scattering of ultrasonic wave due to the propagation medium. To measure absolute attenuation is very difficult, particularly in solid material, such as common structural metals, at the test frequencies usually applied in nondestructive testing i.e. 1 to 20 MHz. This is because

the overall result observed includes other loss mechanisms such as beam spread, field effects, couplant mismatch, transducer bonding and sample geometry. These factors are difficult to isolate perfectly without the special technique and equipment.

In present work new technique is used to measure absolute attenuation at various frequencies using 5 MHz broad band ultrasonic transducer.

Theoretical Aspects

When ultrasound wave propagates through a material, there are energy losses by two main factors absorption and scattering. The mechanism that removes energy from the ultrasound waves is "attenuation". Scattering is due to inhomogeneity in the material, such as inclusion, pores or grain boundaries containing contaminants. The inhomogeneity present a boundary between two materials of different acoustic impedances. Materials having inhomogeneities not only decrease the return ultrasonic signal because of scattering but also reflect ultrasonic wave in directions other than its original direction of propagation.

Ultrasound is absorbed by the medium if part of the wave energy is converted into other form of energy such as heat^{3,9}. When a sound wave propagates through a material it causes particles to oscillate. Due to friction between atoms part of the energy is converted into heat in the material. Absorption usually increases with frequency. The total attenuation of sound energy can be calculated from the relationship:

$$V = V_0 e^{-\alpha x}$$

Where,

- V_0 = Initial voltage or amplitude in % of FSH
- V = Final voltage or amplitude in % of FSH
- X = Distance travelled by ultrasound between the two echoes
- α = Attenuation coefficient
- FSH = Full screen height

If V_1 and V_2 are output voltages at distances x_1 and x_2 for two different echoes.

$$V_1 = V_0 e^{-\alpha x_1} \quad (1)$$

$$V_2 = V_0 e^{-\alpha x_2} \quad (2)$$

From Eqs. (1) and (2)

$$\log_e \frac{V_2}{V_1} = \alpha(x_2 - x_1)$$

$$\alpha = \frac{\log_e \left(\frac{V_2}{V_1} \right)}{(x_1 - x_2)} \text{ Nepers} \quad (3)$$

When expressed in decibels, the above yields

$$\text{Attenuation } \alpha = \frac{20 \log_{10} \left(\frac{V_2}{V_1} \right)}{(x_1 - x_2)} \text{ decibels (dB)/m}$$

$$(1 \text{ Neper} = 8.686 \text{ dB/m})$$

By measuring echo amplitude in volt or in % of full screen echo height of the two echoes and measuring their corresponding ultrasound travel distance, the attenuation coefficient (α) also known as apparent attenuation can be determined for a particular material at certain frequency.

Although the attenuation measured above is good for comparative study of the two materials. But this, includes other beam losses due to couplant mismatch, beam diffraction, *etc.* and hence is not the true attenuation of the material. The technique mentioned below is giving the measurement of true attenuation which includes the effect of absorption and scattering of ultrasound in material. This technique will prove good for predicting the characteristics of material.

When a normal beam longitudinal wave transducer is placed on the curved surface of a circular cylinder, it makes the line contact between transducer and surface of the cylinder. Due to very small width of the contact line, the divergence angle is large and a number of echoes are observed (Fig. 1). The first echo is from diametrically opposite side or back wall (Path -T1). Second echo results when ray of transducer makes an angle of 30° with the diameter and covers a triangular distance (Path -T2). This equilateral triangle path is traversed by longitudinal wave. The third echo observed is from the longitudinal wave, L, mode converted into shear wave, S, and then back to longitudinal wave which is then received by the transducer (Path -T3). The material in which attenuation is to be evaluated, is taken in the form of a rod with minimum two steps. The rod is machined to have two different diameters for measuring pressures through path T1, T2 and T3.

Let d_1 = diameter of rod at one end

d_2 = diameter of rod at another end

For diameter 'd' of rod path T1, T2, T3 can be given as:

$$T1 = 2d$$

- T2 = 3d cos 30
- T3 = 2d cos θ + d cos θ_t
- R₁ = 1 = Reflection coefficient for incident longitudinal ray for path T1
- R₂ = Reflection coefficient for incident longitudinal ray at an angle 30° and reflected longitudinal ray
- R₃ = Reflection coefficient for incident longitudinal ray at an angle θ and reflected transverse ray at angle θ_t.
- R₄ = Reflection coefficient for incident transverse ray at an angle θ_t and reflected longitudinal ray at angle θ.

Let P₁₁, P₁₂ and P₁₃ be pressures of echoes following the path T1, T2 and T3 respectively from rod end of diameter d₁ and P₂₁, P₂₂ and P₂₃ be pressures of these path from rod end of diameter d₂.

Various pressure equations can be written as follows.

$$P_{11} = A_1 \exp(-2 \alpha_l d_1) \quad (4)$$

where A₁ is the acoustic pressure of ray immediately after its entrance in rod of diameter d₁. The reflection coefficient (R₁) has been taken as 1 for normal incidence at metal/air interface.

$$P_{12} = A_1 \exp(-\alpha_l 3d_1 \cos 30).R_2^2 \quad (5)$$

$$P_{13} = A_1 \exp(-\alpha_l 2d_1 \cos \theta - \alpha_t d_1 \sin^2 \theta)R_3 R_4 \quad (6)$$

Similar equations can be written for diameter d₂

$$P_{21} = A_1 \exp(-2 \alpha_l d_2) \quad (7)$$

$$P_{22} = A_1 \exp(-\alpha_l 3d_2 \cos 30).R_2^2 \quad (8)$$

$$P_{23} = A_1 \exp(-\alpha_l 2d_2 \cos \theta - \alpha_t d_2 \sin^2 \theta)R_3 R_4 \quad (9)$$

θ can be determined by relation,

$$\sin \theta = 1/4 \{- V_l/V_s + [(V_l/V_s)^2 + 8]^{1/2} \}$$

It may be noted that reflection coefficients do not change with change in diameter. The initial pressures, of course, may be different. Using Eqs. (4) - (9) attenuation values for longitudinal wave and transverse wave can be determined by the following relations.

$$\alpha_l = - \frac{1}{0.598.(d_2 - d_1)} \cdot \log_e \frac{P_{11} / P_{12}}{P_{21} / P_{22}} \quad (10)$$

$$\alpha_t = \frac{1}{\sin 2\theta} \left\{ \frac{1}{d_1 - d_2} \log_e \frac{P_{12} / P_{22}}{P_{13} / P_{23}} \alpha_l (2.598 - 2 \cos \theta) \right\} \quad (11)$$

Equations (10) and (11) give the attenuation in terms of known angle θ, diameters d₁ and d₂ and measured ratio of echo amplitudes. Here θ is determined by shear (V_s) and longitudinal (V_l) wave velocities of the materials.

Experimental

Cylindrical samples of aluminium and steel each having two different end diameters are used in the experiment. Block diagram and photograph of the experimental set up is shown in Figs. 1, 2. The broad band transducer of nominal frequency 5MHz was put onto the cylindrical surface of the sample with fixed pressure on the transducer. Couplant thickness has been kept minimum possible such that the echo height obtained is constant after a certain pressure. This was done because the line width of contact is minimised up to 1.5 mm. Ultrasonic flaw detector is used to excite the transducer and to receive the echoes. First three echoes for each end of the rod in UFD were separately sampled and stored

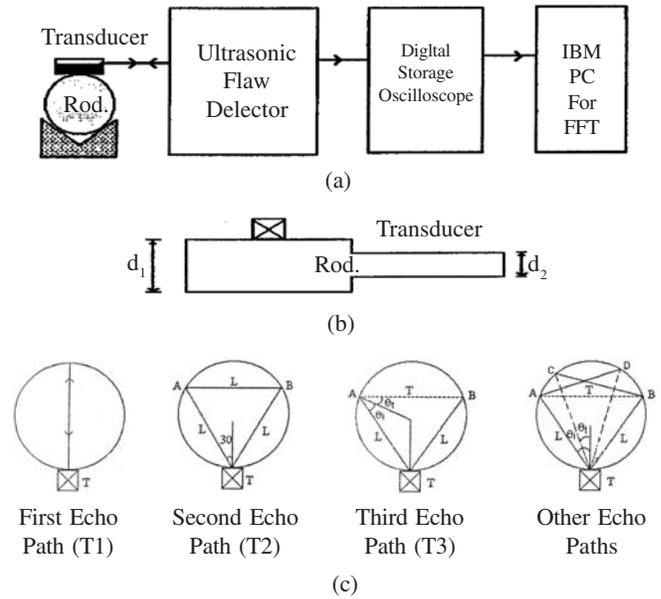


Fig. 1. Block diagram of (a) the experimental setup (b) sample of rod and (c) possible echo paths.



Fig. 2. Photograph of the Experimental Setup.

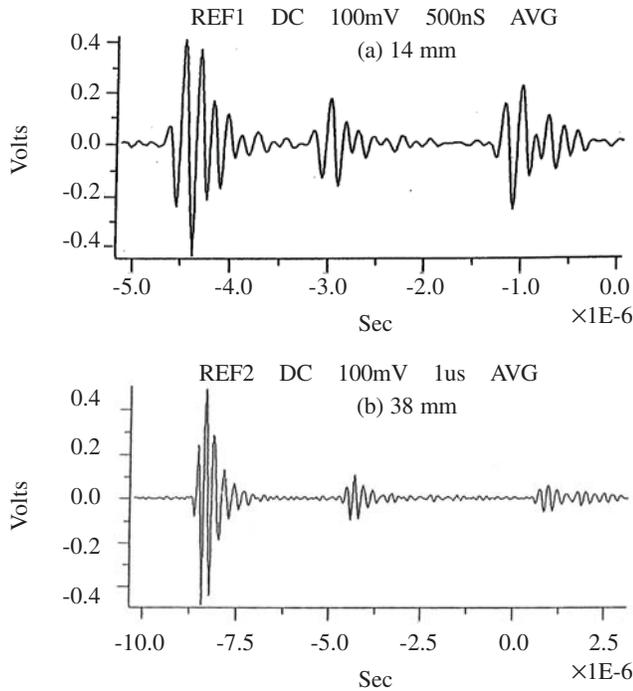


Fig. 3. First three echoes corresponding to path T1, T2 and T3 for Stainless Steel rod of diameter (a) 14 mm and (b) 38 mm

in the digital storage oscilloscope and transferred to PC via GPIB interface. FFT of the stored signal performed to analyse the data by magnitude spectrum using the software. The echoes observed after third echo were not considered in our experiment. Measurements were taken only when all the three echoes were quite steady i.e. pressure between rod and transducer was equal or more than a certain pressure keeping minimum couplant layer. Attenuation for longitudinal and transverse wave was determined according to the Eqs. (10) & (11) respectively.

Results and discussion

Samples of steel and aluminium are taken for rod diameter 14 and 38 mm, 20 and 38 mm, 20 and 30 mm, 45 and 60 mm, 30 and 45 mm. Absolute attenuation values for longitudinal and transverse waves evaluated and are shown in Fig. 4. It is observed that the values for longitudinal wave attenuation obtained between 3.5 MHz and 6 MHz are of the same order of magnitude as the values given in literature for the same material. The values for shear wave attenuation are slightly higher than the longitudinal wave attenuation values, as expected. Method may be explored further by performing measurements and measuring attenuation values after 3 times the near field where the beam diffraction correction is negligible.

Conclusion

Ultrasonic attenuation, apparent or absolute, is very important parameter for characterization of material. Usually apparent is measured for comparison of material with given material or with some standard or reference material. Absolute attenuation is very difficult to measure. New method employs single L-wave normal beam from broad band ultrasonic transducer to measure both longitudinal and shear wave attenuation in isotropic

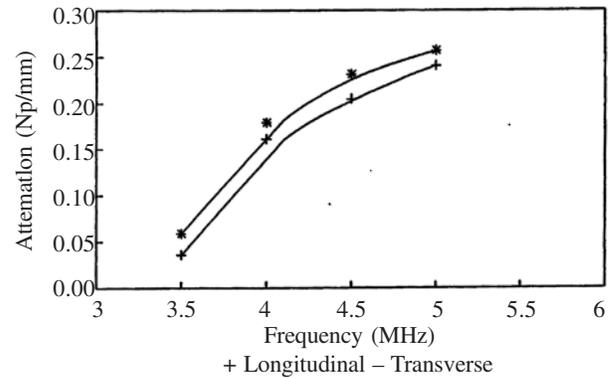


Fig. 4(a). Al alloy rod with end diameter 20 and 38 mm

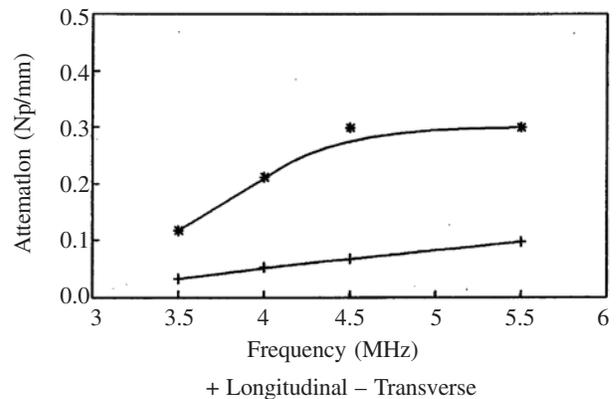


Fig. 4(b). Mild steel rod with end diameters 20 and 30 mm

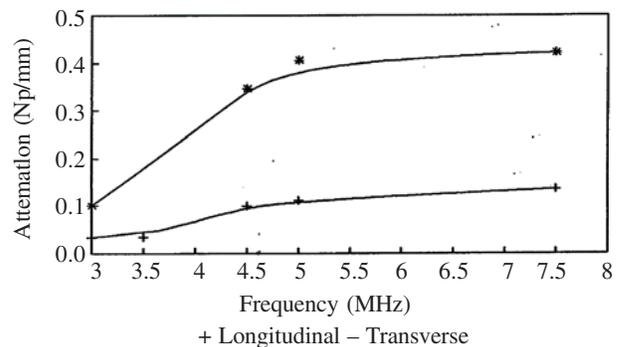


Fig. 4(c). Mild Steel rod with end diameters 45 and 60 mm

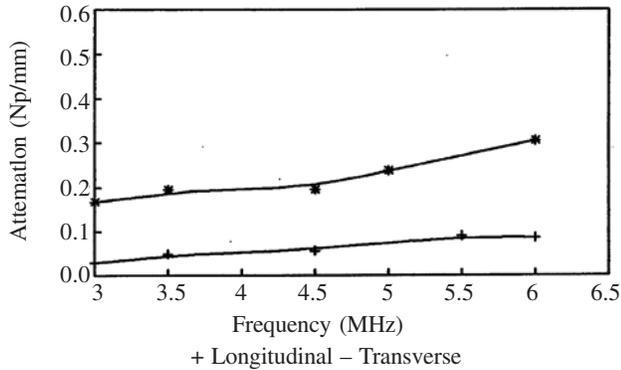


Fig. 4(d). Al alloy rod with end diameter 30 and 45 mm

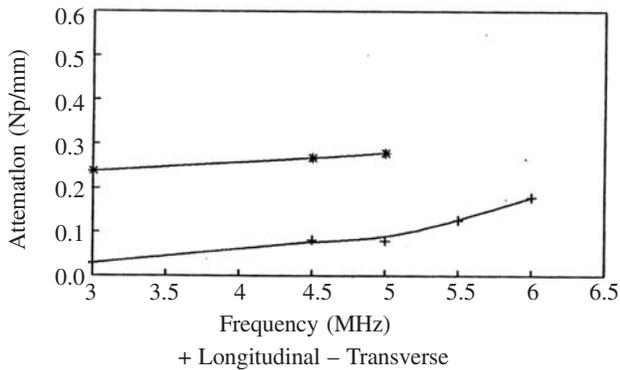


Fig. 4(e). Al alloy rod with end diameters 45 and 60 mm

rod shaped material at different frequencies. First three echoes from rod sample, transducer making line contact, are taken into account for measurement so that the use of diffraction correction and reflection coefficient parameters are eliminated. Ultrasonic attenuation values of Steel and Aluminium alloy is measured with present method for frequency range 3.5 MHz to 6 MHz. The technique requires neither diffraction correction nor reflection or transmission coefficient correction.

Method may be applied for any material by making the sample in rod shape.

Acknowledgement

Author is thankful to Director NPL and Dr. Ashok Kumar for their constant encouragement, support and useful discussion to perform the work.

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Ultrasonic attenuation in NbO at higher temperature phase

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Ultrasonic attenuation for the longitudinal and shear waves due to phonon-phonon interaction and thermoelastic mechanism have been evaluated in NbO along $\langle 100 \rangle$ and $\langle 111 \rangle$ crystallographic directions in the temperature range 100-500K. The second-and third order elastic constants are also evaluated for the evaluation of ultrasonic attenuation and other associated parameters like Grüneisen parameters and acoustic coupling constants. The ultrasonic attenuation due to phonon-phonon interaction is predominant over thermoelastic loss in this material. The obtained results are discussed in correlation with thermoelastic properties of NbO.

Keywords: Elastic constants, ultrasonic velocity, thermal conductivity, ultrasonic attenuation

Introduction

Ultrasonics play an important role in every field of life^{1,2}. Ultrasonic wave measurements in solid structures. Infact, the initial work on ultrasonic attenuation was started with these very species of the crystals. In the cases of silicon and germanium, the results of Lamb *et.al*³, Dobbs *et. al*, and Sykes⁵ are prominent. Oliver⁶ has further enriched this field with his theoretical results for the attenuation of longitudinal waves in many insulating crystals. The ideal crystal for studying the effect of phonon-phonon interactions are the dielectric crystals, unlike metals where a large contribution to the attenuation arises due to electron-phonon interaction *i.e.*, the coupling between sound wave and the free electrons of metals (particularly at low temperature). At frequencies in the GHz region and above, the attenuation in good quality dielectric crystals arises mainly from interaction between the ultrasonic wave and the thermal phonons in the solids. Dielectric materials have many applications throughout the fields electronics, microwave communication, and aerospace industries. The study of ultrasonic attenuation and velocity in dielectric crystals is very useful for studying phonons in two ways. One the low temperature side *i.e.* under the condition $\omega\tau_{th} \gg 1$ (where ω is the angular frequency and τ_{th} the relaxation time) when the sound wave and thermal waves are treated microscopically, the attenuation values provide information about mean free path of phonons constituting the sound wave. On the higher temperature side *i.e.*, when

$\omega\tau_{th} \gg 1$ and the sound wave is treated macroscopically, the attenuation and velocity values are found to be useful have continued to focus on study of dielectric crystals in investigations on the collective properties of thermal phonons. In the present investigation NaCl-type crystal NbO (niobium oxide) is chosen for a number of reasons. These are one of the most structurally perfect crystals and have simple cubic face centered lattice structure. NbO appears as white crystals or powder. Its melting point is 1520°C. Its major application is as a intermediate and in electronics. In packaging it is used in making jars, pails drums, multiply paper bags, bulk bags and fibre board containers. Author has made an attempt on ultrasonic study of NbO along $\langle 100 \rangle$ and $\langle 111 \rangle$ orientations in the temperature range 100-500 K.

Theory

Using Coulomb and Born-Mayer⁷ potential $\Phi(r_0) = A \exp(-r_0/b)$ where r_0 is the nearest neighbour distance and b -Born-Mayer (hardness) parameter; and considering interaction effective to the second nearest neighbour distance, SOECs and TOECs at absolute zero have been obtained following Brügger's⁸ definition of elastic constants. According to the anharmonic theory of lattice dynamics developed by Leibfried⁹ and Mori¹⁰; lattice energy of the crystal changes with temperature, hence adding vibrational energy contribution to the elastic constants at absolute zero, one gets SOECs and TOECs at desired temperatures;

$$C_{UK} = C_{UK}^0 + C_{UK}^{vib} \quad \dots(1)$$

where superscripts 0 and Vib. have used to denote SOECs and TOECs at 0K and vibrational contribution respectively.

In the evaluation of ultrasonic absorption¹¹⁻¹³, SOECs and TOECs play an important role. Also elastic properties of solids are important because they relate to various fundamental solids state phenomena. The thermal relaxation time τ_{th} , the time for the exchange of thermal energy along the direction of propagation may be written as :

$$\tau_{th} = \frac{3K}{C_v V^2 D} \quad \dots(2)$$

K being the thermal conductivity, C_v the specific heat at per unit volume and V_D the Debye average sound velocity.

Experimental results indicate that the relaxation time for longitudinal wave is only about twice that for shear wave. Hence thermal relaxation time

$$\tau_{th} = \tau_{sh} = \frac{1}{2} \tau_{long} \quad \dots(3)$$

The condition $\omega\tau_{th} \ll 1$ is obtained at room temperature. $\tau_{th} \sim 10^{-12}$ s and also $1/\omega \gg \tau_{th}$ means the individual phonon loses its significance and follows statistical model of phonon gas.

Thermoelastic loss is obtained from

$$(\alpha/f^2)_{th} = \frac{4\pi^2 \langle \gamma_i^j \rangle^2 KT}{2\rho V_{long}^5} \quad \dots(4)$$

where ρ is the density and T the temperature in Kelvin scale.

The Akhieser loss (ultrasonic attenuations is given by

$$(\alpha/f^2)_{Akh.} = \frac{4\pi^2 \tau E_o (D/3)}{2\rho V^3} \quad \dots(5)$$

E_o is the thermal energy, D is non-linearity parameter for longitudinal and shear waves given by

$$D = 9 \langle (\gamma_i^j)^2 \rangle - \frac{3 \langle \gamma_i^j \rangle^2 C_v T}{E_o} \quad \dots(6)$$

$\langle \gamma_i^j \rangle$ are the average Grüneisen parameters. V is ultrasonic velocity for longitudinal and shear waves.

Result and discussion

Taking nearest neighbour distance $r_0 = 2.105 \text{ \AA}$ and hardness parameter $b = 0.312 \text{ \AA}$ SOECs and TOECs have been evaluated at the temperature range 100-500K. The calculated values of SOECs and TOECs of NbO are presented in Table 1. SOECs and TOECs have been used to evaluate Grüneisen parameters along $\langle 100 \rangle$ direction for longitudinal wave over 39 pure modes and for shear wave over 18 modes and along $\langle 111 \rangle$ direction for longitudinal wave over 39 pure modes, and for shear wave polarised along $\langle 100 \rangle$ over 18 modes. The values of Grüneisen parameters along with non-linearity coupling constants (D_1 and D_s) are presented in Tables 2-3 along the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions. TOECs are a direct measure of anharmonic nature of crystal lattice giving rise to many important thermal and mechanical properties. In case of NaCl-type crystals C_{111} , C_{112} and C_{116} are negative and C_{123} , C_{456} and C_{144} are positive. The experimental values of SOECs and TOECs of NbO are not available in literature. But the comparison is made with the other NaCl-type dielectrics NaCl, KCl,

Table 1–Second and third order elastic constants (SOEC) and (TOEC) [10^{11} Dyne/cm²] of NbO at temperature range 100-500K.

| Temp. | 100K | 200K | 300K | 400K | 500K |
|-----------|---------|---------|---------|---------|---------|
| SOEC/ | | | | | |
| TOEC | | | | | |
| C_{11} | 7.206 | 7.338 | 7.526 | 7.732 | 7.838 |
| C_{12} | 5.582 | 5.494 | 5.404 | 5.314 | 5.269 |
| C_{44} | 5.701 | 5.716 | 5.736 | 5.756 | 5.567 |
| C_{111} | -90.643 | -96.629 | -97.185 | -97.874 | -98.243 |
| C_{112} | -22.696 | -22.480 | -22.244 | -22.008 | -21.892 |
| C_{123} | 7.961 | 7.616 | 7.274 | 6.933 | 6.762 |
| C_{144} | 8.349 | 8.394 | 8.442 | 8.489 | 8.514 |
| C_{166} | -23.058 | -23.099 | -23.159 | -23.227 | -23.262 |
| C_{456} | 8.297 | 8.297 | 8.297 | 8.297 | 8.297 |

Table 2– Temperature dependent ultrasonic Grüneisen parameter and acoustic coupling constant of NbO along $\langle 100 \rangle$ and $\langle 111 \rangle$ directions.

| Mate- rial | Temp. (K) | $\langle \gamma_i^j \rangle_1$ | $\langle (\gamma_i^j)^2 \rangle_1$ | $\langle (\gamma_i^j)^2 \rangle_s$ | D_1 | D_s |
|-----------------------|--------------|--------------------------------|------------------------------------|------------------------------------|--------|-------|
| $\langle 100 \rangle$ | | | | | | |
| NbO | 100 | 0.681 | 2.836 | 0.557 | 22.458 | 5.013 |
| | 200 | 0.642 | 2.453 | 0.479 | 20.143 | 4.311 |
| | 300 | 0.603 | 2.122 | 0.412 | 17.619 | 3.708 |
| | 400 | 0.569 | 1.866 | 0.362 | 15.569 | 3.258 |
| | 500 | 0.541 | 1.672 | 0.324 | 13.985 | 2.916 |

| <111> | | | | | | |
|-------|-----|--------|-------|-------|--------|--------|
| NbO | 100 | -0.767 | 3.617 | 1.199 | 28.673 | 10.791 |
| | 200 | -0.722 | 3.129 | 1.149 | 25.719 | 10.341 |
| | 300 | -0.677 | 2.698 | 1.100 | 22.418 | 9.900 |
| | 400 | -0.637 | 2.356 | 1.055 | 19.669 | 9.495 |
| | 500 | -0.603 | 2.089 | 1.015 | 17.480 | 9.135 |

KBr and KI¹⁵⁻¹⁷. The order of values of SOECs and TOECs ($\sim 10^{11}$ dyne/cm²) are same with NaCl, KCl, KBr and KI. It is particularly gratifying that the calculated values of D for shear wave polarised along <100> direction are smaller in magnitude to the values of D for compressional wave along <100> and along <111> direction. This material have the same trend of variation with temperature for D_1 and D_s as other NaCl-type crystals like NaCl, KCl, KBr and KI¹⁵⁻¹⁷. The temperature dependent of ultrasonic attenuation due to phonon-phonon interaction is shown in Table 3. It is obvious from the Table 3 that the thermoelastic loss is negligible in comparison to phonon viscosity loss. This is due to lower values of total thermal conductivity in this substance. $(\alpha/f^2)_{th}$ increases with increase in temperature till the temperature 400 K after that it saturates and then it starts decreasing in both directions. The reason behind it is that the values of thermal conductivity (K) increases with increase in temperature and after the temperature 400K it is not going to change with an appreciable value. $(\alpha/f^2)_{Akh.long}$ increases with increase in temperature till 400K after that it saturates along all the directions. This is because of thermal conductivity. $(\alpha/f^2)_{Akh.shear}$ increases linearly with increase in temperature similarly

Table 3– Temperature dependent ultrasonic attenuation (in 10^{-18} Nps²/cm) of NbO along <100> and <111> directions.

| Material | Temp. (K) | $(\alpha/f^2)_{th}$ | $(\alpha/f^2)_{Akh.long}$ | $(\alpha/f^2)_{Akh.shear}$ |
|----------|-----------|---------------------|---------------------------|----------------------------|
| <100> | | | | |
| NbO | 100 | 0.002 | 0.007 | 0.001 |
| | 200 | 0.005 | 0.026 | 0.004 |
| | 300 | 0.006 | 0.048 | 0.008 |
| | 400 | 0.007 | 0.065 | 0.011 |
| | 500 | 0.010 | 0.089 | 0.041 |
| <110> | | | | |
| NbO | 100 | 0.004 | 0.009 | 0.003 |
| | 200 | 0.008 | 0.033 | 0.011 |
| | 300 | 0.010 | 0.062 | 0.022 |
| | 400 | 0.011 | 0.082 | 0.033 |
| | 500 | 0.010 | 0.089 | 0.041 |

as thermal conductivity value changes with temperature. This type of nature is also found in previously investigated materials¹⁸⁻¹⁹.

It is clear that the thermal conductivity is playing very important role for the ultrasonic attenuation. Thus the temperature dependence of ultrasonic attenuation in NbO along different crystallographic orientations can be utilized for the characterization of materials during the processing and after production.

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Ultrasonic treatment in surface modification of sisal fiber

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Ultrasonic wave propagation in solvent mixture is an important technique in fiber engineering technology. Surface bleaching and surface modification of natural fiber can be well maintained when the basic interaction can be studied in natural fiber-reinforced composites with solvent mixture. In the present investigation sisal fiber has been chosen as natural fiber and its surface is treated with solvent mixture of malleic acid with ethanol. The ultrasonic velocities are determined in binary mixture of malleic acid and ethanol with different frequencies (1 MHz, 3 MHz and 5 MHz) at temperature 303 K. The different acoustical properties like intermolecular free length, isentropic compressibility, acoustic impedance and bulk modulus are computed from the ultrasonic velocity and density of the mixture. The variation of these parameters relating to chemical composition of fiber and solvent mixture are discussed in terms of intermolecular interactions.

Keywords: Ultrasonic velocity, binary mixture, intermolecular free length, isentropic compressibility, acoustic impedance, bulk modulus.

Introduction

Interfaces play an important role in the physical and chemical properties of composites^{1,2}. The hydroxyl groups which occur throughout the structure of natural fibres make them hydrophilic, but many polymer matrices are hydrophobic so that sisal-polymer composites have poor interfaces. Also, the hydrophilic sisal fibres will absorb a large amount of water in the composite leading to failure by delamination. Adequate adhesion across the interface can be achieved at desirable levels by better wetting and chemical bonding between fibre and matrix. Maleic acid are important raw materials used in the manufacture of phthalic-type alkyd and unsaturated polyester resins, surface coatings, lubricant additives, plasticizers, copolymers and agricultural chemicals. The present study deals with the ultrasonic study of binary mixture of maleic acid and ethanol which is well used in the surface treatment of sisal fiber for better interlocking and mechanical strength. Ultrasonic speed of sound waves in a medium is fundamentally related to the binding forces between the molecules. The objective of the work is improving

composite-interface adhesion by fiber surface modification using different chemical mixtures which are chemically compatible to each other such that the mixture can improve the surface roughness and hence the interlocking in fibers. The compatibility between chemical mixtures is more distinctible when a sound wave of high intensity is allowed to pass through it. It is observed that if a liquid mixture is subjected to irradiation of high intensity ultrasonic waves, alternate compression and expansion modes takes place which leads to change in some thermodynamic properties of the liquid mixture. As a result of which the variation in speed of ultrasonic waves takes place which affects some of the mechanical properties of the natural fiber. The absorption of ultrasound in polymer composite systems is governed by local modes of motion and cooperative because of the existence of strong intermolecular interaction within the liquid mixture. The manner in which the propagation of the ultrasonic wave is affected by structure of the liquid results in parameters that can lead to the binding between the natural fibers.

Material And Methods

Sisal fibre is a hard fibre extracted from the leaves of the sisal plant (*Agave sisalana*) as in Fig. 1 and were



Fig. 1. Sisal plant.

subjected to dry sun light in open place so as to bring down to lower moisture level to 10-20%. They were chopped to smaller length and further cut in to required size approximately. and stored in suitable bags at dry place The fibres were first dewaxed in 2000 ml solution of benzene and alcohol (methylated spirit), ratio 1:1, by soaking batches of about 200 g of sisal fibres, 300 mm long, in a sealed glass vessel. The fibres were soaked for 24 h, rinsed in alcohol and distilled water. These fibres were then mercerized by soaking in a 0.5 N solution of sodium dioxide, for about 72 h, rinsed in distilled water and dried. The lignocelluloses fibers were obtained by cutting sisal fibers into small pieces of approximately 5cm long 10 mm wide. In the present study the chemicals used are of analytical grade purified by standard procedure³⁻⁶ and redistilled before use. Density was determined with a Pyknometer of 25 cm³ capacity, calibrated with de-ionized double distilled water. Ultrasonic speed was measured by a single crystal variable path ultrasonic interferometer model operating at different frequencies of 1MHz, 3MHz and 5MHz.

The temperature stability is maintained within 0.1K by circulating thermo stated water around the interferometer cell that contains the liquid, with circulating pump. Binary mixtures of maleic acid were prepared with ethanol with varying fraction of maleic acid. The fibers were then extracted for 24 hrs in a soxhlet reflux of binary mixture of maleic acid/ethanol. Subsequently; the discoloured fibers were dried at room temperature. The used fibers are denoted as unmodified.

Experimental Details

The ultrasonic speed of the above liquids and their mixtures were measured using multi-frequency ultrasonic interferometer operating at different frequencies like 1MHz, 3MHz and 5MHz. The accuracy in the measurement of ultrasonic velocity was within $\pm 0.01 \text{ ms}^{-1}$. The working principle used in the measurement of velocity of sound through medium was based on the accurate determination of the wave length of ultrasonic waves of known frequency produced by quartz crystal in the measuring cell⁵⁻⁷. The temperature of the solution was controlled by circulating water at a desired temperature through the jacket of double walled cell within $\pm 0.01 \text{ K}$ using a constant temperature bath and the temperature was monitored with a platinum resistance thermometer with an accuracy of $\pm 0.001 \text{ K}$.

Theory

The experimental measured values of ultrasonic speed and computed values of density are used to compute acoustic parameters such as intermolecular free length (L_f), isentropic compressibility (β), acoustic impedance (Z) and bulk modulus (K) and their excess values. The above acoustic parameters are determined with the help of the following relationship.

$$\text{Isentropic compressibility } (\beta_s) = \frac{1}{\rho C^2} \quad (1)$$

$$\text{Intermolecular free length } (L_f) = k\beta^{1/2} \quad (2)$$

$$\text{Acoustic impedance } (Z) = \rho C \quad (3)$$

$$\text{Bulk modulus } (K) = \rho C^2 \quad (4)$$

and their excess values are calculated as

$$(Y_E) = Y_{mix} - (X_A Y_A + X_B Y_B) \quad (5)$$

where X_A , X_B , Y_A , Y_B and Y_{mix} are mole fraction, isentropic compressibility, inter molecular free length, acoustic impedance and bulk modulus of ethanol, maleic acid and mixture respectively. The constant k is temperature dependent which is given as $[93.875 + (0.375T)] \times 10^{-8}$ as per literature⁸ and T being the absolute temperature.

Result and discussion

Experimentally determined ultrasonic velocity and measured density were used to calculate isentropic compressibility (β), intermolecular free length (L_f), acoustic impedance (Z), bulk modulus (K) and their

excess values using the standard relations with accuracy up to third decimal digit. The variations of these parameters with entire concentration range of maleic acid at different frequencies 1 MHz, 3 MHz and 5 MHz for constant temperature are displayed graphically in Fig. 2 to Fig. 6. The Fig. 2 shows the variation of ultrasonic velocity in binary mixture of ethanol with mole fraction

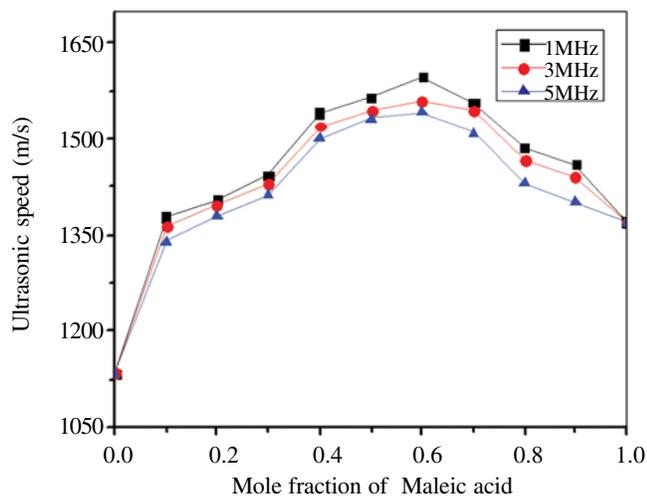


Fig. 2. Ultrasonic speed vs. mole fraction.

of maleic acid which is not linear. It is seen that the ultrasonic velocity increases then decreases with mole fraction of maleic acid depending on the ultrasonic velocity value of second component in the entire sample. The effect of adding a non-polar second component is primarily to disrupt the dipolar interactions of the first component. This may be due to self-association of the solvent molecules and a very weak dipole-induced dipole interaction between the component molecules, which is concentration dependent⁹. Further, in this binary system the interaction becomes more with increase in frequency from 1 MHz-5 MHz for which the ultrasonic velocity is decreases with increase of frequency due to thermal agitation of component molecules. As isentropic compressibility (β) varies inversely with C^2 , the trend in isentropic compressibility with concentration is the reverse of the trend in ultrasonic velocity with concentration. Further, the plots of isentropic compressibility with concentration of maleic acid are non linear suggesting that these system are deviated from the ideal ones. The variations in isentropic compressibility values with concentration indicate that the strength of induced dipole-induced dipole interactions is concentration dependent. The variation of ultrasonic velocity in a solution depends upon the increase or

decrease of intermolecular free length after mixing the components.

According to Eyring and Kincaid⁸ the ultrasonic velocity increases if the intermolecular free length decreases and vice versa.

The plot of excess compressibility and excess intermolecular free length versus mole fraction of acetone in the binary mixture of maleic acid with ethanol are shown in Fig 3 and Fig. 4.

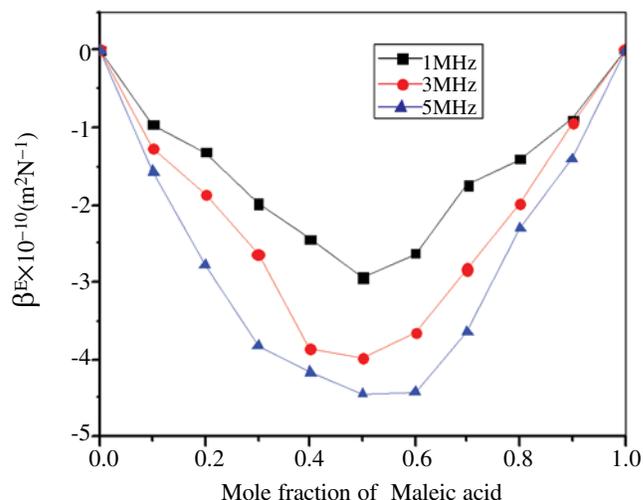


Fig. 3. Excess compressibility vs. mole fraction.

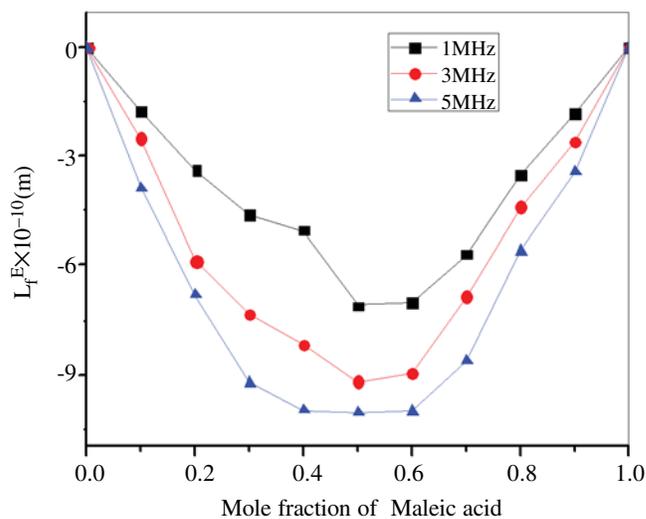


Fig. 4. Intermolecular free length vs. mole fraction.

It is clear from the profiles that the β^E and L_f^E of the mixture increases negatively. It was reported that the negative excess compressibility⁸ is an indication of strong hetro-molecular interactions in the liquid mixtures which are attributed to charge transfer, dipole-induced dipole, dipole-dipole interactions and hydrogen bonding. It is

clear from the profiles that the β^E and L_f^E of the mixture increases negatively for mole fraction of maleic acid. It was reported that the negative excess compressibility⁷ is an indication of strong heteromolecular interactions in the liquid mixtures which are attributed to charge transfer, dipole-induced dipole, dipole-dipole interactions and hydrogen bonding. With increase in frequency, as the polarity is no longer observed, the moment of the molecule is due to intermolecular gap. So the intermolecular free length is more in high frequency range 3MHz and 5MHz for which the molecules are able to move freely. The intermolecular free length sharply decreases up to 50 mole% of maleic acid and then increases in pure maleic acid as the interaction between the maleic acid molecules decreases.

The variation of β^E and L_f^E are also supported by existence of some specific interaction like excess values of acoustic impedance Z^E . The variation of Z^E as shown in Fig. 5 in the system reveals that dispersion is more prominent in the systems but the less magnitude of Z^E suggests that there is possibility of weak dipole-induced

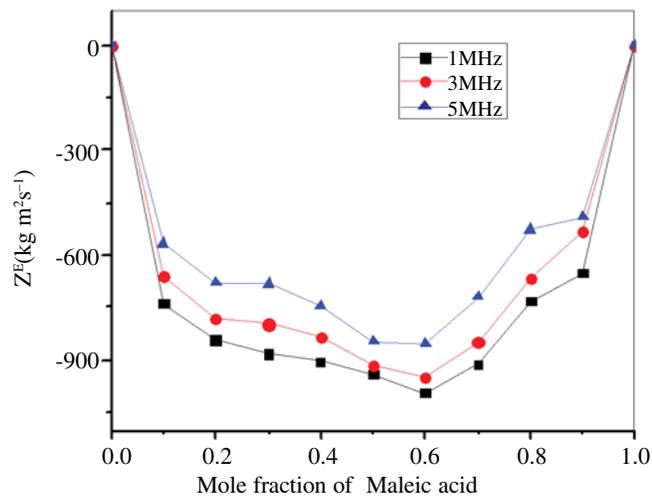


Fig. 5. Acoustic impedance vs. mole fraction.

dipole type of interaction acting between system components. From the nature of the profile it is very clear that in maleic acid and ethanol system the magnitude of Z^E is appreciably more negative suggesting the fact that the dispersion is more prominent and having weak dipole-induced dipole interaction in system. Again considering the effect of frequency it is also informative that with increase of frequency the values of Z^E goes on increasing leads to conformation that the interactions goes on decreasing

From the profiles for excess bulk modulus as shown in Fig. 6 it is informative that with decrease of volume of the mixture pressure increases. As a result of which the intermolecular interaction between the liquid molecules increases and the components of the mixture are tightly bound with each other and also with the chemical composition of the sisal fibers. This results in increase of surface roughness and interlocking in edges of the sisal fibers.

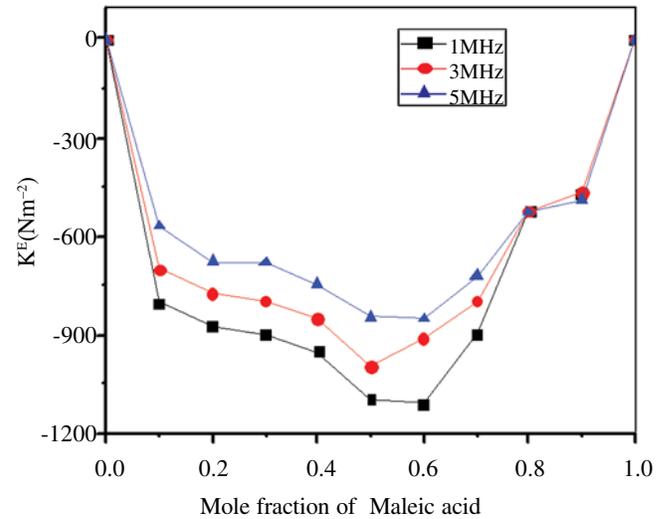


Fig. 6. Bulk modulus vs. mole fraction.

Conclusion

Thus it can be concluded that the interaction of maleic acid I with ethanol is stronger in high frequency as is observed in different acoustic parameters for different frequencies. The dependence of ultrasonic velocity and other derived parameters on composition of the mixture is indicative of the presence of molecular interactions. The sign and magnitude of excess parameter of the mixture and their variations with frequencies reveals that the extent of interaction increases with increase in frequency. When the concentration of ethanol decreases and maleic acid concentration increases there is more than one type interaction like dipole-dipole, dipole-induced dipole, dispersion force may appears in the mixture which basically responsible for such variation. Thus the variation of different acoustic parameters with frequency indicates that the in characterization of different intermolecular interaction frequency plays vital role. Thus it can be concluded that for surface treatment of the sisal fibers the composition of maleic acid and ethanol mixture is more compatible.

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Temperature dependent elastic and ultrasonic properties of silver halide crystals

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The present study deals with the computation of higher order elastic constants and ultrasonic properties of AgCl and AgBr in temperature range 0-300K. The elastic constants are estimated using Coulomb and Born-Mayer potential with two basic parameters *i.e.*, nearest neighbour distance and hardness parameter. The ultrasonic velocity for longitudinal and shear waves along <100>, <110> and <111> orientations for temperature range 100- 300K have been evaluated with second order elastic constant and density of the silver halides. The Debye average velocity, Debye temperature, bulk modulus, Breazeale's non-linearity parameter, Young's modulus and Poisson's ratio are also computed. The fracture/toughness (B/G) ratio is less than 1.75 which shows that the compounds are brittle in nature at room temperature. The materials fulfil the Born criterion of stability. AgCl is stiffer in comparison to AgBr as it has higher values of elastic constants and ultrasonic velocity.

Keywords: Silver halides, elastic properties, ultrasonic properties

Introduction

The ultrasonic non-destructive techniques (NDT) are used for determination of elastic constants, microstructures, discontinuities and mechanical properties of materials¹⁻³ under different physical conditions. The physical properties of materials depend on temperature and pressure. The silver halides compounds are interesting in research because of their unusual properties. Silver halides exhibit rock-salt type structure. There exists experimental and theoretical studies on silver halides in literature. The third and fourth order elastic constants are studied by Shanker and Singh⁴. Endou *et al.*⁵ performed RUS study of elastic constants in silver halides. The analysis of temperature dependent elastic constants of AgCl has been done by Aniya and Sedakuni⁶. Loje and Schuck⁷ studied pressure and temperature derivatives of elastic constants of AgCl and AgBr. Petterson⁸ investigated the thermal conductivity of silver halides. The computational study of AgCl and AgBr has been done by Benmessabih *et al.*⁹. The higher order elastic constants and thermoelastic studies have been made by Shanker and Bhendre¹⁰.

The present work is a detailed study on elastic and ultrasonic properties of AgCl and AgBr using the inter-

ionic potential theory involving nearest neighbour distance and hardness parameter¹¹⁻¹². We investigated the second and third order elastic constants (SOECs and TOECs) for AgCl and AgBr in the temperature range 0-300K. The mechanical properties like bulk modulus, Young's modulus, shear modulus, Poisson's ratio, Breazeale's non linearity parameter and ultrasonic velocities along <100>, <110> and <111> directions are computed and obtained results are compared with available experimental and theoretical results.

Computational Approach

The various steps for theoretical investigation are as follows :

Second and third order elastic constants

The SOECs and TOECs at 0K are calculated using Brugger's definition¹¹ and Coulomb and Born-Mayer potential¹². Since the lattice energy of a single crystal changes with temperature¹²⁻¹⁴ so an addition of vibrational contribution to elastic constants at 0K will provide SOECs and TOECs at a particular temperature.

$$C_{ij} = C_{ij}^0 + C_{ij}^{\text{vib}} \quad \text{and} \quad C_{ijk} = C_{ijk}^0 + C_{ijk}^{\text{vib}} \quad (1)$$

Where superscript 0 has been used to denote SOEC and TOEC at 0K (static elastic constants) and superscript Vib has been used to denote vibrational part of SOEC and TOEC at a particular temperature. The SOECs and TOECs at various temperatures are obtained by the method developed by Mori and Hiki¹³. The second (C_{IJ}) and third (C_{IJK}) order elastic constants of material are defined by following expressions.

$$C_{IJ} = \frac{\partial^2 U}{\partial e_i \partial e_j}; \quad I \text{ or } J = 1, \dots, 6 \quad (2)$$

$$C_{IJK} = \frac{\partial^3 U}{\partial e_i \partial e_j \partial e_k}; \quad I \text{ or } J \text{ or } K = 1, \dots, 6 \quad (3)$$

The elastic energy density is well related to interaction potential between atoms. The potential used to evaluate the SOECs and TOECs is taken as sum of Coulomb and Born-Mayer potentials.

$$\phi(r) = \phi(C) + \phi(B) \quad (4)$$

where $\phi(C)$ is electrostatic/Coulomb potential and $\phi(B)$ is the repulsive/Born-Mayer potential, given as $\phi(C) = \pm(e^2/r_0)$ and $\phi(B) = A \exp(-r_0/b)$. Here e is electronic charge, r is the nearest neighbour distance, b is the hardness parameter and A is the strength parameter.

$$A = -3b \frac{e^2}{r_0} S_3^{(1)} \frac{1}{6 \exp(-\rho_0) + 12\sqrt{2} \exp(-\sqrt{2}r_0)} \quad (5)$$

where $\rho_0 = r_0/b$. The lattice parameter for AgCl and AgBr are 2.775 Å and 2.885 Å¹⁵⁻¹⁶. The hardness parameter¹⁷ is taken as 0.303 Å. The strength of the material is determined by density, Poisson's ratio (ν), Zener's anisotropy (A) and tetragonal moduli (C_2). The relations for these are given in our previous paper¹⁸. The distortion produced due to the propagation of ultrasonic waves characterise the simple harmonic generation of longitudinal waves given by negative ratio of nonlinearity term to the linear term in non linear waves¹⁹.

$$\beta = -(2K_2 + K_3)/K_2 \quad (6)$$

K_2 and K_3 are linear combinations of SOECs and TOECs respectively. The values of K_2 and K_3 are given below along the directions, $\langle 100 \rangle$, $\langle 111 \rangle$, $\langle 110 \rangle$.

| | $\langle 100 \rangle$ | $\langle 111 \rangle$ | $\langle 110 \rangle$ |
|-------|-----------------------|--|---------------------------------------|
| K_2 | C_{11} | $1/3(C_{11} + 2C_{12} + 4C_{44})$ | $1/2(C_{11} + C_{12} + 2C_{44})$ |
| K_3 | C_{111} | $\{1/9(C_{111} + 6C_{112} + 12C_{144} + 24C_{166} + 2C_{123} + 16C_{456})\}$ | $1/4(C_{111} + 3C_{112} + 12C_{166})$ |

Orientation dependence of ultrasonic velocity

The ultrasonic velocities along $\langle 100 \rangle$, $\langle 111 \rangle$, $\langle 110 \rangle$ directions are calculated for longitudinal and shear modes of propagation. The expressions for wave velocities²⁰ are given below:

Along $\langle 100 \rangle$ crystallographic direction;

$$V_L = \sqrt{\frac{C_{11}}{\rho}}; \quad V_{S1} = V_{S2} = \sqrt{\frac{C_{44}}{\rho}} \quad (7)$$

Along $\langle 111 \rangle$ crystallographic direction;

$$\left. \begin{aligned} V_L &= \sqrt{\frac{C_{11} + 2C_{12} + 4C_{44}}{3\rho}}; \\ V_{S1} = V_{S2} &= \sqrt{\frac{C_{11} - C_{12} + C_{44}}{3\rho}} \end{aligned} \right\} \quad (8)$$

Along $\langle 110 \rangle$ crystallographic direction;

$$\left. \begin{aligned} V_L &= \sqrt{\frac{C_{11} + C_{12} + 2C_{44}}{2\rho}}; \\ V_{S1} &= \sqrt{\frac{C_{44}}{\rho}}; \quad V_{S2} = \sqrt{\frac{C_{11} - C_{12}}{\rho}} \end{aligned} \right\} \quad (9)$$

where C_{11} , C_{12} and C_{44} are SOECs and ρ is the density of silver halide single crystal.

The ultrasonic velocities can be worked out using calculated values of SOECs. The Debye average velocity plays a key role to determine the Debye temperature and thermal relaxation time for the material. The expression for Debye average velocity along $\langle 100 \rangle$, $\langle 111 \rangle$, and $\langle 110 \rangle$ directions are

$$\left. \begin{aligned} V_D &= \left[\frac{1}{3} \left\{ \frac{1}{V_L^3} + \frac{2}{V_{S1}^3} \right\} \right]^{-1/3}; \\ &\text{along } \langle 100 \rangle \text{ and } \langle 111 \rangle \text{ direction} \\ &= \left[\frac{1}{3} \left\{ \frac{1}{V_L^3} + \frac{1}{V_{S1}^3} + \frac{1}{V_{S2}^3} \right\} \right]^{-1/3}; \\ &\text{along } \langle 110 \rangle \text{ direction} \end{aligned} \right\} \quad (10)$$

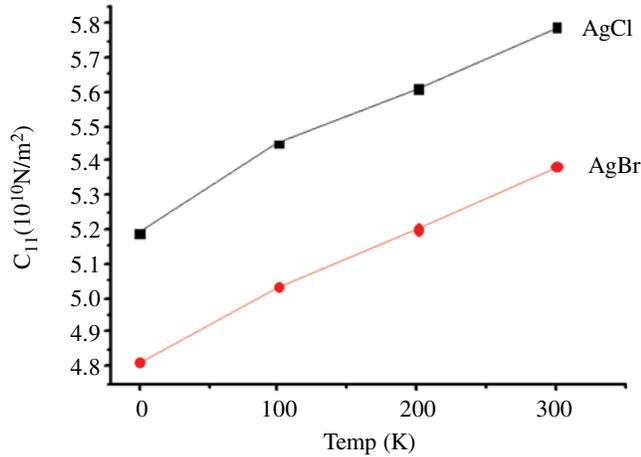
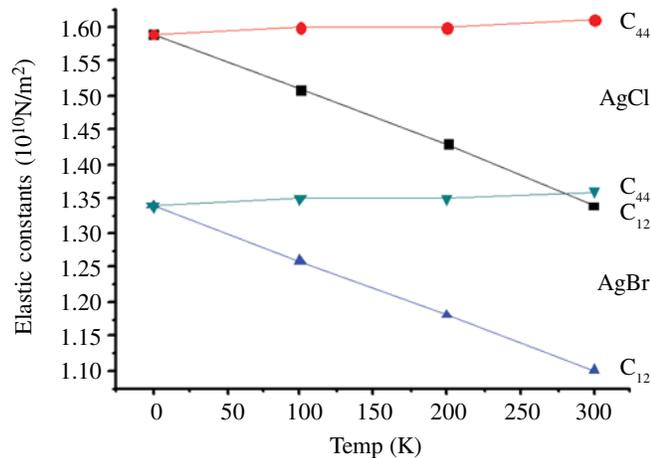
The Debye temperature (θ_D) characterises the excitation of phonons and various lattice thermal phenomena. The expression for Debye temperature is given in literature^{21,22}.

Results and discussion

The SOECs and TOECs are calculated using Eqs (1-4) and are listed in Table 1. It is seen that the values of C_{11} , C_{44} , C_{111} , C_{166} and C_{144} increase with temperature

Table 1–SOECs and TOECs for AgCl and AgBr (in 10^{10} N/m²) for temperature range 0-300K.

| Material | Constants | 0K | 100K | 200K | 300K |
|----------|-----------|--------|--------|--------|--------|
| AgCl | C_{11} | 5.19 | 5.45 | 5.61 | 5.79 |
| | C_{12} | 1.59 | 1.51 | 1.43 | 1.34 |
| | C_{44} | 1.59 | 1.60 | 1.60 | 1.61 |
| | C_{111} | -85.44 | -87.09 | -87.76 | -88.63 |
| | C_{112} | -6.48 | -6.17 | -5.87 | -5.56 |
| | C_{123} | 2.64 | 2.17 | 1.69 | 1.22 |
| | C_{144} | 2.64 | 2.66 | 2.68 | 2.70 |
| | C_{166} | -6.48 | -6.52 | -6.54 | -6.57 |
| | C_{456} | 2.64 | 2.64 | 2.64 | 2.64 |
| AgBr | C_{11} | 4.81 | 5.03 | 5.20 | 5.38 |
| | C_{12} | 1.34 | 1.26 | 1.18 | 1.10 |
| | C_{44} | 1.34 | 1.35 | 1.35 | 1.36 |
| | C_{111} | -81.03 | -82.40 | -83.19 | -84.11 |
| | C_{112} | -5.44 | -5.13 | -4.82 | -4.51 |
| | C_{123} | 2.26 | 1.78 | 1.30 | 0.81 |
| | C_{144} | 2.26 | 2.28 | 2.29 | 2.31 |
| | C_{166} | -5.44 | -5.47 | -5.49 | -5.52 |
| | C_{456} | 2.26 | 2.26 | 2.26 | 2.26 |

Fig. 1. Variation of C_{11} with temperatureFig. 2. Variation of C_{12} and C_{44} with temperature.

and that of C_{12} , C_{112} and C_{123} decrease with temperature while C_{456} remains constant. These variations are shown in Figs.1-2. A similar behaviour is observed in praseodymium monpnictides¹⁸, berkelium monpnictides²¹ and monobismuthides²³. The higher values of elastic constants for AgCl indicate that it is stronger in comparison to AgBr.

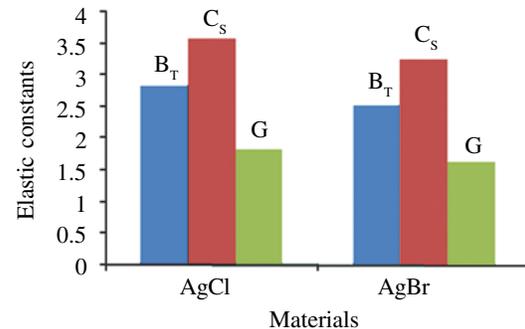
The computed values of bulk modulus (B_T), tetragonal modulus (C_S), C_{44} and θ_D are given in Table 2 at room temperature.

Table 2–Bulk modulus B_T , C_{44} , C_S (in 10^{10} N/m²) and θ_D (in K) at 300K.

| Material | B_T | C_{44} | C_S | θ_D |
|----------|-------|----------|-------|--------------------------------|
| AgCl | 2.82 | 1.61 | 3.57 | $\langle 100 \rangle = 203.8$ |
| | | | | $\langle 111 \rangle = 224.18$ |
| | | | | $\langle 110 \rangle = 235.97$ |
| AgBr | 2.53 | 1.36 | 3.24 | $\langle 100 \rangle = 168.11$ |
| | | | | $\langle 111 \rangle = 191.83$ |
| | | | | $\langle 110 \rangle = 195.95$ |

According to Born criteria²⁴ stability is expressed as:-
 $B_T = (C_{11} + 2C_{12})/3 > 0$, $C_{44} > 0$, $C_S = (C_{11} - C_{12})/2 > 0$

Since all the values are greater than 1, so Born criteria is satisfied. The ratio of bulk modulus to isotropic shear modulus i.e. B/G (fracture/toughness) is less than 1.75 so the materials are brittle. The calculated values of B/G for AgCl and AgBr at 300K are 1.54 and 1.55 respectively. Figure 3 shows the values of B_T , C_S and G for both materials. The nature of bonding forces can be analysed from Poisson's ratio²⁴. For central forces, the value of Poisson's ratio should lie in range $0.25 < \nu < 0.5$. Our values of Poisson's ratio are not in this range. So applied forces are non-central as suggested by Watt and Peselnick²⁵. The value for Poisson's ratio for AgCl is 0.233 and for AgBr is 0.235 in our study. The value of Young's modulus is greater for AgCl (4.51×10^{10} N/m²) than for AgBr (4.03×10^{10} N/m²). Hence AgCl is stiffer than AgBr. It is also seen from Table 1 that the values of

Fig. 3. B_T , C_S and G in unit at room temperature.

C_{111} , C_{112} , and C_{166} are negative whereas the values of C_{123} , C_{144} and C_{456} are positive. C_{111} is highest for both materials at absolute zero value. The value for C_{456} remains constant as the vibrational part vanishes¹³.

Deviation from Cauchy's relation

Cousin²⁶ proposed that Cauchy relation for SOECs and TOECs at 0K are:

$$C_{12}^{\circ} = C_{44}^{\circ}; C_{112}^{\circ} = C_{166}^{\circ}; C_{123}^{\circ} = C_{144}^{\circ} = C_{456}^{\circ} \quad (12)$$

If the atoms of crystal interact through central forces then the Cauchy's relations are satisfied for the material. The temperature dependence of ratios C_{44}/C_{12} and C_{166}/C_{112} are shown in Figs. 4-5. The deviations shown in Figs. 4-5 suggest that the forces become more ionic with rise in temperature. The Cauchy's relation is followed at 0K but deviates at higher temperatures due to vibrational part of energy. The values of C_{144}/C_{456} are same for both materials for all temperatures.

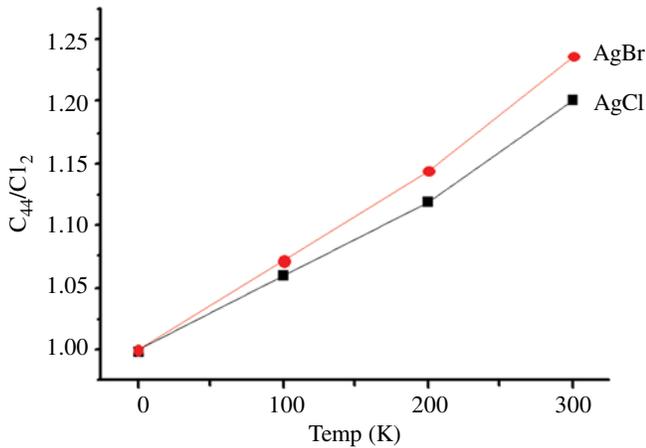


Fig. 4. C_{44}/C_{12} versus temperature.

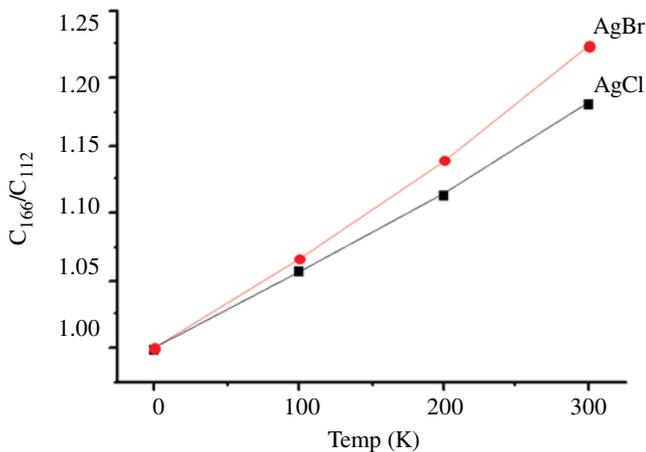


Fig. 5. C_{166}/C_{112} versus temperature.

Ultrasonic velocity, Debye average velocity, Debye temperature and Breazeale's non linearity parameters

The calculated values of ultrasonic velocity, Debye average velocity and Breazeale's non linearity parameter are shown in Table 3. The values of Debye temperature are shown in Table 2 at room temperature.

Table 3. Ultrasonic velocity of silver halide crystals : V_L for longitudinal waves, V_s for shear waves, V_D is Debye average velocity for temperature range 0-300K, β Breazeale's non linearity parameter at 300K.

| Material | Direction | Temp | V_L | V_{S1} | V_{S2} | V_D | β |
|----------|-----------|------|-------|----------|----------|-------|---------|
| AgCl | <100> | 100K | 3.13 | 1.69 | 1.69 | 1.89 | 12.31 |
| | | 200K | 3.17 | 1.70 | 1.70 | 1.90 | |
| | | 300K | 3.22 | 1.70 | 1.70 | 1.90 | |
| | <111> | 100K | 2.98 | 1.82 | 1.82 | 2.01 | |
| | | 200K | 2.98 | 1.86 | 1.86 | 2.05 | |
| | | 300K | 3.0 | 1.90 | 1.90 | 2.09 | |
| | <110> | 100K | 3.01 | 1.69 | 2.66 | 2.09 | |
| | | 200K | 3.03 | 1.70 | 2.74 | 2.18 | |
| | | 300K | 3.05 | 1.70 | 2.83 | 2.20 | |
| AgBr | <100> | 100K | 2.78 | 1.44 | 1.44 | 1.61 | 12.63 |
| | | 200K | 2.83 | 1.45 | 1.45 | 1.61 | |
| | | 300K | 2.88 | 1.45 | 1.45 | 1.63 | |
| | <111> | 100K | 2.58 | 1.62 | 1.62 | 1.78 | |
| | | 200K | 2.58 | 1.66 | 1.66 | 1.82 | |
| | | 300K | 2.59 | 1.70 | 1.70 | 1.86 | |
| | <110> | 100K | 2.63 | 1.44 | 2.41 | 1.87 | |
| | | 200K | 2.65 | 1.44 | 2.49 | 1.88 | |
| | | 300K | 2.66 | 1.45 | 2.57 | 1.90 | |

[Note: all the values of velocities in the units of 10^3 m/s]

Table 3 depicts that the Debye average velocity increase with increase in temperature. It is maximum along <110> and minimum along <100> directions as shown in Fig. 6. The value for ultrasonic velocity for AgCl is greater in comparison to AgBr, so propagation

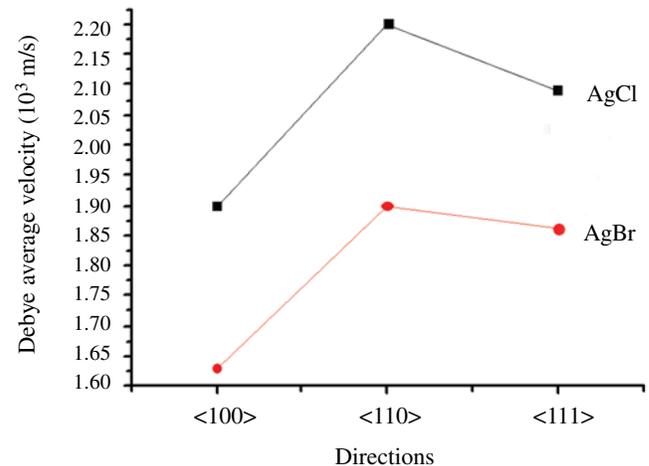


Fig. 6. Debye average velocity at room temperature.

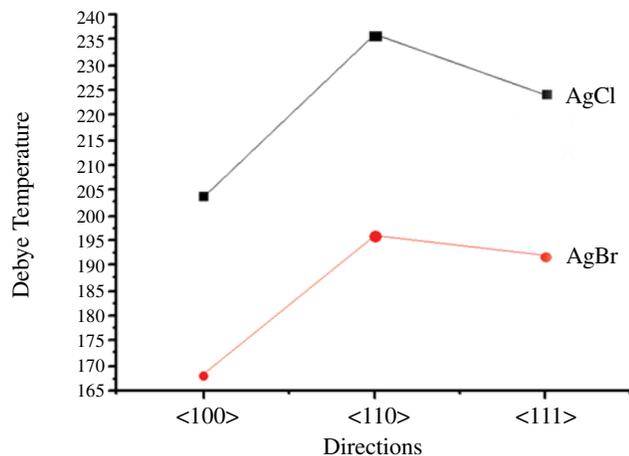


Fig. 7. Debye temperature along different directions.

of sound waves is better in AgCl. The longitudinal wave velocity is highest along $\langle 100 \rangle$ and lowest along $\langle 111 \rangle$ for both materials. The Debye average velocity is highest along $\langle 110 \rangle$ direction and lowest along $\langle 100 \rangle$ direction. The Debye temperature decreases with increase in lattice constant and atomic number as shown in Fig. 7. This type of behaviour is already seen in rare earth mononictides²⁷. The highest values are obtained along $\langle 100 \rangle$ axis and decrease with increase in temperature for both materials while the values remain temperature independent along $\langle 111 \rangle$ direction.

Conclusions

On the basis of discussion of the achieved results, we conclude the following points:

- The Coulomb and Born-Mayer potential has been applied successfully with two basic parameters- lattice parameter and hardness parameter to calculate the higher order elastic constants.
- The SOECs and TOECs are higher for AgCl in comparison to AgBr so the mechanical properties of AgCl are better.
- According to Born, stability criterion is satisfied these materials as $B_T > 0$, $C_S > 0$ and $C_{44} > 0$. So these halides are stable.
- The Cauchy's relations are deviated as we go to higher temperatures. This shows increment in ionic nature of silver halides.
- The fracture/toughness, *i.e.*, B/G values are less than 1.75, so these materials are brittle.
- The ultrasonic velocity is higher for AgCl than for AgBr along all orientations. It means that AgCl will be the most appropriate candidate for wave propagation.

The results obtained in the present work can be used further for calculating ultrasonic Grüneisen parameter thermal conductivity, thermal relaxation time, and ultrasonic attenuation for various applications.

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Epoxy based underwater transducer encapsulation material

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Epoxy materials exhibit a great range of properties (from soft to hard) which leads to a great versatility in application. Epoxy is the material of choice for underwater acoustic window applications as its acoustic impedance can be made to match the acoustic impedance of sea water. Acoustic impedance can be modified over a broad range for epoxy material by changing the resin (prepolymer) to curing agent ratio in the composition. Acoustical and mechanical properties of these epoxy composition have been investigated. Sound velocity and density of materials were measured. Acoustic impedance of the materials were evaluated and compared with the acoustic impedance of sea water. Insertion loss and echo reduction of the materials were measured in the frequency range 15 kHz to 100 kHz. Insertion loss was less than 2 dB and echo reduction was more than 10 dB throughout the frequency range which is suitable for underwater transducer encapsulation material. Mechanical properties like tensile strength, elongation at break and hardness etc. were investigated, which are important for encapsulation materials to withstand hydrostatic or hydrodynamic pressure. Ageing resistance to hot air was also conducted in the present study.

Keywords: Acoustically transparent, acoustic impedance, encapsulation, sound speed, insertion loss, echo reduction and epoxy.

Introduction

Almost all underwater acoustic transducers (projector and hydrophone) are encapsulated in polymeric materials. These coatings protect the underlying sensors & electronics from physical damage and water ingress, while allowing the passage of acoustical energy without significant reflection, loss or distortion¹. It also works as electrical insulator.

Epoxy materials exhibit a great range of properties (from soft to hard) which leads to a great versatility in application. This is mainly due to good adhesive properties, mechanical properties, low expansion coefficients and low viscosity. Epoxy materials can be employed in a typical array as inter-element, passive intra element filler between active transducers, backing material and as acoustic window material². Epoxy is the material of choice for underwater acoustic transmission applications as its acoustic impedance can be made to match the acoustic impedance of sea water. Acoustic impedance can be modified over a broad range for epoxy material by changing the resin (prepolymer) to curing

agent ratio in the composition. At the boundary, there is no reflection of sound waves if the acoustic impedance of the two media is equal³.

Some underwater acoustical applications require a window that is both acoustically transparent and structurally rigid⁴. The paper focuses on the effect of curing agent on acoustic properties of different epoxy composition. Five different types of epoxy composition made with Cresyl glycidyl ether and Triethylene tetramine (TETA) and their acoustical and mechanical properties have been investigated. Care is to be taken while making the epoxy composition such that the epoxy materials housing the sensor elements or transducer are transparent to sound signals in the desired frequency range and have sufficient strength to withstand the hydrostatic/ hydrodynamic pressure exerted on it⁵. The acoustical transparency of epoxy material was studied by measuring the percentage of sound transmitted through and reflected from the sample of material immersed in water. Sound velocity and acoustic impedance of the materials were evaluated and compared

with the acoustic impedance of sea water. Insertion loss and echo reduction of the materials were measured in the frequency range 15 kHz to 100 kHz. Mechanical properties of epoxy materials were studied as per ASTM Standards. Ageing resistance to hot air was conducted for better service life of the materials. Electrical insulation resistance properties of materials checked to avoid short circuit.

Experimental

Material

Epoxy material used in the present study is a two component, room temperature cure system. The component one is a prepolymer of Cresyl glycidyl ether and it is prepared by the reaction between Cresyl and Epichlorohydrin. It is a liquid resin having viscosity of 225 Pa.s. The component two is curing agent or catalyst and it is an aliphatic amine i.e, Triethylene Tetramine (TETA). It is black colour liquid having viscosity of 25 Pa.s. Epoxy Resin / Curing agent is a black, filled epoxy adhesive which, by varying the amount of catalyst used, can adjust the hardness from flexible to rigid. It has an easy mix ratio range and can be cured at room temperature or rapidly at elevated temperatures. It bond well to wide variety of substrate.

Sample preparation

Five different types of epoxy composition made with varied proportion of prepolymer resin and curing agent. The epoxy compositions used in the present study are summarized in Table I. Both prepolymer resin and curing agent taken separately in to a clean container. Both the chemicals were degassed under vacuum. The prepolymer resin and curing agent weighed as per mixing ratio and mixed thoroughly with the help of stirrer. The mixed chemicals were degassed under vacuum. The mixture was immediately poured into a mould of size 300mm × 300mm × 6mm for acoustic measurement and 150mm × 150mm × 2mm for mechanical and other properties measurement. Samples were cured at room temperature for 24 hours.

Table 1 – Composition

| Ingredients | Weight in grams Composition | | | | |
|--------------|-----------------------------|-----|-----|-----|-----|
| | A | B | C | D | E |
| Epoxy Resin | 100 | 100 | 100 | 100 | 100 |
| Curing Agent | 50 | 75 | 100 | 125 | 150 |

Acoustical Properties

Sound Velocity

The velocity of sound is the distance traveled during unit time by a sound wave propagating through an elastic medium. Ultrasonic Thickness Gauge (Model 25HP Plus of OLYMPUS, USA make) was used to measure the sound velocity of materials. Ultrasonic non-destructive testing introduces high frequency sound waves into a epoxy sheet or test sample to obtain information about the object without altering or damaging the material. In this instrument, the time of flight or the amount of time for the sound wave to travel through the sample sheet is measured. Based on thickness of material as input data and time of flight data, the sound velocity is calculated directly by the instrument as follows⁶.

$$T = ct_s/2 \quad (1)$$

where, T = Thickness of material, t_s = Time of flight and c = Sound velocity of material

Acoustic Impedance

The acoustic impedance is a measure of the acoustic behavior of a material. It is the opposition to displacement of its particles by sound waves⁶. Acoustic impedance (Z) of a material is defined as the product of its density (ρ) and sound velocity (c).

$$Z = \rho c \quad (2)$$

where, Z = acoustic impedance, ρ = density of material and c = sound velocity of material

It is important to determine the transmission and reflection of sound waves at the boundary of two materials having different impedances. The boundary between two materials of different acoustic impedances is called acoustic interface. When sound strikes an acoustic interface at normal incidence, some amount of sound energy is reflected and some amount of sound energy is transmitted across the boundary⁶. But at the boundary, there is maximum transmission of sound energy with minimum reflection of sound waves if the acoustic impedance of the two media is equal.

Acoustic impedances of the materials were calculated and matched with acoustic impedance of sea water (1.55 M-Rayls at 20°C). Acoustic Impedance of sea water is calculated as :

$$\begin{aligned} Z &= \rho c = 1030 \text{ kg.m}^{-3} \times 1500 \text{ m.s}^{-1} \\ &= 1.55 \times 10^6 \text{ kg.m}^{-2}.\text{s}^{-1} \\ &= 1.55 \text{ M-Rayls} \end{aligned} \quad (3)$$

Insertion Loss and Echo Reduction

For acoustical transparency measurements, a sheet of size 300 mm × 300 mm × 6mm was made by open casting. The epoxy sheet was tested in an acoustic tank by panel method. Standard transducers (projector and hydrophone) ITC-1042 were used for acoustic measurement. A high frequency pulse of short duration was applied to a standard transducer (projector), that sends out a beam of sound waves into the liquid (water) and picked up by a standard hydrophone (receiver) placed in the acoustic path. The specimen (epoxy sheet) was introduced into the sound path and from the relative amplitudes measured on the oscilloscope before and after introduction of the sample between the transmitter and receiver, the insertion loss and echo reduction are calculated. Measurements are carried out in the frequency range of 15 kHz to 100 kHz. The schematic view of the experimental set-up for measurement of insertion loss and echo reduction is shown in Fig. 1.

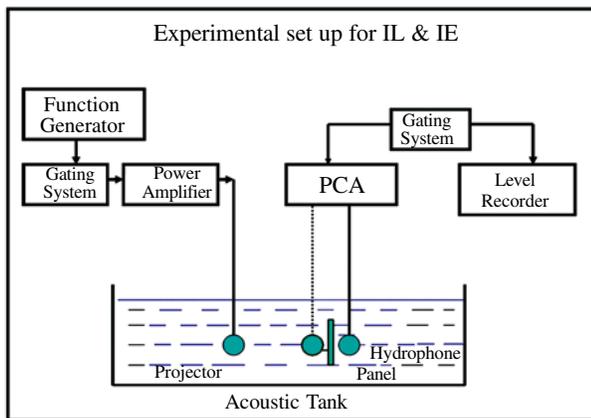


Fig. 1. Schematic view of the experimental set up for measurement of IL and ER of material.

Insertion loss measurement:

Sample sheet was positioned inside the water at a depth of 2 meter from the top. Both Projector and Hydrophone were also positioned inside water at 2 m depth. Standard hydrophone is positioned just behind the sample to receive the transmitted signal. The projector transmits the sound waves and the transmitted sound waves through the test sample were received by the standard hydrophone. Then the test sample was removed from the acoustic path and the sound waves transmitted by projector were measured by the hydrophone. This is the direct or incident sound pressure. Insertion loss is calculated as follows;

$$\text{Insertion Loss, } dB = 20 \log \left(\frac{\text{Incident sound pressure/}}{\text{Transmitted sound pressure}} \right) \tag{4}$$

Echo reduction measurement:

It is a measure of how much incident sound pressure is reduced after reflection. Here the hydrophone is placed in front of the test sample. The projector transmits the sound waves and the reflected sound waves from the test sample were measured by the hydrophone. Echo reduction is calculated as follows;

$$\text{Echo Reduction, } dB = 20 \log \left(\frac{\text{Incident sound pressure/}}{\text{Reflected sound pressure}} \right) \tag{5}$$

Mechanical properties

The tensile properties of these materials were carried out in a Universal Testing machine (Hungta, Taiwan) according to ASTM D 412 a test method using dumb-bell shaped specimen at a cross-head speed of 500 mm/min at room temperature (25±2°C). Hardness was measured as per ASTM D-2240 standard with the help of Universal Hardness tester (Bareiss, Germany).

Accelerated Ageing (Hot air ageing)

Materials resistance to hot air was studied as per ASTM D-573 standard. Test samples were kept in a hot air oven at reference temperature. After different time intervals, samples were removed from oven and their changes in properties like tensile strength, elongation at break and hardness were measured.

Results and Discussion

Acoustical Properties

Sound Velocity and Acoustic Impedance

Initially sound velocity and density of materials were measured. Then acoustic impedance of materials was calculated by multiplying sound velocity and density data. All the values are shown in the Figs.2-3 respectively.

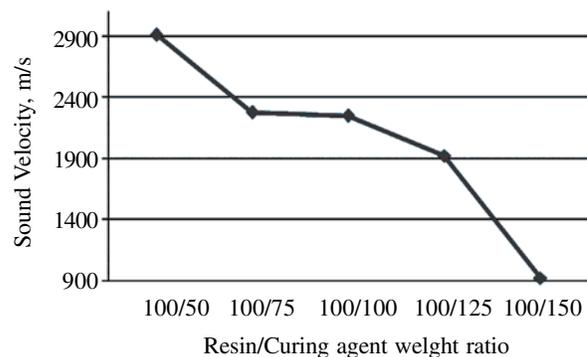


Fig. 2–Effect of Curing agent on Sound velocity.

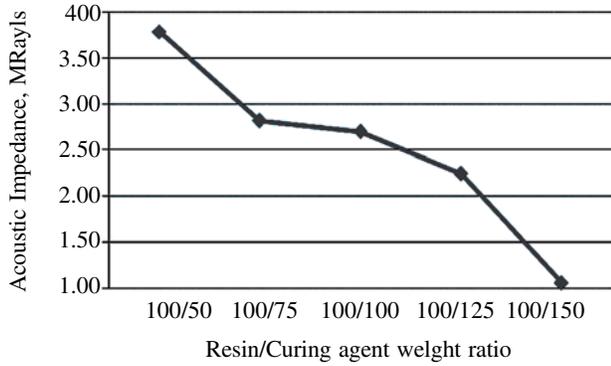


Fig. 3. Effect of Curing agent on Acoustic impedance.

Sound velocity of material decreases with the increase of amount of curing agent (catalyst-15) per 100 parts of resin i.e, curing agent increases from 50 to 150 parts per 100 parts of resin. This is due to as the curing agent increases, the chain length increases by chain extension reaction. This gives more flexibility to the material with reduced modulus. Modulus of material is directly proportional to the sound velocity of material i.e, sound travels faster through media with higher modulus of elasticity and vice-versa.

Insertion Loss & Echo Reduction

Insertion loss and Echo reduction were measured for all the five materials in the frequency range of 15 kHz to 100 kHz at room temperature. Figures. 4-5 show the effect of increase in amount of curing agent (catalyst-15) per 100 parts of resin on insertion loss and echo reduction of the materials respectively.

Insertion loss values for Composition-B, C and D (i.e, resin to curing agent weight ratio 100/75, 100/100 and 100/125) are less than 2 dB throughout the frequency

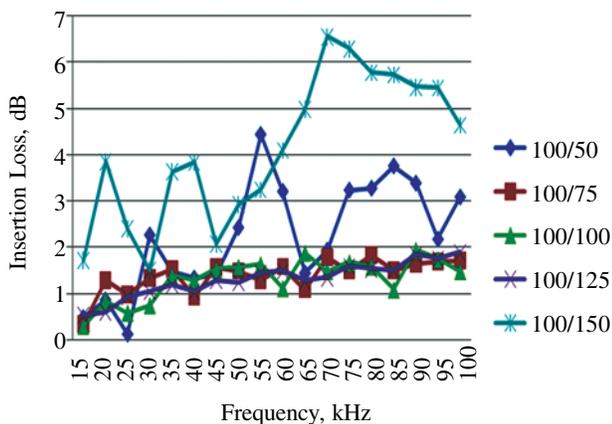


Fig. 4. Effect of Curing agent on Insertion loss.

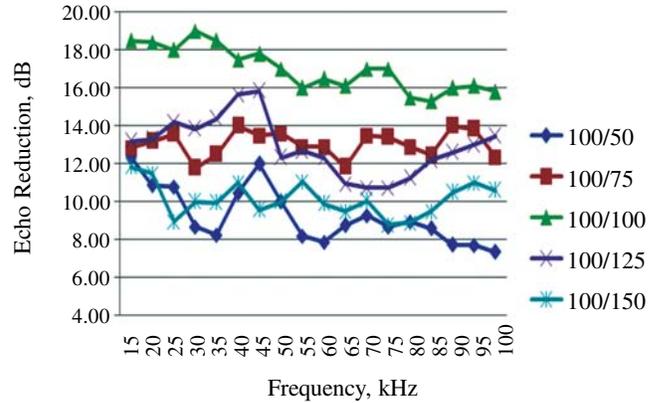


Fig. 5. Effect of Curing agent on Echo Reduction.

range of 15 kHz to 100 kHz, which is suitable for acoustically transparent materials. The insertion loss values for Composition-A (i.e, resin/curing :100/50) vary from 0.13 to 4.44 dB in the frequency range of 15 kHz to 100 kHz. This may be due to the higher acoustic impedance value of composition-A as compared to acoustic impedance of sea water. The insertion loss values for Composition-E (i.e, resin/curing :100/150) vary from 1.51 to 6.56 dB in the frequency range of 15 kHz to 100 kHz. This may be due to the lower acoustic impedance value of composition-A as compared to acoustic impedance of sea water.

Echo reduction values for Composition-B, C and D (i.e, resin to curing agent weight ratio 100/75, 100/100 and 100/125) are more than 10 dB throughout the frequency range of 15 kHz to 100 kHz, which is suitable for acoustically transparent materials. The Echo reduction values for Composition-A (i.e, resin/curing :100/50) vary from 7.36 to 12.39 dB in the frequency range of 15 kHz to 100 kHz. This may be due to the higher acoustic impedance value of composition-A as compared to acoustic impedance of sea water. The Echo reduction values for Composition-E (i.e, resin/curing :100/150) vary from 8.80 to 11.85 dB in the frequency range of 15 kHz to 100 kHz. This may be due to the lower acoustic impedance value of composition-A as compared to acoustic impedance of sea water.

Mechanical properties

Tensile strength, elongation at break and hardness of five composition are shown below in the Table 2. Hardness and tensile strength of material decreases with the increase of amount of curing agent (catalyst-15) per 100 parts of resin i.e, curing agent increases from 50 to 150 parts per 100 parts of resin. This is due to, as the

Table 2 – Mechanical Properties

| Properties | Composition | | | | |
|------------------------|-------------|------|-------|------|------|
| | A | B | C | D | E |
| Hardness, Shore-A/D | 60 D | 40D | 70A | 50A | 33A |
| Tensile Strength, MPa | 15.85 | 14.6 | 10.36 | 3.80 | 2.25 |
| Elongation at Break, % | 4 | 14 | 65 | 83 | 145 |

curing agent increases, the percentage of hard block (*i.e.* weight percentage of resin) decreases in the composition which leads to decrease in hardness and tensile strength.

Accelerated Ageing (Hot air ageing)

Test samples were kept in a hot air oven at 70°C temperature for 7 days. Their change in properties like tensile strength, elongation at break and hardness were measured. Results are shown in the Table 3. Change in properties like tensile strength, elongation at break and hardness are satisfactory. Hence from hot air ageing value, it is clear that, these materials will resist the deterioration of physical properties with time caused by oxidative and thermal ageing.

Electrical properties

Insulation Resistance of all the five materials was measured with 500 Volt Megger. The values are more than 500 MΩ which is suitable for underwater transducer encapsulation applications.

Conclusions

On the basis of above discussion following points are concluded as :

- Five different epoxy compositions have been made. (*i.e.* resin to curing agent weight ratio 100/50, 100/75, 100/100, 100/125 and 100/150)
- Acoustical, mechanical, electrical and ageing properties of these materials have been investigated.
- Acoustic impedance of all the materials was calculated from sound velocity and density of materials. Acoustic impedance vary from 1.06×10^6 to 3.79×10^6 $\text{kg.m}^{-2}.\text{s}^{-1}$ which is close to the acoustic impedance of sea water (1.55×10^6 $\text{kg.m}^{-2}.\text{s}^{-1}$).
- Insertion loss and echo reduction of all the materials were measured in the frequency range of 15 kHz to 100 kHz. For composition-B, C and D (*i.e.* resin to curing agent weight ratio 100/75, 100/100 and 100/125), the insertion loss values were less than 2dB

Table 3 – Hot Air Ageing Properties

| Properties | Composition | | | | |
|----------------------------------|-------------|-------|------|-------|-------|
| | A | B | C | D | E |
| Change in Hardness, Shore-A/D | +4 | +3 | +4 | +5 | +3 |
| Change in Tensile Strength, % | -5.05 | -4.7 | -3.5 | -7.8 | -8.0 |
| Change in Elongation at Break, % | -1.5 | -4.65 | -3.6 | -8.43 | -10.3 |

and echo reduction values were more than 10dB throughout the frequency range, which is suitable for underwater transducer encapsulation material. So this composition-B, C and D can be used for encapsulation of underwater transducers.

- For composition-A (100/50), though the properties like mechanical, electrical and ageing properties are good but both insertion loss and echo reduction values are poor. Similarly, for composition-E (100/150), both acoustic and mechanical properties are poor. So these two compositions are not suitable for underwater electro-acoustic transducer encapsulation applications.

Acknowledgments

The authors are thankful to Shri C.D. Malleswar, Scientist-G, Director, NSTL for encouraging during the course of work and permitting us to submit the paper. Authors would like to express sincere thanks to Shri VVS Bhaskara Raju, Scientist-F, Head Rubber Technology division and Dr K. Trinath, Scientist-G, Head Sensor division for their encouragement during the course of work. The author is also grateful to Shri Ch.S.R.K. Sharma, Scientist-D, Shri I.R. Abisekaraj, Scientist-D, Shri M. Prasad and Shri NVN. Rao, for their cooperation and assistance during the course of work.

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Ultrasonic study of binary solutions of triethyl amine with alcohols

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Triethyl amine as well as methanol and ethanol are important aliphatic organic amino compound, which draw their importance as excellent solvents. The densities(ρ) and ultrasonic velocities(u) of binary mixtures of triethyl amine with methanol and ethanol have been determined experimentally at 298.15K, 303.15K and 308.15K respectively. Isentropic compressibility, intermolecular free length, molar volume, available volume and free volume have been computed utilizing these experimental data. The nonlinear variation of these parameters shows the presence of interaction and their excess values is indicative of interaction between the components molecules in both systems.

Keywords: Ultrasonic velocity, binary mixtures of triethylamine with alcohols, compressibility, molecular interaction.

Introduction

The compositional dependence of thermodynamic properties has proved to be very useful tool in understanding the nature and extent of molecular aggregation resulting from inter molecular interaction between components molecules¹⁻⁴. The acoustic and thermodynamic study is a very powerful means of characterizing the various aspects of physicochemical behavior of liquid mixtures and interaction between molecules. The mixing volume effect is significant phenomenon in many practical applications mainly in paints, varnishes, printing ink industries and bio-medical where volume effects are involved⁵.

Present study of binary mixture of triethylamine and alcohols is extension of our previous work⁶. In order to have a clear understanding of intermolecular interaction between the component molecules, densities, ultrasonic velocities of at three different temperatures over the entire composition range is being reported here. The experimental values of densities and ultrasonic velocities have been used for computation of isentropic compressibility's, inter molecular free length volumes, available volumes and free volumes. These parameters have been found to be sensitive to the interactions between component molecules, which enables use to have a better understanding of behaviour of liquid

mixture.

Experimental methods

All the chemicals namely triethylamine (Pfizer), methanol (BDH AR) and ethanol (BCPW), used in present study were further purified using standard procedures⁷. The ultrasonic velocity was measured with an variable path ultrasonic interferometer⁸ at 2 MHz with an accuracy of $\pm 0.2 \text{ ms}^{-1}$. The temperature was controlled by a thermostat with an electronic relay controlling the flow of water with an accuracy of $\pm 0.01^\circ\text{C}$. The density was measured with a double walled pycnometer and single pan electrical balance with accuracy of the results $\pm 0.01 \text{ g/ml}^{-1}$. Double distilled water and benzene were used for the calibration of pycnometer. The reliability of the experimental data may be ascertained by comparing the densities of pure organic liquids as obtained in present study with their values as per literature⁹ as presented in Table 1 which are in close agreement with each other.

Theory

According to Eyring et al. free volume V_f can be calculated from the velocity of sound in the liquid medium (u_l) and that in the vapour Phase (u_g) by the

Table 1–Comparison of experimental values of density and ultrasonic velocity with literature⁹ Values of pure component liquids at 303.15K

| Component liquids | Density (ρ) x 10 ⁻³ (g ml ⁻¹) | | Viscosity (η) x 10 ³ (cP) | |
|-------------------|---|-------------|---|-------------|
| | Experi-mental | Litera-ture | Experi-mental | Litera-ture |
| Triethylamine | 0.719 | 0.719 | 0.323 | 0.323 |
| Methanol | 0.782 | 0.782 | 0.510 | 0.510 |
| Ethanol | 0.781 | 0.781 | 1.003 | 1.003 |

relation given below, V being the molar volume.

$$V_f = V \left(\frac{u_g}{u_l} \right)^3 \quad \dots(1)$$

This equation has been used to calculate the free volume in the above binary mixtures. The value of u_g for each component of mixture was obtained from the relation obtained by combining the well known Laplace's equation with that of Berthelot's equation of state.

$$u_g = \left(\frac{C_p}{C_v} \times \frac{RT}{M} \left\{ 1 + \frac{9}{128} \times \frac{PT_c}{P_c T} \left(1 - 6 \frac{T_c^2}{T^2} \right) \right\} \right)^{1/2} \quad \dots(2)$$

Where M is the molecular weight, P is the pressure, T is the temperature in absolute degree, T_c and P_c are the critical temperature and critical pressure respectively, C_p and C_v are the two specific heats and R is the gas constant. C_p and C_v in the vapour phase were obtained by the method of Dobratz. For the calculation of V_f The value of v_g have been computed according to equation (1) assuming the additivity of u_g in the case of mixtures.

The available volume (V_a) was calculated from the following expression obtained by combining the equations of Jacobson and Schaff.

$$V_a = V \left(1 - \frac{u_l}{u_\infty} \right) \quad \dots(3)$$

Where V is the molar volume, at u_l is the ultrasonic velocity in the liquid and $u_\infty = 1600 \text{ ms}^{-1}$.

The intermolecular free length (L_f), that is, the distance covered by a sound wave between the surfaces of the two molecules is given by the equation.

$$L_f = K\beta_s^{1/2} \quad \dots(4)$$

Where K is the Temperature dependent constant and β_s is the isentropic compressibility which is given by relation $\beta_s = u^2 \rho^{-1}$, where ρ is the density of liquid.

The excess value of A^E of these thermodynamic parameters have been obtained by subtracting the ideal value from the experimental value

$$A^E = (A_{\text{exp}}) - X_1 A_1 + X_2 A_2 \quad \dots\dots\dots (5)$$

Where A represents the parameter such as intermolecular free length, molar volume, available volume and free volume, and X_1 and X_2 are the mole fractions of components whose parameters are A_1 and A_2 respectively.

Results and Discussion

The results of the measurements of ultrasonic velocity and density at 298.15K, 303.15K, and 308.15K are given in Tables 2 and 3. A perusal of these data demonstrate the trend of change of ultrasonic velocity and density with the change in composition to binary mixtures as well as with temperature. Deviation from the linearity was found in both binary mixtures at all three temperatures, which demonstrates the presence of molecular interaction between unlike molecules.

The results presented in Tables 2 and 3, show non linear behaviour of isentropic compressibility, intermolecular free length, molar volume, available volume and free volume which is further substantiated by their excess values (Tables 4 and 5). All three organic compounds, namely triethylamine, methanol and ethanol are a polar organic compounds having dipole moments 0.66D, 1.70D and 1.69D respectively. Normally more the dipole moment, stronger is the intermolecular attraction, which results in decreasing of free space between molecules and increase in the ultrasonic velocity. Similar results have been also reported by Reddy et al¹⁰ in case of solutions of ethyl acetate and cresols.

It is evident from Tables 4 and 5 for the system I and system II that the excess isentropic compressibility is negative over the entire range of composition and at all three temperatures. More over it's negative value has increased with increase in temperature. These values are indications of stronger molecular interaction in the system I as compared to the system II.

The values of excess free length (L_f^E), are negative over the entire range of composition in system I as well as in system II at each temperature of study as evident from Tables 4 and 5. Table 4 shows an decrease in L_f^E with the increase in concentration of triethylamine and a minima occurs at about 0.3029 mole fraction of triethylamine. Table 5 shows an increase in L_f^E with the increase in concentration of triethylamine and occurrence of a maxima at about 0.2963 mole fraction of triethylamine. The structural changes are responsible to affect the variation of intermolecular free length which

Table 2–Values of density (ρ),ultrasonic velocity(u),isentropic compressibility(β_s),intermolecular free length(L_f), molar volume (V), available volume (V_a) and free volume (V_f) properties for binary liquid mixtures of Triethylamine and methanol.

| X_1 | ρ (g ml ⁻¹) | u (ms ⁻¹) | $\beta_s \times 10^{12}$ (cm ² dyne ⁻¹) | $L_f \times 10^8$ (cm) | $V \times 10^6$ (ml mol ⁻¹) | $V_a \times 10^6$ (ml mol ⁻¹) | $V_f \times 10^6$ (ml mol ⁻¹) |
|-------------------------------------|---------------------------------|----------------------------|---|---------------------------|--|--|--|
| Temperature (298.15 ± 0.01)K | | | | | | | |
| 0.0000 | 0.7868 | 1112 | 102.78 | 0.633 | 40.72 | 12.42 | 0.826 |
| 0.0311 | 0.7855 | 1121 | 101.31 | 0.629 | 43.53 | 12.88 | 0.835 |
| 0.0676 | 0.7834 | 1144 | 97.53 | 0.617 | 46.86 | 13.36 | 0.815 |
| 0.1242 | 0.7815 | 1163 | 94.60 | 0.608 | 51.99 | 14.20 | 0.789 |
| 0.1618 | 0.7803 | 1173 | 93.14 | 0.603 | 55.40 | 14.78 | 0.772 |
| 0.2247 | 0.7778 | 1189 | 90.94 | 0.596 | 61.17 | 15.71 | 0.743 |
| 0.3029 | 0.7727 | 1182 | 92.63 | 0.601 | 68.57 | 17.91 | 0.708 |
| 0.4033 | 0.7658 | 1178 | 94.10 | 0.606 | 78.25 | 20.64 | 0.662 |
| 0.5368 | 0.7565 | 1155 | 99.09 | 0.622 | 91.42 | 25.43 | 0.601 |
| 0.7227 | 0.7438 | 1153 | 101.13 | 0.628 | 110.26 | 30.81 | 0.516 |
| 1.0000 | 0.7255 | 1120 | 109.88 | 0.655 | 139.48 | 41.84 | 0.389 |
| Temperature (303.15 ± 0.01)K | | | | | | | |
| 0.0000 | 0.7819 | 1098 | 106.08 | 0.650 | 40.98 | 12.86 | 0.903 |
| 0.0311 | 0.7811 | 1112 | 101.70 | 0.636 | 43.77 | 13.08 | 0.864 |
| 0.0676 | 0.7797 | 1126 | 101.16 | 0.635 | 47.09 | 13.78 | 0.842 |
| 0.1242 | 0.7777 | 1152 | 96.89 | 0.621 | 52.24 | 14.63 | 0.828 |
| 0.1618 | 0.7770 | 1155 | 96.48 | 0.620 | 55.64 | 15.47 | 0.825 |
| 0.2247 | 0.7746 | 1170 | 95.94 | 0.618 | 61.42 | 16.51 | 0.793 |
| 0.3029 | 0.7696 | 1168 | 96.23 | 0.619 | 68.85 | 18.59 | 0.784 |
| 0.4033 | 0.7623 | 1159 | 98.50 | 0.626 | 78.61 | 21.67 | 0.769 |
| 0.5368 | 0.7542 | 1143 | 101.49 | 0.636 | 91.70 | 26.19 | 0.728 |
| 0.7227 | 0.7398 | 1120 | 107.76 | 0.655 | 110.86 | 33.26 | 0.634 |
| 1.0000 | 0.7186 | 1096 | 114.99 | 0.677 | 140.81 | 44.44 | 0.432 |
| Temperature (308.15 ± 0.01)K | | | | | | | |
| 0.0000 | 0.7771 | 1073 | 111.77 | 0.673 | 41.23 | 13.58 | 0.995 |
| 0.0311 | 0.7763 | 1105 | 105.49 | 0.654 | 44.04 | 13.62 | 0.930 |
| 0.0676 | 0.7759 | 1117 | 103.30 | 0.647 | 47.31 | 14.28 | 0.616 |
| 0.1242 | 0.7741 | 1131 | 100.99 | 0.639 | 52.48 | 15.38 | 0.898 |
| 0.1618 | 0.7729 | 1146 | 98.52 | 0.632 | 55.93 | 15.87 | 0.868 |
| 0.2247 | 0.7724 | 1152 | 97.56 | 0.629 | 61.60 | 17.25 | 0.851 |
| 0.3029 | 0.7654 | 1151 | 98.62 | 0.632 | 69.22 | 19.43 | 0.842 |
| 0.4033 | 0.7582 | 1148 | 100.08 | 0.637 | 79.04 | 22.33 | 0.815 |
| 0.5368 | 0.7486 | 1134 | 103.88 | 0.649 | 92.38 | 26.91 | 0.768 |
| 0.7227 | 0.7355 | 1111 | 110.15 | 0.668 | 111.51 | 34.08 | 0.669 |
| 1.0000 | 0.7138 | 1075 | 121.23 | 0.701 | 141.76 | 46.51 | 0.453 |

affects the flow rate of the liquid mixtures. There is small increase in the negative value of L_f^E in both systems increases with increase in temperature in indicating structural readjustment.

A perusal of Tables 4 and 5 reveal that the values of excess molar volume (V^E) are negative in both systems and increases with increase in the concentration of triethylamine in its binary mixtures at all three temperatures 298.15 K, 303.15 K and 308.15K till it attains a minimum value at the mole fraction of 0.40 of

triethylamine. Generally V^E can be considered to arise from two types of interactions¹¹ between component molecules. (i) Physical interaction consisting mainly of dispersion forces or weak dipole- dipole interaction and making a positive contribution. (ii) Chemical or specific interactions, including formation of H bond, charge-transfer, and other complex forming interactions, difference in size and shapes of the component molecules of the mixtures, affecting the structure of component molecules which result in a negative contribution. When

Table 3– Values of density (ρ), ultrasonic velocity (u), isentropic compressibility (β_s), intermolecular free length (L_f), molar volume (V), available volume (V_a) and free volume (V_f) properties for binary liquid mixtures of Triethylamine and ethanol.

| X_1 | ρ (g ml ⁻¹) | u (ms ⁻¹) | $\beta_s \times 10^{12}$ (cm ² dyne ⁻¹) | $L_f \times 10^8$ (cm) | $V \times 10^6$ (ml mol ⁻¹) | $V_a \times 10^6$ (ml mol ⁻¹) | $V_f \times 10^6$ (ml mol ⁻¹) |
|-------------------------------------|---------------------------------|----------------------------|---|---------------------------|--|--|--|
| Temperature (298.15 ± 0.01)K | | | | | | | |
| 0.0000 | 0.7851 | 1160 | 94.66 | 0.608 | 58.68 | 16.13 | 0.567 |
| 0.0218 | 0.7850 | 1181 | 91.33 | 0.597 | 60.22 | 15.77 | 0.538 |
| 0.0446 | 0.7847 | 1189 | 90.14 | 0.593 | 61.84 | 15.88 | 0.528 |
| 0.0953 | 0.7844 | 1194 | 89.42 | 0.591 | 65.43 | 16.60 | 0.521 |
| 0.1529 | 0.7832 | 1196 | 89.26 | 0.590 | 69.58 | 17.57 | 0.517 |
| 0.2192 | 0.7799 | 1195 | 89.79 | 0.592 | 74.56 | 19.13 | 0.507 |
| 0.2963 | 0.7745 | 1194 | 90.57 | 0.595 | 80.57 | 20.44 | 0.508 |
| 0.3870 | 0.7674 | 1189 | 92.33 | 0.601 | 87.83 | 22.61 | 0.502 |
| 0.4956 | 0.7592 | 1175 | 95.40 | 0.610 | 96.66 | 25.67 | 0.496 |
| 0.6275 | 0.7496 | 1165 | 98.29 | 0.619 | 107.60 | 29.25 | 0.474 |
| 1.0000 | 0.7255 | 1120 | 109.88 | 0.655 | 139.48 | 41.84 | 0.389 |
| Temperature (303.15 ± 0.01)K | | | | | | | |
| 0.0000 | 0.7808 | 1139 | 98.72 | 0.627 | 59.00 | 17.00 | 0.615 |
| 0.0218 | 0.7807 | 1146 | 97.53 | 0.623 | 60.55 | 17.18 | 0.606 |
| 0.0446 | 0.7805 | 1154 | 96.21 | 0.619 | 62.17 | 17.33 | 0.594 |
| 0.0953 | 0.7803 | 1164 | 94.59 | 0.613 | 65.77 | 17.92 | 0.579 |
| 0.1529 | 0.7789 | 1166 | 94.43 | 0.613 | 69.97 | 18.98 | 0.574 |
| 0.2192 | 0.7704 | 1163 | 95.97 | 0.618 | 81.00 | 22.12 | 0.565 |
| 0.2963 | 0.7631 | 1158 | 97.72 | 0.624 | 88.32 | 24.40 | 0.558 |
| 0.3870 | 0.7550 | 1145 | 101.03 | 0.634 | 97.20 | 27.64 | 0.553 |
| 0.4956 | 0.7494 | 1138 | 102.97 | 0.640 | 103.49 | 29.88 | 0.542 |
| 0.6275 | 0.7454 | 1136 | 103.96 | 0.643 | 108.21 | 31.38 | 0.527 |
| 1.0000 | 0.7186 | 1095 | 114.99 | 0.677 | 140.81 | 44.44 | 0.432 |
| Temperature (308.15 ± 0.01)K | | | | | | | |
| 0.0000 | 0.7764 | 1120 | 102.68 | 0.645 | 59.34 | 17.80 | 0.666 |
| 0.0218 | 0.7762 | 1132 | 100.54 | 0.638 | 60.90 | 17.81 | 0.646 |
| 0.0446 | 0.7760 | 1138 | 99.51 | 0.635 | 62.53 | 18.06 | 0.637 |
| 0.0953 | 0.7758 | 1152 | 97.13 | 0.627 | 66.16 | 18.52 | 0.614 |
| 0.1529 | 0.7750 | 1154 | 95.89 | 0.626 | 70.32 | 19.60 | 0.608 |
| 0.2192 | 0.7661 | 1150 | 98.70 | 0.632 | 81.45 | 22.91 | 0.602 |
| 0.2963 | 0.7590 | 1140 | 101.38 | 0.641 | 88.80 | 23.53 | 0.602 |
| 0.3870 | 0.7508 | 1128 | 104.68 | 0.651 | 97.74 | 28.83 | 0.595 |
| 0.4956 | 0.7452 | 1120 | 106.98 | 0.658 | 104.07 | 31.22 | 0.585 |
| 0.6275 | 0.7410 | 1115 | 108.55 | 0.663 | 108.85 | 32.99 | 0.574 |
| 1.0000 | 0.7138 | 1075 | 121.23 | 0.703 | 141.76 | 46.51 | 0.543 |

triethylamine is mixed with alcohols H-bond of alcohols of alcohols polymers are broken and specific intermolecular interaction leading to the bond formation like (-H...N-) takes place causing decrease in excess molar volume (V^E).

A perusal of Tables 4 and 5 also reveal that the values of excess free volume (V_f^E) are negative and become positive with the increase in concentration of triethylamine beyond mole fraction 0.30 of triethylamine in both binary mixtures at all three temperatures. The

observed value of V_f^E over whole range of composition suggest the weak interaction between component molecules. These Tables also reveal the change in value of V_f^E with increase in temperature which signifies the increase in the molecular interaction with temperature while weakening of molecular association leading to a large free volume available for molecules motion. Similar results have also been found in other binary liquid mixtures¹².

It is evident from Tables 4 and 5 that the value of

Table 4– Excess values of isentropic compressibility (β_s^E), intermolecular free length (L_f^E), molar volume (V^E), available volume (V_a^E) and free volume (V_f^E) properties for binary liquid mixtures of Triethylamine and methanol.

| X_1 | $\beta_s^E \times 10^{12}$ ($\text{cm}^2 \text{dyne}^{-1}$) | $L_f^E \times 10^8$ (cm) | $V^E \times 10^6$ (ml mol^{-1}) | $V_a^E \times 10^6$ (ml mol^{-1}) | $V_f^E \times 10^6$ (ml mol^{-1}) |
|-------------------------------------|--|-----------------------------|---|---|---|
| Temperature (298.15 ± 0.01)K | | | | | |
| 0.0000 | 0.00 | 0.000 | 0.00 | 0.00 | 0.000 |
| 0.0311 | -1.69 | -0.005 | -0.26 | -0.55 | 0.004 |
| 0.0676 | -5.73 | -0.018 | -0.53 | -1.05 | -0.006 |
| 0.1242 | -9.06 | -0.028 | -0.99 | -1.87 | -0.005 |
| 0.1618 | -10.79 | -0.034 | -1.29 | -2.40 | -0.005 |
| 0.2247 | -13.43 | -0.042 | -1.74 | -3.32 | -0.007 |
| 0.3029 | -12.30 | -0.039 | -2.06 | -3.42 | +0.029 |
| 0.4033 | -11.54 | -0.036 | -2.30 | -3.65 | +0.050 |
| 0.5368 | -7.50 | -0.023 | -2.31 | -2.78 | +0.086 |
| 0.7227 | -6.79 | -0.021 | -1.83 | -2.87 | +0.048 |
| 1.0000 | 0.00 | 0.000 | 0.00 | 0.00 | 0.000 |
| Temperature (303.15 ± 0.01)K | | | | | |
| 0.0000 | 0.00 | 0.000 | 0.00 | 0.00 | 0.000 |
| 0.0311 | -4.66 | -0.015 | -0.31 | -0.76 | -0.025 |
| 0.0676 | -5.52 | -0.017 | -0.64 | -1.68 | -0.21 |
| 0.1242 | -10.30 | -0.032 | -1.14 | -2.15 | -0.017 |
| 0.1618 | -11.04 | -0.034 | -1.49 | -2.50 | -0.002 |
| 0.2247 | -12.14 | -0.038 | -1.99 | -3.45 | -0.004 |
| 0.3029 | -12.55 | -0.039 | -2.37 | -3.83 | +0.023 |
| 0.4033 | -11.17 | -0.035 | -2.63 | -3.93 | +0.056 |
| 0.5368 | -9.37 | -0.023 | 2.87 | -3.62 | +0.078 |
| 0.7227 | -4.76 | -0.014 | -2.27 | -2.43 | +0.071 |
| 1.0000 | 0.00 | 0.000 | 0.00 | 0.00 | 0.000 |
| Temperature (308.15 ± 0.01)K | | | | | |
| 0.0000 | 0.00 | 0.000 | 0.00 | 0.00 | 0.000 |
| 0.0311 | -6.57 | -0.020 | -0.31 | -0.94 | -0.048 |
| 0.0676 | -9.11 | -0.028 | -0.71 | -1.44 | -0.042 |
| 0.1242 | -11.95 | -0.037 | -1.23 | -2.14 | -0.030 |
| 0.1618 | -14.78 | -0.045 | -1.56 | -2.83 | -0.039 |
| 0.2247 | -16.34 | -0.050 | -2.22 | -3.45 | -0.022 |
| 0.3029 | -16.02 | -0.049 | -2.46 | -3.75 | +0.011 |
| 0.4033 | -15.51 | -0.047 | -2.73 | -4.03 | +0.039 |
| 0.5368 | -12.97 | -0.039 | -2.81 | -0.68 | +0.064 |
| 0.7227 | -8.46 | -0.025 | -2.37 | -2.40 | +0.066 |
| 1.0000 | 0.00 | 0.000 | 0.00 | 0.00 | 0.000 |

excess available volume are typically negative for both systems at all three temperatures. Similar results were also obtained by Prakash *et al*¹³ for binary mixtures of ketones. The depolymerisation of hydrogen bonded alcohols aggregates and decrease in dipolar association of component molecules leads to expansion of volume dominating interstitial accommodation which causes positive value of excess available volume but it is compensated by charge transfer complex formation between hydrogen of alcohols and nitrogen of

triethylamine.

The change in molar volume, free volume and available volume with change in composition in these systems, indicate the variations in cohesive forces of these systems¹⁴. A perusal of the sign and magnitude of the excess values of the parameters (β_s^E), (L_f^E), (V^E), (V_f^E) and (V_a^E) show that the strength of the molecular interaction between the component molecules. The present study points out clearly that in both systems triethylamine is involved in the charge transfer interaction

Table 5– Excess values of isentropic compressibility (β_s^E), intermolecular free length (L_r^E), molar volume (V_E), available volume (V_a^E) and free volume (V_f^E) properties for binary liquid mixtures of Triethylamine and ethanol.

| X_1 | $\beta_s^E \times 10^{12}$ ($\text{cm}^2 \text{ dyne}^{-1}$) | $L_r^E \times 10^8$ (cm) | $V^E \times 10^6$ (ml mol^{-1}) | $V_a^E \times 10^6$ (ml mol^{-1}) | $V_f^E \times 10^6$ (ml mol^{-1}) |
|-------------------------------------|---|-----------------------------|---|---|---|
| Temperature (298.15 ± 0.01)K | | | | | |
| 0.0000 | 0.00 | 0.000 | 0.00 | 0.00 | 0.000 |
| 0.0218 | -3.66 | -0.012 | -0.22 | -0.92 | -0.024 |
| 0.0446 | -5.20 | -0.017 | -0.44 | -1.40 | -0.031 |
| 0.0953 | -6.69 | -0.021 | -0.95 | -1.98 | -0.029 |
| 0.1529 | -7.73 | -0.025 | -1.45 | -2.49 | -0.022 |
| 0.2192 | -8.20 | -0.026 | -1.83 | -2.64 | -0.021 |
| 0.2963 | -8.60 | -0.027 | -2.05 | -3.31 | -0.006 |
| 0.3870 | -8.22 | -0.025 | -2.12 | -3.47 | +0.004 |
| 0.4956 | -6.80 | -0.021 | -2.06 | -2.72 | +0.017 |
| 0.6275 | -5.92 | -0.018 | -1.78 | -3.01 | +0.019 |
| 1.0000 | 0.00 | 0.000 | 0.00 | 0.00 | 0.000 |
| Temperature (303.15 ± 0.01)K | | | | | |
| 0.0000 | 0.00 | 0.000 | 0.00 | 0.00 | 0.000 |
| 0.0218 | -1.54 | -0.005 | -0.24 | -0.41 | -0.006 |
| 0.0446 | -3.24 | -0.010 | -0.48 | -0.89 | -0.013 |
| 0.0953 | -5.68 | -0.018 | -1.03 | -1.69 | -0.019 |
| 0.1529 | -6.78 | -0.021 | -1.54 | -2.22 | -0.013 |
| 0.2192 | -7.57 | -0.023 | -2.24 | -3.01 | +0.004 |
| 0.2963 | -7.30 | -0.022 | -2.34 | -3.22 | +0.014 |
| 0.3870 | -5.75 | -0.017 | -2.35 | -2.96 | +0.029 |
| 0.4956 | -5.04 | -0.015 | -2.24 | -2.80 | +0.031 |
| 0.6275 | -4.97 | -0.014 | -2.13 | -2.84 | +0.027 |
| 1.0000 | 0.00 | 0.000 | 0.00 | 0.00 | 0.000 |
| Temperature (308.15 ± 0.01)K | | | | | |
| 0.0000 | 0.00 | 0.000 | 0.00 | 0.00 | 0.000 |
| 0.0218 | -2.54 | -0.008 | -0.23 | -0.59 | -0.015 |
| 0.0446 | -4.00 | -0.012 | -0.48 | -0.96 | -0.019 |
| 0.0953 | -7.32 | -0.023 | -1.04 | -1.90 | -0.031 |
| 0.1529 | -8.63 | -0.027 | -1.62 | -2.40 | -0.025 |
| 0.2192 | -9.46 | -0.029 | -2.31 | -3.03 | -0.001 |
| 0.2963 | -8.48 | -0.025 | -2.43 | -5.90 | +0.019 |
| 0.3870 | -7.19 | -0.022 | -2.35 | -2.59 | +0.035 |
| 0.4956 | -6.29 | -0.019 | -2.21 | -2.27 | +0.041 |
| 0.6275 | -5.77 | -0.017 | -2.21 | -2.05 | +0.042 |
| 1.0000 | 0.00 | 0.000 | 0.00 | 0.00 | 0.000 |

with alcohols. The nitrogen atom of triethylamine being strongly electronegative would have tendency to attract electro positive hydrogen of alcohols, resulting in the formation of new species, showing the negative value of excess thermodynamic properties. Similar results have also been reported by Mehra *et al*¹⁴.

The deviation from Raoult's law upon mixing two non electrolytic liquids demonstrates molecular interaction between unlike molecules which is attributed to adhesive and cohesive forces. The dispersion forces are

responsible for positive deviations where the size of molecules are taken into considerations. The negative deviations of high magnitude lead to the unstable complex formation between the heteromolecules of the mixtures. In the present study the negative excess volume indicates the breaking of hydrogen bond of alcohol polymers, as alcohol is diluted with triethylamine and association between unlike molecules causing contraction with increasing concentration of triethylamine. Therefore it can be concluded that AB type

strong specific interaction take place leading to a bonding like (-H ...N -) which results in the formation of a complex of the type O - HN - C₂ H₅.

The results reveal that the intermolecular interaction decreases with the increasing size of the alcohol molecules. Hydrogen bonding strength also decreases with decreasing dipolemoment of the alcohol molecules. Thus the interaction between triethylamine and methanol molecule is stronger than between triethylamine and ethanol molecule.

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Ph.D. Thesis Summary

Analysis of Anharmonic Behaviour of Sodium Halides and Oxide of Cd, Co, Fe, and Te Using Ultrasonic Techniques

(Ph.D. thesis awarded to Dr. Jitendra Kumar by Bundelkhand University, Jhansi 2012)

Ultrasonic applications cover a number of fields of human importance like medical, research, industry, defence and many more. Although ultrasound competes with other forms of medical imaging, such as X-ray techniques and magnetic resonance imaging, it has certain desirable features. Ultrasonic methods offer the possibility to identify and characterize microstructure properties, as well as defects in the materials, controlling material behavior on the basis of physical mechanisms that forecast the properties of the materials, structural inhomogeneities, elastic constants, precipitates, dislocations, grain phase transformation, porosity, cracks, electrical resistivity, thermal conductivity, specific heat, and many other physical properties are well connected with temperature-dependent ultrasonic parameters.

Elastic constants of the materials provide valuable insight into the nature of the atomic binding forces. In this study the higher order (second, third and fourth) elastic constants, the first order pressure derivatives of second and third order elastic constants and second order pressure derivatives of second order elastic constants are evaluated for sodium halides and oxides of Cd, Co, Fe and Te using Coulomb and Born-Mayer potentials and the temperature variation of these anharmonic properties is studied and analysed at elevated temperatures. Also the Grüneisen parameter, ultrasonic wave velocity, thermal relaxation time, ultrasonic attenuation are evaluated along different crystallographic directions for CaO crystal and the temperature variation of these

ultrasonic properties is studied. The propagation of ultrasonic wave velocity for some organic and inorganic pathological compounds at different ultrasonic frequencies is studied using ultrasonic interferometers and on that basis their characteristic properties are discussed. The Grüneisen parameter plays a significant role in study of thermoelastic properties of materials; it also describes the volume and strain dependence of lattice vibration frequency and depends on elastic constants. The ultrasonic velocity is a key parameter in ultrasonic characterization and can provide information about crystallographic texture. The temperature dependent part of acoustic attenuation has been explained in terms of model in this study, where the acoustic phonon interacts with number of thermal phonons in the lattice.

The present study will be helpful in making qualitative understanding of elastic behaviour in monovalent and divalent fcc structured solids. These parameters may be correlated with the optical and thermoelastic parameters in the broad temperature range. Due to the simplicity of the method used in the study, it can be applied to the more complicated solids, like minerals of geophysical importance and applications. These results, together with other well-known physical properties of these materials, may be expanded as further prospects for the application of halides and oxides under investigation. The achieved results in the present work can be used for further investigations using other methods such as polarizing microscope, X-rays scattering, surface tension, viscosity, NMR and various transport phenomena.

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