

CHARACTERISATION OF EPOXY MATERIALS USED IN THE DEVELOPMENT OF ULTRASONIC ARRAYS

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Abstract: The increasing popularity of piezocomposite technology is largely due to the improvements in mechanical and electro-acoustical properties over for example monolithic piezoelectric elements. Polymer materials are extensively used in the manufacture of ultrasonic transducers. Epoxy resins 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, low expansion coefficients and low viscosity. A variety of epoxies may be used in order to suit a particular application e.g. isolation of piezo-electric rods within the matrix material. Furthermore loaded epoxy is often used as a backing material due to possibility of achieving high impedance in the order of 11 Mrayl and attenuation values of about 15 to 20 dB/cm.

Investigations have been performed on epoxy materials to provide a basic knowledge of how such materials are influenced by such factors as temperature and pressure. It is expected that the piezo-ceramic will only be minimally influenced by changes in temperature up to 200 °C but within this range dramatic changes can occur in a polymer material leading to a reduction in often impedance and variations in attenuation. By employing customised sensors and equipment, experiments were performed in an oilbath at temperatures up to 180 °C. Measurement of mechanical moduli, linear expansion coefficients are also employed to understand variations in the physical properties of the pure material.

The objective is to determine which factors define the suitability of such materials for applications under high temperatures and pressures such as occur in the line of oil rigging.

Introduction: As discussed by Splitt¹ piezocomposite materials have several advantages over their conventional monolithic piezoceramic counterpart especially for specialist applications². There is a clear technology trend in many imaging fields towards the adoption of array technology to enhance system versatility, reliability and efficiency³. Epoxy materials can be employed in a typical array as inter-element, passive intra element filler between active transducers, and as backing material. For an array used at or close to room temperature the resin systems corresponding to the above applications can be described in very basic terms as a hard/glassy epoxy for the interelement, a medium to soft epoxy as intra element filler and a soft generally heavily loaded (e.g. with Tungsten particles) attenuating epoxy as backing. This is a general description as these materials may include small volumes of additives depending on such factors as impedance, attenuation, thermal expansion etc. which will depend on a given application. However, the main physical factor which differentiates the three types of epoxies mentioned is the glass rubber transition temperature or T_g . The primary relaxation associated with motions of polymer chain segments is referred to as alpha relaxation α or T_g . At T_g a drop in the modulus of several orders occurs and it is therefore often referred to as softening point or range. The hardness or stiffness of a polymer is measured as a modulus, a ratio of stress to strain at a certain stage of deformation. Epoxies are viscoelastic materials and as a result their mechanical and acoustical properties will depend very much upon measurement frequency and temperature. It should be taken into account that T_g as referred to in this article always refers to dynamic and not static T_g which usually refers to low frequency techniques or dilatometric techniques⁴. Therefore the rough description (above) which is sufficient for epoxy materials for piezo-composite transducers at room temperature is often not valid even over a small temperature range. In this article this will be demonstrated on two epoxy materials.

The objective of present work and the results illustrated is to develop a better understanding of the relationship between mechanical and acoustical properties and their association with the glass transition temperature and frequency. This is quite a wide scope and therefore this paper concentrates on experiments on two homogenous epoxy samples and compares low frequency

moduli (E^* , G^*) obtained from Dynamic Mechanical Analysis with the ultrasound longitudinal modulus at high frequencies. Furthermore, the relationship between the elastic modulus and the acoustic parameters (sound velocity and attenuation) and their application will be considered.

Materials: Two epoxy materials with different glass transition temperatures have been investigated. Firstly a two component low T_g (-20°C) epoxy gel referred to as Stycast 1265 supplied by Emerson and Cuming. This material is intended for encapsulation of electronic components and has an attenuative gel/rubbery consistence at room temperature. The second epoxy resin is a two component transparent epoxy resin/hardener system with the trade name L385:340 fom Martin G. Scheuffler. This is an epoxy normally used in the construction of light airplanes or gliders. It has a T_g of about 80°C .

Dynamic Mechanical Analysis, DMA: For the dynamic mechanical analysis a Torsional Pendulum from Myrenne, Germany was used. With this instrument it is possible to measure the shear G' and G'' shear loss modulus at 1 Hz. Young's modulus and loss were measured using a Netzsch DMA 242C instrument using a dual cantilever test set-up. Measurement can take place in a frequency range between 0.01 and 100 Hz. Although two different elastic moduli are measured, the measurement principles remain similar, a sinusoidal strain is imposed on a rectangular sample as a function of temperature. Measurements can take place in a range from -180°C to 500°C .

Thermal Mechanical Analysis, TMA: Density from the materials is calculated using the Archimedes principle at room temperature. It is possible using Thermal Mechanical Analysis to measure the change in length of a linear rectangular (60x5x1 mm) sample. From the change of length, the change in volume can be calculated. Mass is taken as constant and the density is calculated over a temperature range using the room temperature as a reference value.

Ultrasound Apparatus: For ultrasound measurements two samples with different thickness' were monitored in through transmission. Attenuation is calculated from the ratio of the two amplitudes measured. In this manner boundary effects such as on the surface of the sample or absorption from oil can be neglected. The samples were clamped between the two sensors and the whole assembly placed in an oilbath. The assembly in Figure 1 was originally designed for measurements in an autoclave at high temperatures and pressures (outside the scope of this paper) and is therefore a robust construction. For oilbath measurements the oilbath is heated to 200°C and cooled slowly.

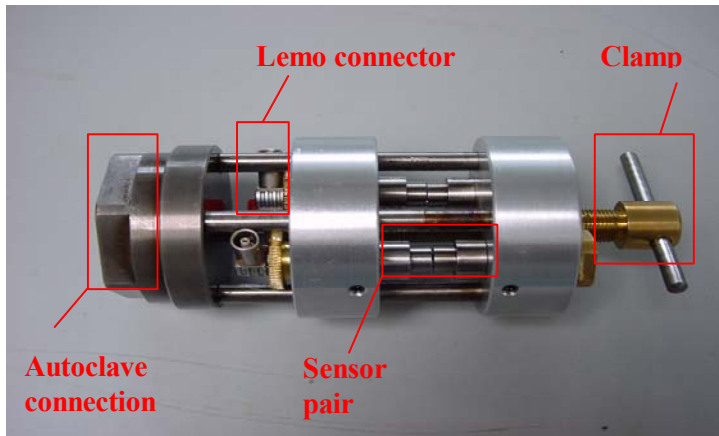


Figure 1: Measuring cell designed for HT/HP conditions

This guarantees that the samples have reached the maximum degree of cure i.e no rest reaction occurs before measurement start and the slow cooling rate ensures homogenous temperatures in the sample. A temperature sensor was placed in contact with the sample's surface. Measurement showed that due to the low cooling rate both samples had almost the exact same temperature. In

general samples with an average diameter of 12mm and thickness' or lengths for the two samples of 3 and 6 mm. Slight differences in thickness may occur due to sample preparation and were considered later. Increased sample length would increase the accuracy of measurement but has the disadvantage that the attenuation is often very high and secondly one can assume with samples of similar geometry that a homogenous temperature distribution is achieved. A scans were recorded over the whole temperature range and analysed using FFT (Fast Fourier Transformation). The amplitudes were evaluated at a middle frequency of 2 MHz. The attenuation per unit length was calculated as follows, where A_1 is the amplitude for thickness L_1 and A_2 is the amplitude for thickness L_2 .

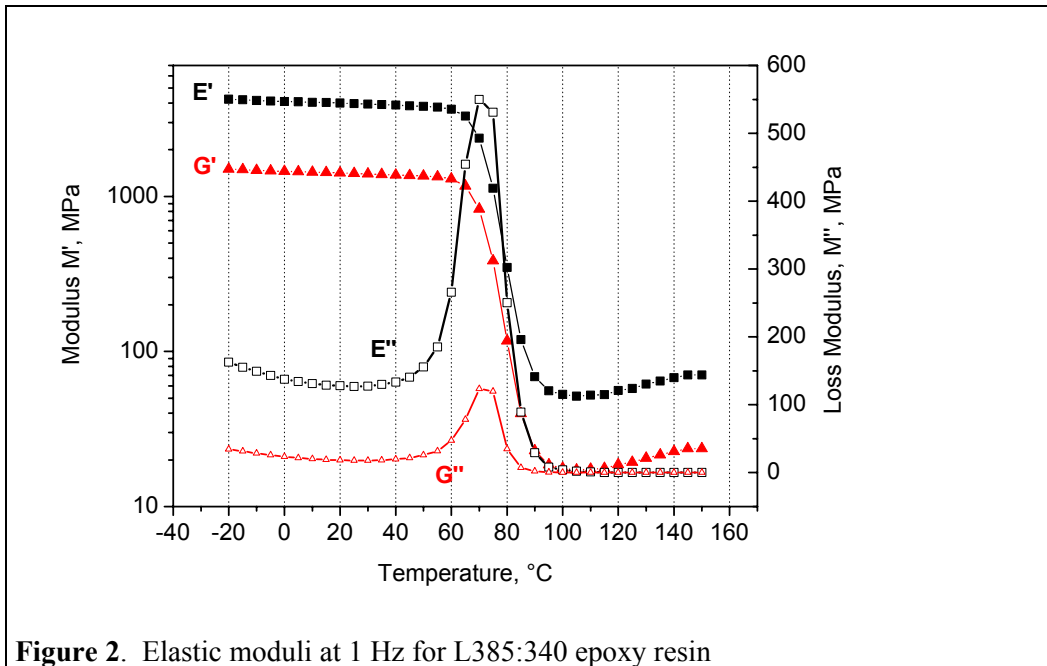
$$\alpha = 20 \log \left(\frac{A_1}{A_2} \right) \frac{1}{\Delta L} \quad [dB/mm]$$

Eq.1

Sensors from Typ K4V from Krautkrämer were employed in combination with the US-Plus[®] Multiplexer system, originally designed for cure monitoring and described elsewhere⁵.

Results and Discussion: In the past several authors and most distinguishably Mason⁶ and Ferry⁷ have discussed the relationship between the elastic constants and in particular Hooke's law, relating stresses to strain and the inter-relationship between the different moduli. For dynamic experiments the modulus is complex M^* and is given by $M^* = M' + iM''$ whereby M' describes the elastic or energy storage component of the modulus and M'' the loss of energy as heat in a cycle deformation. This is valid for E^* the complex Young's modulus, G^* complex shear modulus, L^* complex longitudinal modulus or K^* complex bulk modulus. The moduli are related according to the following expression $K^* = L^* - 4/3G^*$, and most recently described by Lellinger⁸ for high frequency measurements on epoxy materials.

In Figure 1, the shear G' , G'' and Young's modulus and loss E' , E'' are illustrated for a 1 Hz measurement. The results are taken from a cooling run from 150 °C. Following the storage modulus measurement a large drop of several orders of magnitude occurs between 60 and 100 °C. Below 60 °C the epoxy has a hard glasslike state and above 100 °C it is rubberlike. This transition zone between the these two material states is known as the glass transition region and the specific T_g is defined by a large peak in the loss factor E'' and G'' at approximately 77 °C. This typical profile is also described by Lellinger⁸ and Nguyen⁹ for the longitudinal modulus L' and L'' with a loss peak and modulus drop correlating with the other moduli. Simply stated one can expect the same elastic behaviour for E^* , G^* , K^* and L^* as long as the same measurement conditions are observed. The absolute values will differ as shown in Figure 2.



As stated previously the T_g is highly frequency dependent. To illustrate this point E' , E'' over a frequency range between 0.1 Hz and 100 Hz were measured (Fig. 3). If the epoxy is above its T_{g} i.e under 80 °C then the periodic stresses occur faster than the material can relax and the measured modulus will be that of a stiff glass. The shorter the period between stresses (or the higher the frequency) the higher the temperature required for the polymer to relax at that frequency. In Figure 3, a shift in the loss factor peak from 72 °C at 0.1 Hz to 84 °C at 50 Hz is observed. This corresponds to a shift in T_g of about 5 °C per decade increase in the frequency. The modulus of a viscoelastic material is a function of time as well as temperature which is the basis for time-temperature superposition principles⁷ which may be used to predict the temperature-frequency behaviour of a polymer. Such analysis will be published at a later date. In this paper the basic behaviour is just examined.

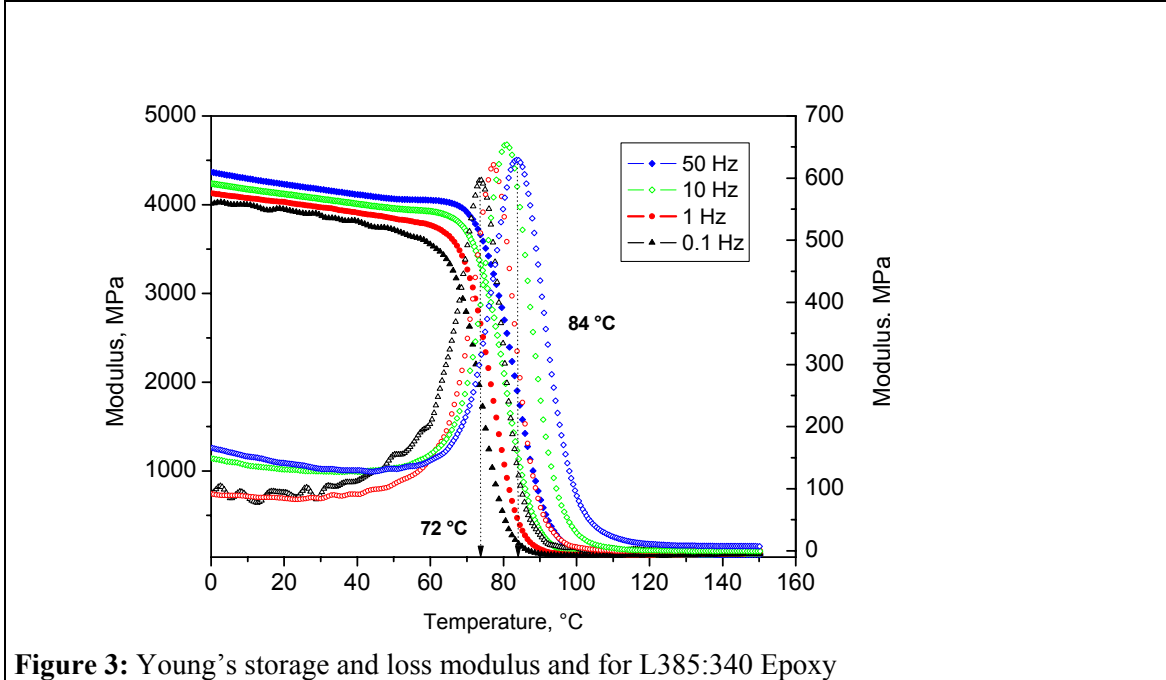


Figure 3: Young's storage and loss modulus and for L385:340 Epoxy

The same material was investigated in an oilbath using two different sample thickness' at a middle frequency of 2 MHz (see Fig. 4). The material was first heated to approximately 200 °C and cooled slowly to ensure a good temperature distribution in the samples. The sound velocity for the two samples, as well as the attenuation and density are illustrated as a function of temperature. The acoustic impedance Z is given as follows:

$$Z = \rho v \quad \rho = \text{density and } v = \text{sound velocity}$$

The impedance provides an estimate of the acoustic compatibility of two materials and varies between 1.5 Mrayl at approx. 180 °C and 3 Mrayl at approx. 20 °C. The change in density over the whole temperature range is < 8%. Density at room temperature is 1.14 g/cm². Therefore due to the small change in density impedance can be calculated relatively easily and only sound velocity is illustrated. The density profile is only shown to 150 °C as TMA measurements were not performed at higher temperatures. A broad attenuation peak is observed which passes through a maximum of 4 dB/mm at 120 °C.

To compare low frequency DMA techniques with high 2 MHz frequency ultrasound, the elastic storage modulus referred to as longitudinal wave modulus L' and L'' were calculated from the sound velocity and the attenuation using Eq. 5 and 6 where v_L , ρ , α and f refer to the longitudinal sound velocity, the density, the attenuation and the frequency. :

$$L' = v_L^2 \rho \tag{5}$$

$$L'' = \frac{\rho v_L^3}{\pi f} \alpha \tag{6}$$

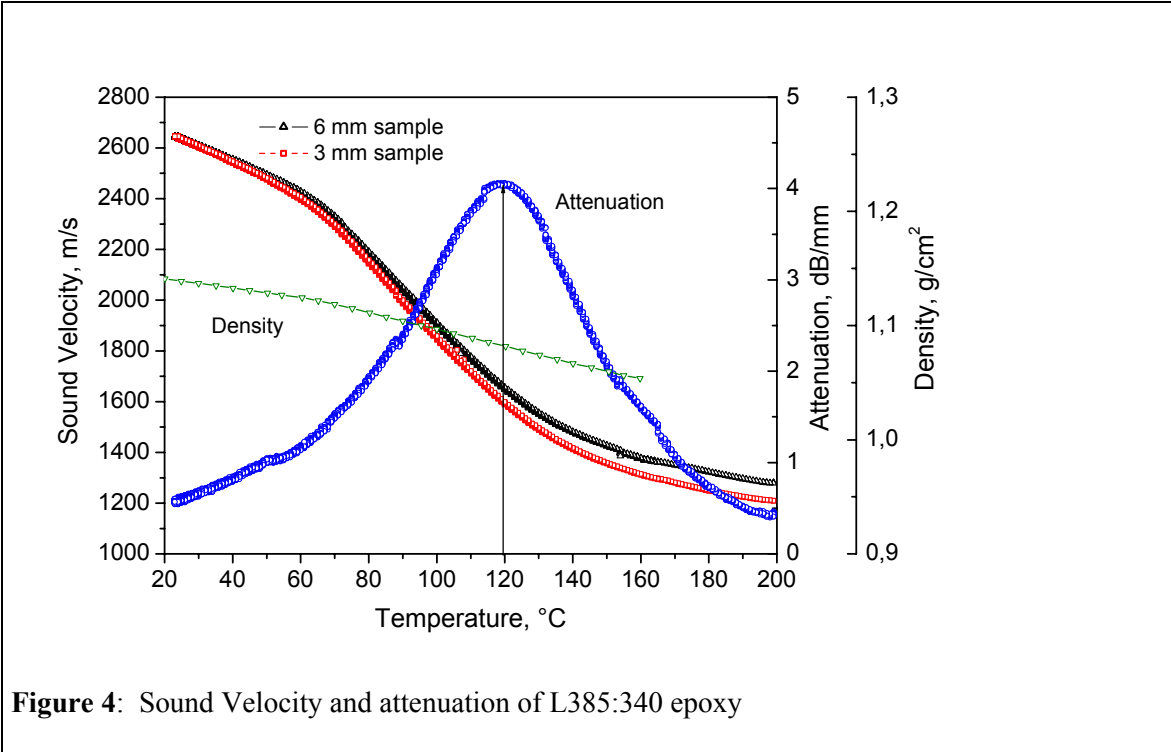


Figure 4: Sound Velocity and attenuation of L385:340 epoxy

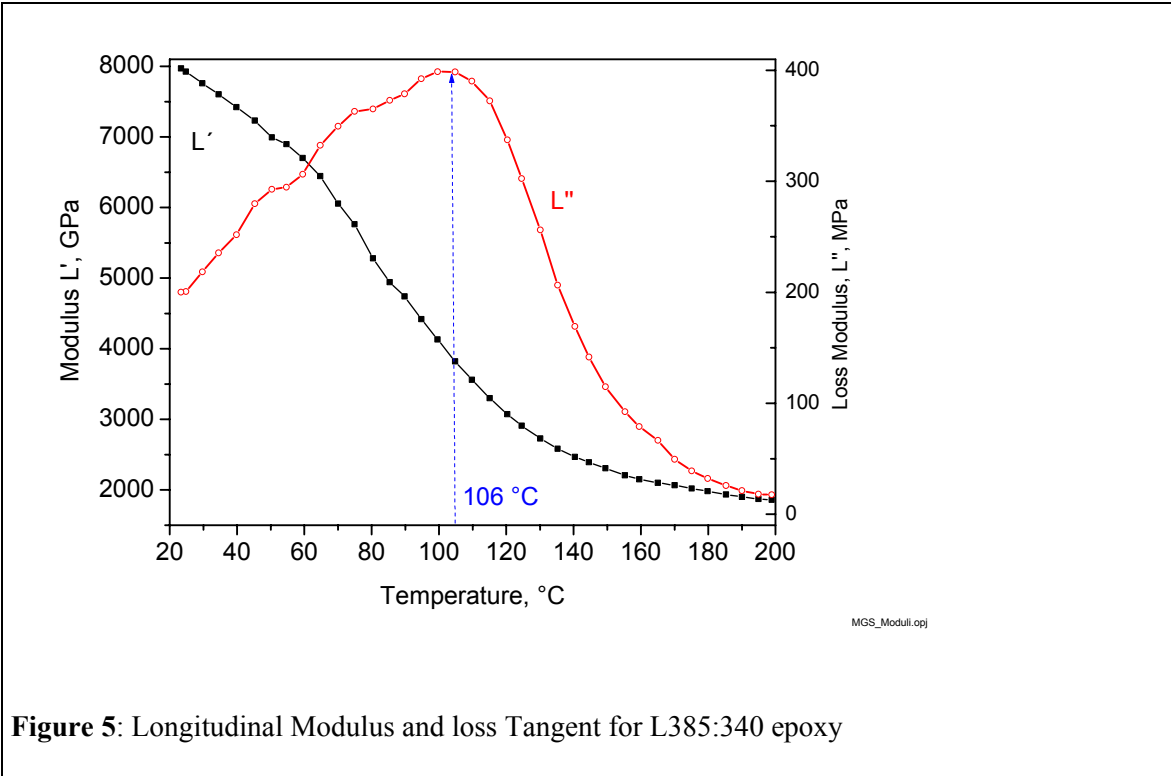
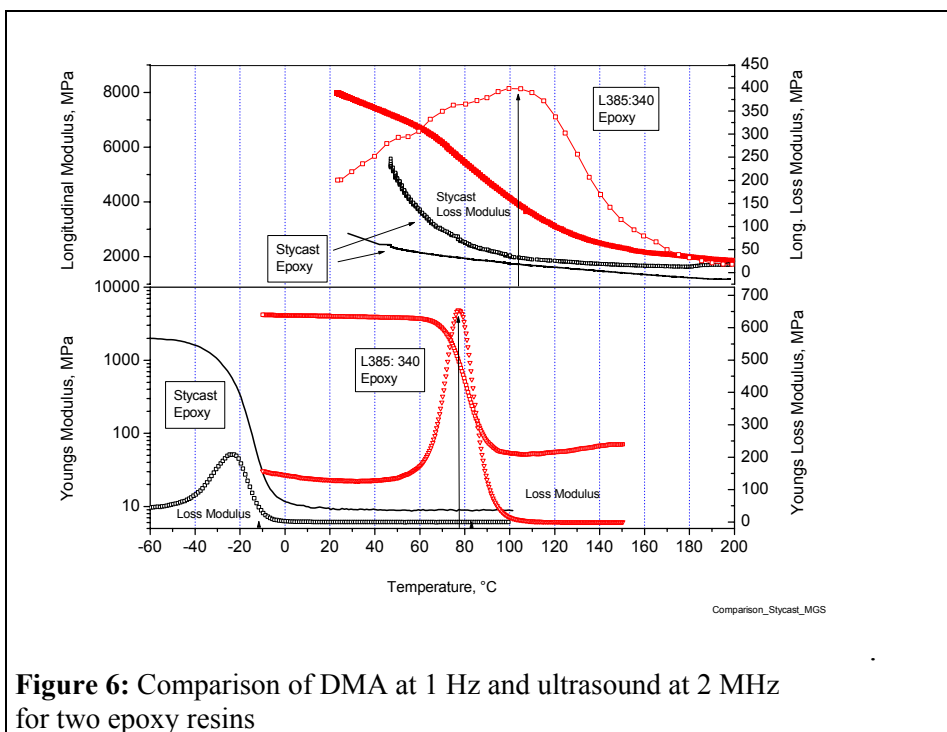


Figure 5: Longitudinal Modulus and loss Tangent for L385:340 epoxy

If Figure 5 is compared to Figs.2 and 3, then an obvious shift in the loss peak M'' is observed. At 2 MHz in the case of L385:340 epoxy, a peak is observed 106 °C whereas for DMA measurements at 1 Hz the peak maximum is at 76 °C. This corresponds to a shift of about 6 °C/pro decade which compares well with the estimate of 5 °C for the Youngs modulus measurements between 0.1 and 50 Hz. This shift in glass transition temperature explains the large attenuation peak in Figure 4.

In Figure 6 a low temperature gel epoxy named Stycast is compared with the L385:340 resin. The gel epoxy which as the name suggests is rubberlike at room temperature has a T_g of about -25 °C measured at 1 Hz. One would expect to observe a loss peak for this resin at about 5 °C, using the 5 to 6°C pro decade shift observed from the L385:340 as a guideline. However, it was not possible in an oil bath to perform measurement at such low temperatures and the experiments will be completed at a later date with another set-up. There are similarities to the L385:340 (after it passed through T_g with increasing temperature) as a large non linear decrease in L'' and a corresponding decrease in L' seem to verify that a loss peak would occur in the expected region. In this experiment the loss modulus was only measured to 40 °C as contact problems occurred with one of the samples, making an evaluation of the attenuation and L'' impossible.



Conclusion: The results show that a good correlation between the ultrasonic properties attenuation and sound velocity and the elastic modulus. It is possible using DMA to make a good estimation in which temperature range certain polymers can be employed for ultrasound applications. The glass transition temperature occurs about 30 °C later at 2 MHz than at 1 Hz using DMA. For applications of passive epoxies in composite arrays it is therefore recommended

to choose a high T_g material to avoid a drop in both impedance and attenuation which can occur as shown in Fig. 4.

Without the aid of DMA such conclusions would be difficult as normally one would expect that a decrease in sound velocity would cause an increase in attenuation or vice versa which depending on T_g is not always the case. Due to the stability of the measurement set-up, accurate measurements of attenuation could be achieved over a large temperature range. On passing through T_g a large increase in attenuation from approx. 3 to 4 dB/mm may be achieved. In the future such information is useful for developing backing material which will function over a wide temperature range. For example, the Stycast material is suitable as a loaded backing at room temperature. At the present time comparisons have only been made for pure material. As an example in this case the pure epoxy has an attenuation of about 4 dB/mm at room temperature. this drops to about 1,5 dB/mm at 60 °C and above 100 °C to 0,5 db/mm. This will mean that even in a loaded state at higher temperatures a dramatic drop in acoustical properties (attenuation and impedance) properties will occur above 60 °C.

As the results presented are part of ongoing research following points will be covered in more detail by the authors, the evaluation of all results e.g time (frequency) – temperature analysis are incomplete and will be presented in September. Secondly, the equipment developed is currently being employed for testing materials under high pressure. At the time of writing insufficient results were available to be included in this paper. Thirdly, loaded materials for backing applications will also be considered in the future.

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