Relationship between the Mechanical and Ultrasound Properties of Polymer Materials

Jarlath MC HUGH, Joachim DÖRING, Wolfgang STARK, BAM, Berlin, Germany
Jean Luc GUEY, Imasonic, Besancon, France

Abstract. In the past the BAM authors have shown that the parameters ultrasound velocity and attenuation are very sensitive to changes in polymer properties e.g. ultrasound cure monitoring of fibre reinforced epoxy materials in aircraft manufacture. More recently, research work (EC Grow Project GRD-CT-2002-000689) has concentrated on the characterisation of polymer materials for application in phased arrays also over a large temperature and pressure range (approx. 180 °C and up to 1400 bar). In the laboratory Dynamic Mechanical Analysis DMA is a well known and standardised technique employed to characterise the mechanical (modulus) properties of polymers. Similar to DMA, ultrasound can measure a dynamic modulus. In addition, ultrasound techniques have the advantage that they can be incorporated into the industrial process, are not confined to the laboratory and modern sensors can be employed over a practical temperature range. The objective of this research field is to increase the understanding of the sensitivity of ultrasound parameters to changes in the mechanical properties of polymers and at the same time increase the potential for practical application of such techniques.
The elastic properties of a polymer can be characterised using longitudinal sound waves. It is principally possible to compare the temperature profile from the measured ultrasound wave modulus with the modulus (shear or Young's modulus) from conventional low frequency DMA techniques, such as commonly employed to characterise polymer materials over a large temperature range. However, several additional factors such as measurement frequency, elastic modulus, physical polymer properties, temperature and their interaction must also be considered. In this presentation the link between ultrasound parameters and mechanical properties of polymer materials will be discussed and illustrated with the aid of practical examples.

Introduction

Dynamic Mechanical Analysis DMA describes techniques whereby a time dependent sinusoidal disturbance is applied to a sample and the resulting behaviour is measured as a function of time, temperature or frequency. Tensile, shear or bulk stresses are common. Similarly ultrasound shear or longitudinal waves may be employed to characterise the behaviour of polymers at higher frequencies. However, shear waves have the limitation that they do not propagate in liquids or very soft gel type materials and it is difficult to achieve good coupling especially at higher temperatures. Therefore experimental results presented here are only for longitudinal waves. Sinusoidally varying stresses are normally expressed as a complex quantity and the modulus is given by $M^* = M' + iM''$. M' is referred to as the real component and describes the elastic or energy storage component of the modulus. M'' is the imaginary part or loss modulus and for example describes the energy dissipated as heat in a cycle deformation. These laws are valid for all modulus including E^* the complex Young's modulus E^*, G^* complex shear modulus, L^* complex longitudinal modulus or K^*

complex bulk modulus. The modulus are related according to the following expression K* = L*-4/3G*, and illustrated experimentally by Lellinger et al. [1] on thin films. Early textbooks [2] illustrate the derivation of the complex modulus for sound waves. For example in accordance with the above complex modulus, the longitudinal modulus L´ and loss L´´ are normally defined as follows:

$$L'_{LongForm} = \rho v^2 \frac{\left(1-\left(\frac{\alpha v}{\omega}\right)^2\right)}{\left(1+\left(\frac{\alpha v}{\omega}\right)^2\right)^2} \qquad \text{Eq.1}$$

$$L''_{LongForm} = 2\rho v^2 \frac{\left(\frac{\alpha v}{\omega}\right)}{\left(1+\left(\frac{\alpha v}{\omega}\right)^2\right)^2} \qquad \text{Eq. 2}$$

Equations 1 and 2 can be simplified under the condition that the attenuation per wave vector $k = \frac{2\pi}{\lambda}$ is very small or $\frac{\alpha v}{\omega} = \frac{\alpha\lambda}{2\pi} << 1$. In this situation the equations 1 and 2 can be shortened to Eq.3 and 4.

$$L'_{ShortForm} = \rho v_L^{\,2} \text{.....when } \frac{\alpha v}{\omega} << 1 \qquad \text{Eq.3}$$

$$L''_{ShortForm} = \frac{2\rho v^3 \alpha}{\omega} \text{.....when } \frac{\alpha v}{\omega} << 1 \qquad \text{Eq.4}$$

This is an important assumption. In this article an epoxy material is investigated which on cooling from 200 °C passes through the T_g region (high attenuation effects are investigated). It is therefore not assumed that in this region the short form for L´ and L´´ (Eq. 3 and 4) are valid. For this reason the notation “long form” is applied to Eqs. 1 and 2 and “short form” to Eqs. 3 and 4 and their validity will be investigated.

To describe viscous losses in a material L´´ or tan δ can be employed. Tan δ describes the relationship between the real and imaginary components of the complex modulus (tan δ = E´´/E´) and has no real units. It is related to the mechanical damping or energy lost in a viscoelastic material due to internal friction. If Eq. 6 (for low attenuation) is studied, it is observed that tan δ describes the attenuation (Np/m) per wavelength at specific frequencies.

$$Tan\delta_{Long} = \frac{L''}{L'} = \frac{2\frac{\alpha v}{\omega}}{\left(1-\left(\frac{\alpha v}{\omega}\right)^2\right)} \qquad \text{Eq.5}$$

$$Tan\delta_{Short} = 2\frac{\alpha v}{\omega} = \frac{\alpha v}{\pi f} = \frac{\alpha\lambda}{\pi} \text{.....when } \frac{\alpha v}{\omega} << 1 \qquad \text{Eq.6.}$$

The term $\frac{\alpha v}{\omega}$ is often referred to as “r” and is a dimensionless parameter. Interestingly “r” is half of tan δ (Eq.6). In conventional DMA (Fig.2) at low frequencies (0.1 to 100 Hz) the actual values of the loss modulus have moderate importance (values depend strongly on sample geometry and testing setup) and the actual profile as a function of temperature, for example if an increase/decrease or peak is observed, is of much higher interest.

Experimental Methods

Ultrasound Apparatus: As shown in Figure 1, the ultrasound rig consists of two separate measuring channels. Each channel contains 2 sensors and a sample (not shown) is clamped with minimal clamping pressure between the two transducer heads. Measurements take place in through transmission. Modified sensors from Krautkrämer K4V were employed. The sensors have a resonance frequency of 3 MHz (average bandwidth 5 MHz). *The advantage of using a technique employing two samples with different thicknesses is that boundary effects such as reflections on the surface of the sample or absorption from oil can be neglected*. The oilbath, although messy, has the advantage that it is relatively easy to maintain consistent temperatures across a samples volume. The assembly was originally designed for characterising polymer materials in an autoclave at high temperatures and pressures (up to 180 °C and 1400 bar) as part of the EU Project GRD-CT-2002-000689. The oilbath is heated to 200 °C and cooled slowly. A-Scans are recorded at regular temperature intervals. A temperature sensor was placed in contact with each sample. A similar arrangement is employed for measurements in the kHz range. Sensors were prototype array sensors with 9 array elements wired parallel and switched simultaneously i.e. same principle as a conventional mono-element piezo-composite. The kHz sensors have a middle frequency of 350 kHz (average bandwidth 600 kHz). The actual prototype sensor was developed by Imasonic (France) with support from BAM in the framework of the above named EU project.

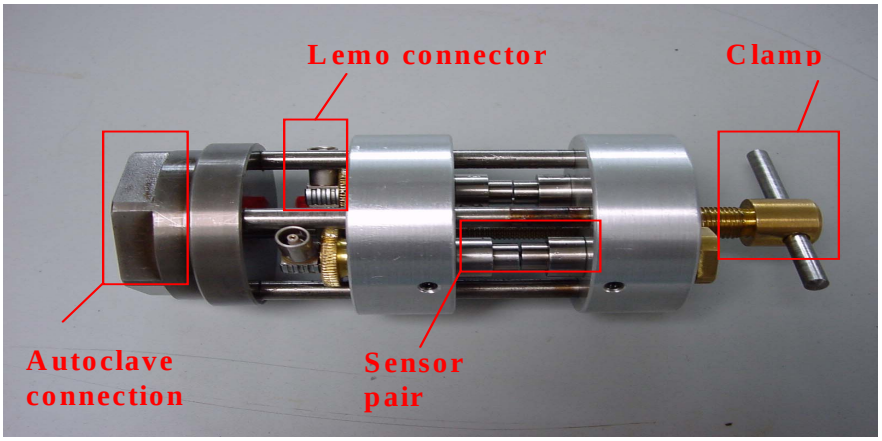

Fig 1: Measuring cell designed for HT/HP conditions

A-scans were recorded on a Yogogawa oscilloscope used in combination with a pulse receiver Model 5800 from the Panametrics company. Care was taken that the High and Low Pass filter settings were set outside the relevant measuring frequency range so that no effects should be observed in the frequency spectrum.

***Dynamic Mechanical Analysis, DMA*:** Young's modulus and loss were measured using a Netzsch DMA 242C instrument using a dual cantilever test set-up. Sample length is typically 30 mm. Measurement can take place in a frequency range between 0.01 and 100 Hz. 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. In this case measurements took place in a Myrenne Torsional Pendulum. 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.

***Material*:** The epoxy resin is a two component transparent epoxy resin/hardener system with the trade name L385:340 from the company Martin G. Scheuffler (MGS). It is normally used in the construction of light airplanes or gliders and has also found application in wind turbine blades. It has a glass-rubber transition T_g measured using static or low frequency techniques (e.g. at 1 Hz) of approximately 80 °C. It has been chosen because of the industrial relevance and also because it offers the opportunity to study the influence of T_g within the measurement range of the ultrasound measurement system. Density of the material at room temperature was 1.141 g/cm².

Calculation of attenuation, group and phase velocity

In general samples with an average diameter of 12mm and thicknesses of 3 and 6 mm for measurements at a middle frequency of 3 MHz and 10 and 16 mm for measurements at 350 kHz were employed. A scans, similar to those illustrated in Fig.2, were recorded at specific temperatures over the whole temperature range. The sound velocity was calculated from the peak arrival times according to Eq. 7. The notation 1 and 2 refers to the thin and thick samples respectively. t_1 and t_2 are the time of flight or transmission times required for the sound wave to travel through individual samples.

$$v_{TOF} = \frac{[d_2 - d_1]}{[t_2 - t_1]} = [\text{m/s}] \qquad \text{Eq.7}$$

The attenuation was determined by comparing the peak amplitudes (e.g. negative peak) from the thin d_1 (left in figure 2) and thick d_2 (right in figure 2) samples and calculated according to Eq.8. Peak amplitudes are referred to as A_1 and A_2.

$$\alpha_{PR} = 20\log\left(\frac{A_1}{A_2}\right)\frac{1}{\Delta d} \quad [dB/mm] \qquad \text{Eq. 8}$$

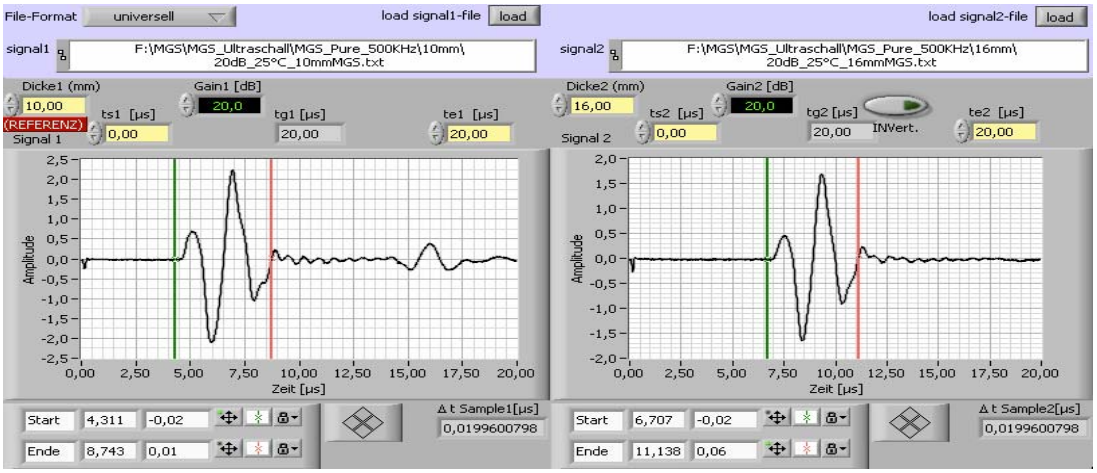

Fig.2 Screen shot of Labview based analysis software. Illustrated are the 2 A-scans from 10 and 16 mm epoxy samples

In order to differentiate between this direct evaluation technique and FFT analysis, the sound velocity calculated is referred to as v_{TOF} (time of flight) and attenuation as α_{PR} (peak relation). The A-scans recorded at a range of temperatures are saved in ASCII format and can be read into a program written in Labview® written specifically for Fourier analysis of acoustic signals. The actual data to be analysed is placed in a rectangular window as shown in the above. Zero on the time axis is the actual start of the evaluation window and the red

line the finish. Full length of the time domain signal is analysed. The amplitude of all points before the green line (not to be confused with the start of evaluation window) are set to null, otherwise unwanted signal noise occurs in the frequency spectrum. The end of the evaluation window (red line) is where possible on the same zero baseline as the start of the window. The frequency resolution was 50 KHz (0.05 MHz) for all experiments although the resolution may be varied slightly using "zero padding" techniques. Attenuation is calculated according to Eq.8 whereby in this case A_1 and A_2 are the amplitudes from the FFT magnitude spectrum taken at specific frequencies. The phase velocity is calculated as follows based on the work of Sachse and Pao [3] and Freemantle et al [4].

$$\text{Phase Velocity } v = \frac{2\pi D}{(\phi(f)_{s1} - \phi(f)_{s2})} . f = \frac{2\pi fD}{(\phi(f)_{s1} - \phi(f)_{s2})} \qquad \text{Eq. 9}$$

where $\frac{2\pi D}{(\phi_{s1}(f) - \phi(f)_{s2})} = \lambda$

ϕ_{s1} Phase angle for sample thickness 1 e.g. 10 mm @500 kHz

ϕ_{s2} Phase angle for sample thickness 2 e.g. 16 mm @500 kHz

D = Thickness difference (d_2-d_1)

Experimental Results:

Fig.3 illustrates the DMA results using a dual cantilever setup in the frequency range 0.1 to 33 Hz. From the Young's Modulus E´ curves 3 distinguishable domains are observed as the material is heated. At low temperatures, the polymer is stiff/frozen and has a high modulus E´ and low damping tan δ. As the temperature increases, the polymer eventually obtains

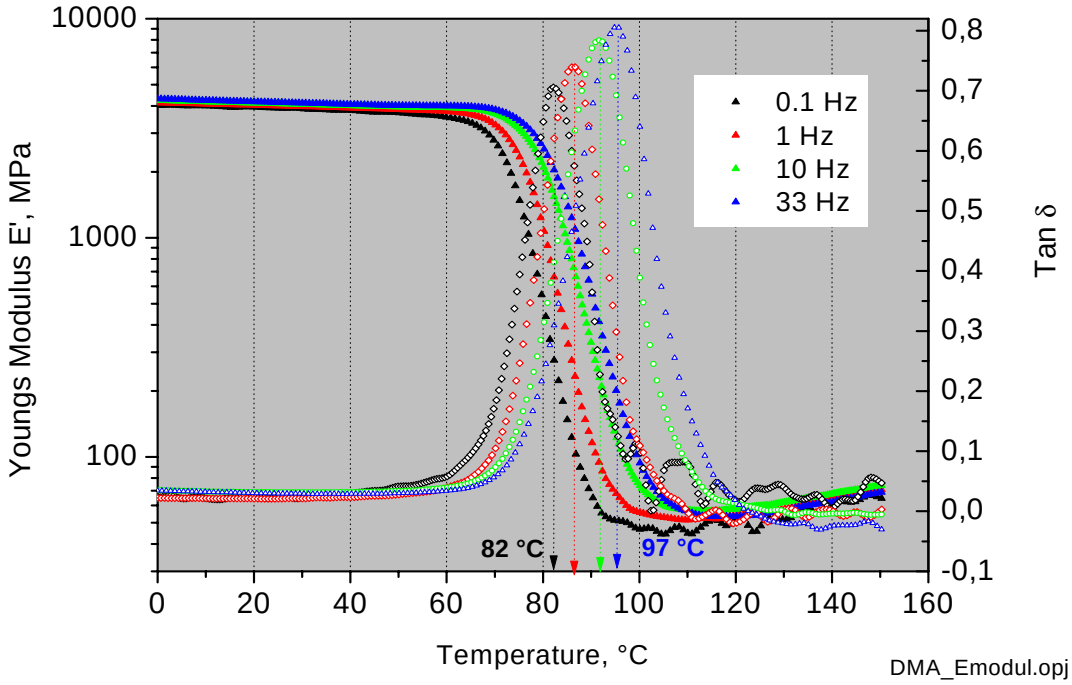

Fig.3: E Modulus and Tan δ as a function of temperature using DMA

sufficient thermal energy to enable its chains to move freely enough to make it behave like

a rubber. In analogy with this process a drop in modulus occurs and the loss factor tan δ forms a peak (high damping). This transition from a hard stiff polymer to a rubber-like polymer and the associated loss peak is referred to as glass transition. Qualitatively T_g can be interpreted as the onset of long range, co-ordinated molecular movement. Below T_g only 1-4 chain atoms are involved in molecular movement while above T_g 10-50 chain atoms attain sufficient thermal energy to move in a co-ordinated manner. When a sinusoidal stress is applied to a linear viscoelastic system, the resulting stress will also be sinusoidal but out of phase when there is energy dissipation or damping in the polymer. This is reflected by the tan δ values. Obviously segmental movement is strongly time dependent and therefore chain mobility will depend on the rate of applied load or measurement frequency. In the example provided using conventional DMA a shift in the tan δ peak is observed from 82°C at 0.1 Hz to 92°C at 10 Hz i.e. approx. 5°C per decade increase in frequency.
At low frequencies the molecular segments have much more time to follow the applied stress than, for example at ultrasound frequencies. At such high frequencies (kHz/MHz) the polymer has to be considerably softer i.e. at higher temperature before the chain segments can respond to the applied (sinusoidal stress), which is in the microsecond range. This peak shift can be described using Time-Temperature Superposition principles [5]. A general rule taken from dielectric measurements [6] over a large frequency range is that the maximum of a tan δ loss peak will change by approximately 7 K per decade increase in frequency. Variations in the relaxation behaviour (DMA as revealed in Fig.3 showed a 5 K peak shift per decade) can be related to the Arrhenius type behaviour of the relaxation times such as discussed by Alig [7].
The same measurement regime as for DMA analysis was performed using longitudinal wave measurement at a range of frequencies. Evaluation of sound velocity and attenuation

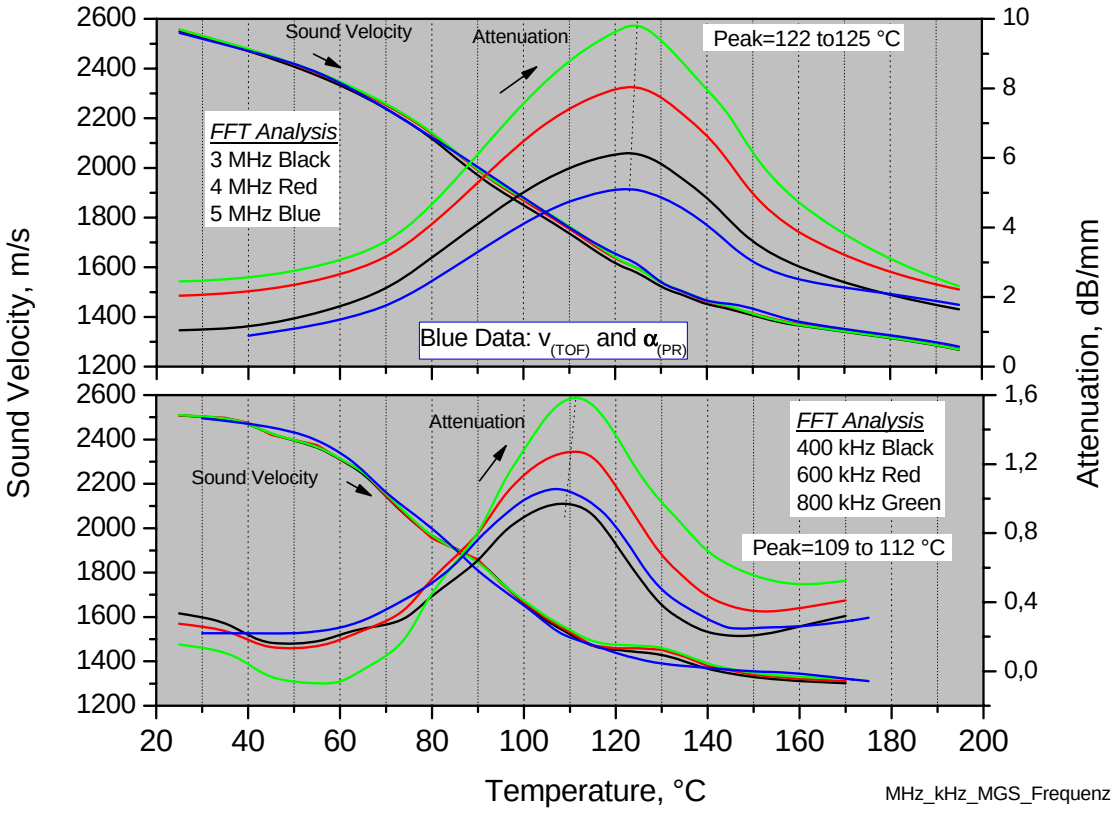

Fig.4: Velocity and attenuation as a function of temperature for MGS Epoxy

took place using v_{TOF}, α_{PR} and FFT analysis techniques (see Fig.4). A first impression reveals clear trends very similar to DMA. A decrease in sound velocity over the temperature range combined with a peak in attenuation is observed. Even within a small frequency range (3 to 5 MHz) a small shift in the attenuation peak to higher frequencies is observed (122 to 125 °C). This becomes clearer if the measurement taking places in the kHz are compared to MHz frequency range as shown. The same physical processes as already described for the DMA are involved but at a higher frequency and therefore the T_g is observed at higher temperatures, the higher the measurement frequency Before employing the ultrasound technique to describe the DMA material properties, it is necessary to investigate the relationship between the complex moduli and the sound velocity and attenuation as shown in Fig.5. Density data as a function of temperature was available from TMA measurements and it was possible to calculate accurate values for the all parameters according to equations 1 to 6.
This is illustrated for measurements in the MHz range in Fig.5. As discussed calculation of L´ can be simplified if $r << 1$. Taking the example given at 4 MHz, a maximum in attenuation of 8 dB/mm is achieved at approx. 123 °C (Fig.4). In Fig 5 the results are illustrated using the approximations for L´ and tan δ at 3, 4 and 5 MHz. These results are compared to the long form (see full Eqs. 1 and 5) for L´ and tan δ. As observed a maximum error of about 6 % is introduced using the approximations for L´ and tan δ. Values for "r" found for this epoxy passing through T_g do not exceed 0.08. If we take the above example with a maximum attenuation of 8 dB/mm and a wavelength of 0.54 mm then:

$$r = \frac{\alpha v}{\omega} = \frac{\alpha \lambda}{2\pi} = \frac{8(0.54)}{2\pi(8.686)} = 0.08$$

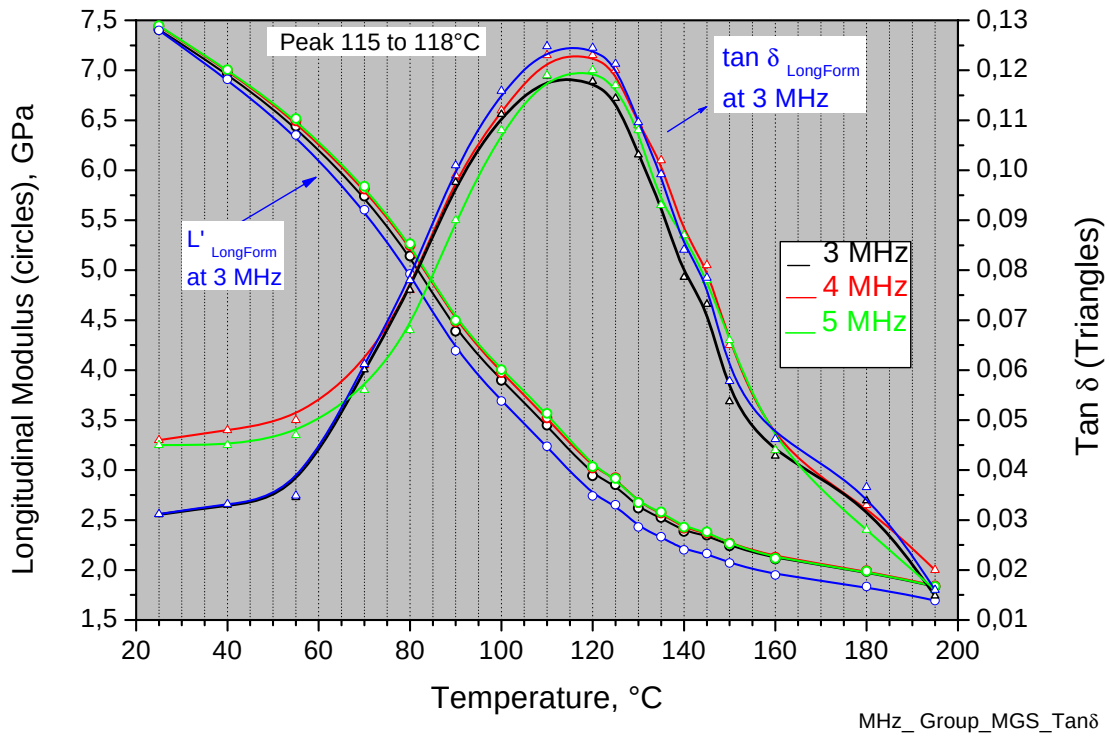

Fig.5: Calculated longitudinal modulus L´ and tan δ as a function of temperature for MGS Epoxy

For this reason it is acceptable to employ the approximations for L′, L′′ and tan δ even when measuring at frequencies that are in the higher MHz range. The attenuation will increase but the wavelength will also decrease in the calculation of values for 'r'.
Tan δ was chosen as the most suitable parameter to illustrate the loss factor in ultrasonic studies, firstly because it can be compared to tan δ for oscillatory Young's modulus measurements at low frequencies as for both techniques it describes the relationship between the storage modulus E′ (Young's) or L′ (longitudinal storage modulus) to the loss moduli E′′ and L′′. Secondly, in respect to ultrasound measurements it describes the attenuation per wavelength (Eq.6) so it is closely related to the measured attenuation (see Fig. 6).For the above reasons tan δ or attenuation would seem to be more suitable for describing the dynamic loss behaviour at ultrasonic frequencies. In order to differentiate between the two parameters, an example is shown illustrating attenuation and tan δ for 2 and 5 MHz measurements. Both parameters clearly show the typical shift of the loss peak to higher temperatures as the frequency is increased from 2 to 5 MHz. Independent of frequency the tan δ is observed at about 5 °C lower temperatures than attenuation.
This offset of the tan δ peak in relation to attenuation is also observed for measurements in the kHz range although not illustrated here. Interestingly the same results are achieved when the data is analysed using PR evaluation technique (cyan colour). It is therefore not caused by analysis technique.

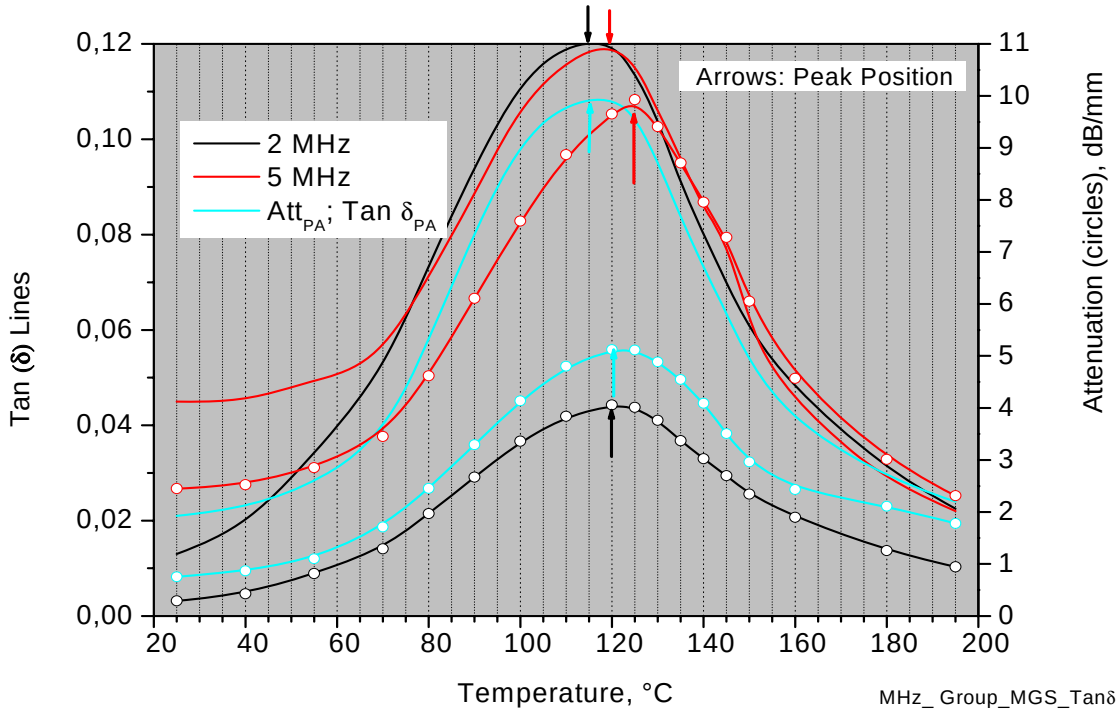

Fig. 6: Comparison measured attenuation and tan δ as a function of temperature for MGS epoxy

Conclusions

It was shown over a kHz/MHz frequency range that ultrasound measurements can be employed to describe dynamic mechanical material behaviour. However, the question arises, which ultrasound parameters are the most suitable for describing the complex

material properties. It was shown that for an epoxy resin material passing through the glass rubber transition region (high peak values of attenuation expected) that approximate values for L´ (Eq. 3) and L´´ (Eq.4) as well as tan δ (Eq.6) are sufficient to describe the dynamic mechanical behaviour, even in the region of T_g .
Similar to DMA techniques operating at low frequencies, an ultrasound attenuation peak that is associated with the T_g is observed. T_g is a frequency dependent transition and it is shown that the transition from glass to rubber state (peak in attenuation) occurs at higher temperatures the higher the measurement frequency. For example a tan δ peak is observed at 86 °C at 1 Hz and 122 °C at 3 MHz. This corresponds to a shift of approx. 6 °C per decade. Between 0.1 and 10 Hz for low frequency measurements a shift of approx. 5 to 6°C per decade is also observed.
Tan δ representation of the damping results, is very similar in form to attenuation (Fig.6), shows less scattering than L´´ (to be presented) and corresponds well with low frequency analysis (tan δ peak shift). As shown in Eq. 6 it can be calculated as the attenuation per wavelength or from the relationship L´´/L´. Taking these factors into account it would seem to be more suitable to describe polymer physical loss properties than L´´ at ultrasonic measurement frequencies.
From physical principles it makes little difference whether v or L´ are employed to describe the elastic mechanical polymer behaviour. It was shown that approximate values for $L´=\rho v^2$ are quite sufficient to describe the longitudinal modulus of an epoxy polymer even in the T_g region. If the density change is taken as constant which is the normal case for DMA measurements then v is roughly proportional to √L´.
Lastly in regard to evaluation techniques, sound velocity and attenuation values were determined from FFT analysis and also by using TOF and PR (comparison of reference peaks) techniques. As shown in Fig. 4 and 6 both techniques delivered comparable results. Sound velocity and attenuation calculated using TOF and PC were comparable to measurements at sensor middle frequencies (see Fig. 4 and 6) e.g. 350 kHz and 3 MHz. The FFT analysis technique has however the advantage that it delivers accurate information over a frequency spectrum with the only limitation being the sensor bandwidth. This means it is more suitable for investigating dispersion effects caused by frequency dependent damping. Presently a TOF and PR based technique with customised software is being employed for the industrial cure monitoring of thermosetting polymers.

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