On the Modelling of Ultrasonic Bulk Wave Propagation in Epoxies.

R. E. Challis, F. Blarel, M. E. Unwin and X. Guo.

Applied Ultrasonics Laboratory, Electrical Systems and Optics Division, Faculty of Engineering, University of Nottingham, University Park, Nottingham, NG7 2RD, UK.
E-mail: Richard.challis@nottingham.ac.uk

Abstract. Bulk wave attenuation in epoxies has been found experimentally to be a linear function of frequency. Anecdotal evidence suggests that the formulations used for bulk wave attenuation to be input to computational propagation models, including models for guided waves, can take many forms: Either the simple linear relationship between attenuation and frequency can be input directly, or any of a number of analytic models could, in principle, be used – examples being the Maxwell, Kelvin-Voigt and Zener anelastic solid models, or the hysteretic damping model sometimes employed for studies of structural vibrations. This paper considers the physical bases of these various models, as well as multiple degree of freedom models that have their origins in dielectric theory. It is shown that a simple two degree of freedom adaptation of the Zener model provides a good simulation of experimentally observed data for both attenuation and phase speed over a wide frequency band.

1. Introduction

In the context of non-destructive testing (NDT) and materials evaluation there is frequently a need to develop mathematical/computational models that simulate bulk and/or guided ultrasonic wave propagation in structures or their constituent materials. Epoxy polymers or composites formed of them represent an important class of materials used in safety critical applications such as aerospace, automotive, rail and marine, and it is therefore important to study wave propagation in them. Of particular interest is the fact that wave attenuation in epoxies is close to a linear function of frequency over a wide frequency band. This is true both for the fully cured material and throughout the cure cycle [1,2]. For simulation of this behaviour, the essential problem lies in the formulation of the complex elastic moduli which govern wave propagation, which lead to frequency dependent attenuation and, to a lesser extent, a frequency dependent phase speed through the Kramers-Kronig relationships [3,4]. This paper draws on results from a recent publication [5] to discuss a number of formulations for the complex elastic moduli, and their applicability to models of wave propagation.

2. Broad band behaviour of attenuation and phase speed

We have recently attempted to measure bulk shear wave attenuation in a cured epoxy [2]. Four techniques were used to measure attenuation either directly using conventional ultrasound transducers in pitch-catch, or indirectly using different methods across a wide frequency band – dynamic mechanical analysis (DMA) for frequencies below 200 Hz, a microwave excitation technique [6] for frequencies around 20 kHz, and a novel guided wave technique for frequencies around 500 kHz [2]. The results are shown on Fig.1 in which the dotted line represents a linear fit corresponding to an attenuation of 340×10^{-6} Np m^{-1} Hz^{-1}. The corresponding results for phase speed are shown on Fig. 2, on which the dotted line corresponds to a Kramers-Kronig calculation based on the attenuation data. Whilst these results are not ‘perfect’, they do indicate the close to linear...
relationship over five decades of frequency as well as reasonable compatibility with the Kramers-Kronig relationship.

![Graph showing bulk shear wave attenuation versus frequency for the 2011 epoxy, calculated from measurements using the four techniques. The dashed line on the attenuation curve is a straight line fit corresponding to 340x10^{-6} Np Hz^{-1}.](image1)

Fig.1. Bulk shear wave attenuation versus frequency for the 2011 epoxy, calculated from measurements using the four techniques. The dashed line on the attenuation curve is a straight line fit corresponding to 340x10^{-6} Np Hz^{-1}.

![Graph showing shear velocity versus frequency for the 2011 epoxy, calculated from measurements using the four techniques. The dashed line was calculated on the basis of the Kramers-Kronig relationships applied to the attenuation data with the speed at 100 Hz taken as 705 ms^{-1}.](image2)

Fig.2. Bulk shear wave phase speed corresponding to the attenuation data on Fig.1. The dashed line was calculated on the basis of the Kramers-Kronig relationships applied to the attenuation data with the speed at 100 Hz taken as 705 ms^{-1}.

3. Basic wave propagation model

Our working follows the classical results of McSkimin [7] which define a complex elastic modulus governing bulk wave propagation

\[ M(\omega) = M_s(\omega) + jM_i(\omega) \]  

(1)

In terms of real quantities in epoxies the real part of the compression and shear moduli at radio frequencies (10 MHz, say) is found to be between one and three times the static (zero frequency) value, depending on the material. At the same high frequencies the values of the imaginary parts of the moduli are, typically, up to 5% of the real part for compression disturbances, and up to 12% for shear disturbances. It is therefore reasonable to make the assumption that \( M_i(\omega) \ll M_s(\omega) \), under which the phase speed is

\[ c^2(\omega) = \frac{M_s(\omega)}{\rho} \]  

(2)
Where $\rho$ is density. Under the same assumption the attenuation coefficient is

$$\alpha(\omega) = \frac{\omega M_s(\omega)}{2\rho c^2(\omega)} = \frac{\omega M_\ell(\omega)}{2c(\omega)M_s(\omega)}$$

(3a),

and the attenuation per wavelength is

$$\alpha \lambda = \pi \frac{M_\ell(\omega)}{M_s(\omega)} = \pi \tan \delta(\omega)$$

(3b),

where $\tan \delta(\omega)$ is the loss tangent. The complex modulus is sometimes expressed in an alternative form

$$M(\omega) = M_0\left[1 + r(1 - H(\omega))\right]$$

(4),

where $M_0$ is the low frequency value and the parameter $r$ represents the strength of the loss process. The frequency dependence incorporated in $H(\omega)$ represents the physics governing the loss process.

The real and imaginary parts of $M(\omega)$ become

$$M_s(\omega) = M_0\left[1 + r(1 - H_s(\omega))\right]$$

(5) and

$$M_\ell(\omega) = -rM_s H_\ell(\omega)$$

(6)

Given knowledge of $H(\omega)$ and $r$ the attenuation and phase speed are calculated using eqs. (2) and (3).

4. Basic loss models

We now consider five basic loss models that have been suggested by various workers in the context of wave modelling.

(i) Maxwell series element [8]

This arrangement is shown in Fig. 3a, and is commonly referred to as representing relaxation in a general sense; the corresponding complex modulus is

$$M(\omega) = M_0 \frac{j\omega \tau}{1 + j\omega \tau}$$

(7)

where $\tau = \eta/M_0$ and $\eta$ represents viscous reaction proportional to frequency. Clearly, at low frequency such a modulus would not support bulk wave propagation, and so it cannot represent an epoxy.

(ii) Kelvin-Voigt [9,10]

This a parallel combination of a ‘spring’ and a ‘dashpot’, shown in Fig. 3b, and is sometimes referred to as representing the creep phenomenon; the complex modulus is

$$M(\omega) = M_0\left(1 + j\omega \tau\right)$$

(8)

This function results in a realistic phase speed but an attenuation that rises as the square of frequency – which does not match the linear function observed in epoxies.

(iii) Zener anelastic solid [11]

This model can be regarded as a combination of the foregoing series and parallel cases, Fig. 3c; the most convenient way to express the modulus is through the function $H(\omega)$ in eq. (4), thus

$$\frac{M_s - M(\omega)}{M_s - M_0} = H(\omega) = \frac{1}{1 + j\omega \tau}$$

(9)

where the relaxation time constant is
\[ \tau = \frac{\eta}{M_o - M_o} \]  

(10),

and the loss parameter is

\[ r = \frac{M_o}{M_o} - 1 = \frac{c_o^2}{c_0^2} - 1 \]  

(11)

where \( c_o \) and \( c_0 \) are the high- and low-frequency asymptotic limits to the phase speed. If \( r \) is much less than unity, the attenuation is

\[ \alpha(\omega) = \frac{r\omega^2 \tau}{2c_o(1 + \omega^2 \tau^2)} \]  

(12)

and the phase speed is

\[ c(\omega) = \frac{1 + (r + 1)^2 \omega^2 \tau^2}{1 + \omega^2 \tau^2} \]  

(13)

The attenuation initially rises as frequency squared and, as we will demonstrate, this gives a reasonable but by no means perfect match to measured results over a narrow frequency band. The phase speed changes by a small amount between low- and high-frequency asymptotes.

Fig. 3. Basic viscoelastic models: (a) Series - Maxwell [12], (b) Parallel - Kelvin Voigt [13, 14], and (c) Anelastic solid - Zener [19].

(iii) Hysteretic damper [12]

This model has found use in studies of vibration damping in civil structures. It consists of an elastic element (‘spring’) in parallel with a damper whose reaction does not depend on sliding speed; the modulus is

\[ M = M_o + jm \]  

(14)

The attenuation from eq. (3) is

\[ \alpha(\omega) = \frac{om}{2c_o M_o} \]  

(15)

This is a linear function of frequency and could, in principle, represent propagation in an epoxy. However, the phase speed is
$$c(\omega) = c_o = \left( \frac{M_o}{\rho} \right)^{\frac{1}{2}}$$

(16)

This is independent of frequency, and does not comply with expectation on the basis of the Kramers-Kronig relationships, given the finite and frequency dependent attenuation. Thus, whilst such a model may be sufficient for practical purposes, it remains unsatisfactory in a more philosophical sense.

5. Multi-compartment models

There are many parallels between studies of mechanical loss and dielectric loss, and much past research has focused on physical explorations and mathematical models which could explain the behaviour of complex dielectric permittivity where changes in the frequency domain extend over a much larger bandwidth than would be expected of a simple single time constant Debye formulation such as we have alluded to earlier in eq. (9). A more detailed treatment of these ideas is to be found in McCrum et al [13]. Three of the most commonly cited empirical formulas for the frequency function $H(\omega)$ are:

Davidson and Cole [14]

$$H(\omega) = \frac{1}{1 + (j\omega\tau)^\gamma}$$

(17)

Cole and Cole [15]

$$H(\omega) = \frac{1}{1 + (j\omega\tau)^{1-\gamma}}$$

(18)

Havriliak and Negami [16]

$$H(\omega) = \frac{1}{[1 + (j\omega\tau)^{1-\gamma}]^\beta}$$

(19)

In a number of unpublished experiments we have found that the Cole-Cole formulation gives the best fit to measured attenuation and phase speed over the limited frequency range between 2 MHz and 20 MHz, see results, below. We now hypothesize that these models can be represented by groups of single time constant processes operating in parallel,

$$H(\omega) = \frac{1}{1 + (j\omega\tau)^{1-\gamma}} = \sum_{n=1}^{N} \frac{g_n}{1 + j\omega\tau_n}$$

(20)

where $g_n$ and $\tau_n$ are the weight and the time constant of the $n$th process; the weights $g_n$ sum to unity. We have used fitting between the right and left sides of eq. (20) to estimate a series of values for $g_n$ and $\tau_n$. Fig. 4 shows the imaginary part of $H(\omega)$ corresponding to a Cole-Cole distribution, with an equivalent set of Debye processes superimposed as vertical arrows where the heights correspond to the process weights $g_n$. Clearly, the seven processes shown would represent considerable complexity in the relaxation behaviour of an epoxy. It is therefore of interest to consider how few processes would be required to give an acceptable representation of attenuation over a limited frequency range that is typical of current laboratory measurements. Fig 5 shows attenuation as a function of frequency calculated on the basis of eq. (3) for three forms of $H(\omega)$: a direct implementation of the Cole-Cole model, the seven Debye processes shown on Fig. 4, and just two Debye processes, eq (20) with $N=2$. The parameters of these two processes are (strength, frequency) = (0.28, 2.51 MHz) and (0.72, 15.8 MHz). It is clear that the three calculated attenuation curves are practically coincident.

6. Experimental results

We now compare experimental measurements of attenuation and phase speed with expectation from a selection of the models described above. Compression wave attenuation over a limited frequency range was measured using techniques we have described previously [1,17,18]. The epoxy material used was Araldite 2015 (Huntsman Advanced Materials, Evenberg, Belgium); measurements were taken 20 minutes into cure at 40°C, at which point the elastic moduli would
have developed to approximately 50% of their final (end of cure) values. Fig. 6 compares the experimental data with a best fit single time constant Debye process. The fitted parameters were $c_0 = 1450$ ms$^{-1}$, $r = 0.31$ and $\tau = 40$ ns. The attenuation prediction is acceptable at frequencies below 8 MHz whilst the phase speed fit is poor. Fig. 7 shows the equivalent data for a fitted full Cole-Cole function with the same parameter values and the coefficient $\gamma$ set to 0.51. The match to both attenuation and phase speed is much improved. Finally, referring to Fig. 5, we note that an equivalent fit to just two Debye processes with the parameter values given earlier would be equally effective.

**Fig. 4.** Imaginary part of $H(\omega)$ corresponding to a Cole-Cole distribution, with an equivalent set of discrete relaxation process superimposed as vertical arrows where the heights represent the process weights $g_n$.

**Fig. 5.** Calculated attenuation on the basis of (solid curve) a direct implementation of the Cole-Cole model, (dots) the relaxation frequency distribution of figure 4, and (dashes) just two concurrent Debye single relaxation time processes of (strength, frequency) = (0.28, 2.51 MHz) and (0.72, 15.8 MHz). The curves are coincident.
Fig. 6. 2015 epoxy, 20 minutes into cure at 40°C: Attenuation (top) and phase speed (bottom) versus frequency. The solid curves represent fits of a single Debye process to the experimental data which are represented as dots.

Fig. 7. The same experimental results as Fig. 6 (dots) together with the fitted Cole-Cole model (solid curves).

7. Discussion and concluding remarks
The motivation behind this work was to provide models of ultrasonic loss in epoxies which were both physically realistic and, at the same time, based on relatively uncomplicated physical ideas. We argued that the simple Maxwell and Kelvin-Voigt models were not appropriate. The hysteretic damper model, whilst giving attenuation as a linear function of frequency, would not simulate dispersion in phase speed. Whilst this would not lead to significant errors in most propagation modelling exercises, the conflict with expectation on the basis of the Kramers-Kronig relationships was philosophically unsatisfactory. Formulations for elastic loss based on ideas from dielectrics
research, particularly that of Cole and Cole [15], gave accurate simulations of both attenuation and phase speed. They did, however, invoke underlying physical processes that were quite complicated in terms of their equivalence to a relatively large number of concomitant single time constant loss processes. However, a simple model consisting of just two Debye processes operating in parallel would give predictions of attenuation and phase speed over a narrow frequency band that are as accurate as those obtained with the more complex Cole-Cole model.

In this work we have not addressed the major scientific question as to what physical processes underpin the efficacy of the simple two-compartment model. To achieve this would require a major experimental programme involving many different epoxy materials, with different internal molecular structures. However, at this stage we are prepared to conjecture that the two degrees of freedom implied by the two compartment model are associated with two distinct aspects of the epoxy molecular arrangement. These could be the mean length of the epoxy polymer chains and the mean length of the cross-linking molecular segments.

The principal conclusion is that a simple two Debye process formulation will provide an effective and practical means to model bulk wave attenuation and phase speed in epoxy materials over the commonly used frequency band up to 20 MHz.

References
[1] R.E. Challis, R. J. Freemantle, R P. Cocker, D.L.Chadwick, D.J. Dare, C.M. Martin, A. Mendrasingham, and W. Fuller. Ultrasonic measurements related to the evolution of structure in curing epoxy resins. Plastics, Rubber and Composites, Vol. 29, pp. 109-118, 2000.
[2] Y. Wang, R.E. Challis, A.P-Y.Phang and M.E. Unwin. Bulk shear wave propagation in an epoxy: Attenuation and Phase Velocity over five decades of frequency. IEEE Trans. UFFC, Vol. 56, No. 11, pp 2504-2523, 2009.
[3] R. Kronig and H.A. Kramers. Absorption and dispersion in X-ray spectra. Zeits. F. Phys. Vol 48, pp. 174-179, 1928.
[4] M. O'Donnell, E.T. Haynes and J.G. miller. Kramers-Kronig relationship between ultrasonic attenuation and phase velocity. J. Acoust. Soc. Am. Vol. 69, pp. 696-701, 1981.
[5] R.E. Challis, F. Blarel, M.E. Unwin, J. Paul and X. Guo. Models of ultrasonic wave propagation in epoxy materials. IEEE Trans. UFFC, Vol. 56, No. 6, pp 1225-1237, 2009.
[6] A.R.H. Henni, C. Bacon and B. Hosten. In-plane vibration of thin circular structures submitted to pulse microwave. J. Acoust. Soc. Am, Vol. 119, No. 6, pp. 3782-3792, 2006.
[7] H.J. McSkimin, In: Physical Acoustics, Vol. 1A, ed W P Mason, Academic Press, New York, 1964.
[8] J.C. Maxwell. On the dynamical theory of gases. Philos. Trans. Roy. Soc. Vol 157, pp. 49-86, 1867.
[9] W.P. Thompson (Lord Kelvin). Article on Elasticity, Encyclopedia Britannica, 1875.
[10] W. Voigt. Uber innere Reibung fester Korper, insbesondere der Metalle. Ann. D. Phys. Vol. 47, pp. 671-693, 1892.
[11] C. Zener. Elasticity and Anelasticity of Metals. University of Chicago Press, Chicago, 1948.
[12] D.J. Ewins. Modal Testing: Theory and Practice. Research Studies Press, John Wiley and Sons Inc. New York, 1986.
[13] N.G. McCrum, B.E. Read and G. Williams, Anelastic and Dielectric Effects in Solids, Wiley, New York, 1967.
[14] D.W. Davidson and R.H. Cole, Dielectric relaxation in glycol, propylene glycol, and n-propanol. J. Chem. Phys., Vol. 19, pp. 1484-1490, 1951.
[15] K.S. Cole and R.H. Cole, Dispersion and absorption in dielectrics I. Alternating current characteristics. J. Chem. Phys., Vol. 9, pp. 341-351, 1941.
[16] S. Havriliak and S. Negami, A complex plane representation of dielectric and mechanical relaxation processes in some polymers. Polymer, Vol. 8, pp. 161-211, 1967.

[17] R.E. Challis, T. Alper, A.K. Holmes and R.P. Cocker, Near-plane-wave acoustic propagation measurements in thin layers of adhesive polymer. Meas. Sci. Technol., Vol. 2, pp. 59-68, 1991.

[18] R.J. Freemantle and R.E. Challis. Combined compression and shear wave ultrasonic measurements on curing adhesive. Meas. Sci. Technol. Vol. 9, pp. 1291-1302, 1998.