Proceedings of the Institute of Acoustics

ON ULTRASONIC COMPRESSION WAVE ABSORPTION IN UNFILLED AND FILLED POLYMERS

R. E. Challis, R. J. Freemantle and A. K. Holmes, Ultrasonics and Digital Signal Processing Laboratory, Keele University, Staffs, ST5 5BG, UK. Tel: -44-1782 583315; Fax: -44-1782 711093; E-mail: R.E.Challis@elec.keele.ac.uk

ABSTRACT

The increasing use of ultrasound for testing engineering structures that incorporate polymer components brings with it the need for analytical models by which wave absorption and phase velocity may be estimated as functions of frequency. Simple spring/dashpot ideas, whilst scientifically long outmoded, can provide a basis for such estimates, although there is some confusion as to which combination of springs and dashpots is appropriate. This paper identifies, by *reductio ad absurdum*, the appropriate model for unfilled polymers as being the anelastic solid, attributable to Zener. In polymers containing fillers, scattering brings about a significant increase in ultrasound absorption. It is shown that established theories of scattering account for absorption in excess of that expected in the continuous polymer phase.

INTRODUCTION

The increasing use of polymers, and particularly adhesives, in engineering has brought about new requirements for NDT of structures and their constituent materials. Ultrasonic methods are much to the fore, and in support of technological development there is presently much activity in simulating ultrasonic wave propagation in multilayered components that incorporate, for example, polymer and metal layers[1]. A requirement that has arisen in a number of centres is a compact method of providing estimates of ultrasonic wave absorption, and possibly phase velocity, in polymers as functions of frequency for input to more complex simulations. Members of the engineering community have for some time considered simple phenomenological models based on springs and dashpots as bases for working approximations to reality, following the lead of a number of text books, for example Auld[2]. There is some confusion as to which models are appropriate for this task, and it is one of the purposes of this paper to consider the implications of three of them - the series and parallel spring-dashpot combinations of Maxwell[3] and Kelvin-Voigt[4a,b], and the anelastic solid model attributed to Zener[5], fig 1. It could be said that this work takes science in a retrograde direction in that the models have long been superseded by much development in polymer science. However an appropriate choice of phenomenological model will enable the engineer to include wave absorption quantitatively, and by means of a few parameters, into a more complex simulation of wave propagation in a composite structure. The absorption and phase velocities that would be expected on the basis of the three models is derived, and it is shown that only the anelastic solid model yields results that match observed phenomena.

Many engineering polymers include filler particles for bulking and/or property modification, and scattering at fillers is expected to significantly increase wave absorption over that in the base polymer. The second part of this paper applies conventional scattering theory[6] to the problem of adhesives containing mineral fillers. It is shown that such theory gives a good estimate of measured absorption in filled materials, and that the effect of fillers is indeed to greatly increase absorption.

EMPIRICAL THEORY: UNFILLED POLYMERS

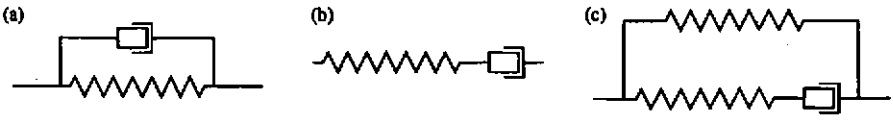


Fig. 1. Phenomenological models of viscoelasticity. (a) Kelvin-Voigt[3], (b) Maxwell[4] (c) Zener[5].

We approach this problem through the somewhat idealised case of the one dimensional plane wave equation that incorporates loss mechanisms in the form of a complex frequency dependent modulus. With the time variable transformed to real frequency ω we have

$$-\omega^2 y\ (x,\omega) = \frac{M(\omega)}{\rho}\ \frac{\delta^2 y\ (x,\omega)}{\delta x^2} \qquad (1)$$

$M(\omega)$ is the modulus, ρ the density, and y the wave dependent variable, pressure, say, and x is the propagation direction. $M(\omega)$ has real and imaginary parts

$$M(\omega) = M_R + M_I \qquad (2)$$

For forward travelling waves eq 1 has solutions of the form

$$y(x,\omega) = y(0,\omega)e^{-\alpha(\omega)x}\ e^{-j\beta(\omega)x} \qquad (3)$$

Where $\alpha(\omega)$ and $\beta(\omega)$ are the imaginary and real parts of the wavenumber. Following McSkimin[7] it can be shown that

$$\alpha^2 = \frac{\omega^2\rho}{2M_R F^2}\ (F-1) \qquad (4)$$

and

$$\beta^2 = \frac{\omega^2\rho}{2M_R F^2}\ (F+1) \qquad (5)$$

where

$$F = \frac{|M(\omega)|}{M_R(\omega)} \qquad (6)$$

Phase velocity is obtained from eq 5, noting that $\beta = \omega/c(\omega)$

$$c^2(\omega) = \frac{2M_R}{\rho}\ \frac{F^2}{(F+1)} \qquad (7)$$

Absorption per wavelength is obtained from eqs 4 and 5, noting that $(\alpha\lambda) = 2\pi\alpha/\beta$.

$$\alpha\lambda = 2\pi\left(\frac{F-1}{F+1}\right)^{1/2} \tag{8}$$

Each of the models of viscoelasticity mentioned in the introduction imply a particular form of $M(\omega)$ and F, and through these the behaviour of the absorption coefficient and phase velocity as functions of frequency can be obtained. For the simple parallel element (fig 1a) we get,

$$M = M_0 + j\omega\eta = M_0(1 + j\omega\tau) \tag{9}$$

with appropriate manipulations of eqs 4-8. This yields phase velocity, attenuation per wavelength and attenuation thus, with $c_0^2 = M_0/\rho$,

$$c(\omega) = c_0\left[\frac{2(1 + \omega^2\tau^2)}{(1 + \omega^2\tau^2)^{1/2} + 1}\right]^{1/2} \tag{10}$$

$$\alpha\lambda = 2\pi\left[\frac{(1 + \omega^2\tau^2)^{1/2} - 1}{(1 + \omega^2\tau^2)^{1/2} + 1}\right]^{1/2} \tag{11}$$

$$\alpha(\omega) = \frac{\omega}{c_0}\left[\frac{(1 + \omega^2\tau^2)^{1/2} - 1}{2(1 + \omega^2\tau^2)}\right]^{1/2} \tag{12}$$

For the series case (fig 1b) we get

$$M = M_0\, j\omega\tau/(1 + j\omega\tau) \tag{13a}$$

where

$$\tau = \eta/M_0 \tag{13b}$$

and

$$c(\omega) = c_0\left[\frac{2\omega\tau}{\omega\tau + (1 + \omega^2\tau^2)^{1/2}}\right]^{1/2} \tag{14}$$

$$\alpha\lambda = 2\pi\left[\frac{(1 + \omega^2\tau^2)^{1/2} - \omega\tau}{(1 + \omega^2\tau^2)^{1/2} + \omega\tau}\right]^{1/2} \tag{15}$$

$$\alpha(\omega) = \frac{\omega}{c_0}\left[\frac{(1 + \omega^2\tau^2)^{1/2} - \omega\tau}{2\omega\tau}\right]^{1/2} \quad (16)$$

For the anelastic solid case (fig 1c) we get

$$M = M_0\frac{(1 + j\omega\tau a)}{(1 + j\omega\tau/a)} \quad (17)$$

where $\tau = \frac{\eta}{\Delta M}\left(\frac{M_0 + \Delta M}{M_0}\right)^{1/2}$ and $a^2 = (M_0 + \Delta M)/M_0$

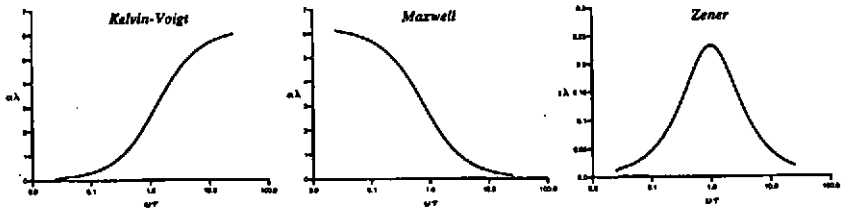
For $\Delta M << M_0$ this yields

$$c(\omega) = c_0\left[\frac{1 + \omega^2\tau^2a^2}{1 + \omega^2\tau^2}\right]^{1/2} \quad (18)$$

$$\alpha\lambda = \pi(a - 1/a)\frac{\omega\tau}{1 + \omega^2\tau^2} \quad (19)$$

$$\alpha(\omega) = (a - 1/a)\frac{\omega^2\tau}{2c_0(1 + \omega^2\tau^2)^{1/2}(1 + \omega^2\tau^2a^2)^{1/2}} \quad (20)$$

The velocities and absorption per wavelength for the three phenomenological models are plotted on fig 2, from which their applicability as engineering approximations to compression wave propagation in polymers will become clear.



(a) (b) (c)

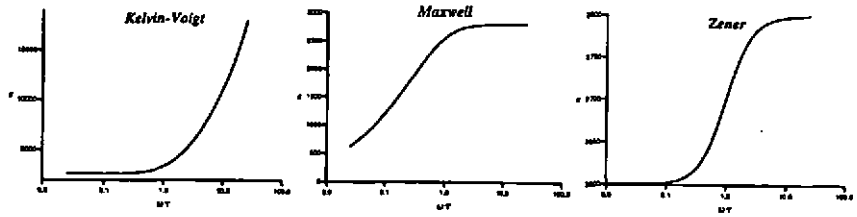


Fig. 2. Absorption per wavelength, Np, and phase velocity, ms^{-1} as predicted on the basis of the three models, a,b, and c of fig. 1.

(i) Parallel elements (fig 1a):
($\alpha\lambda$) rises asymptotically to $2\pi N_\rho$ at high frequency. In most polymers $\alpha\lambda$ peaks around $\omega\tau = 1$ and falls as frequency increases thereafter; the peak value is generally around an order of magnitude less than 2π. The phase velocity $c(\omega)$ can take a realistic value at low frequencies, but would be expected to rise indefinitely at high frequencies. In most polymers $c(\omega)$ rises from a low frequency value to a slightly higher value (+3%, say) at frequencies $>>1/\tau$.

(ii) Series elements (fig 1b):
($\alpha\lambda$) has the high value, $2\pi N_p$ at low frequency and falls to zero at high frequency. Phase velocity is zero at low frequency, and rises to a value at high frequency governed by the elastic element and material density $c_0 = (M_d/\rho)^{1/2}$. Attenuation and velocity functions of this kind are unlikely to be observed in polymers.

(iii) Anelastic solid (fig 1c):
($\alpha\lambda$) rises to a peak value at $\omega\tau = 1$ and falls off at high frequency. Phase velocity rises from a low frequency value to a value slightly greater at high frequencies, $\omega\tau>>1$. Both these behaviours are observed in a wide range of polymers. Fig 3 shows an LMS fit of measured absorption to an anelastic solid model for a cured epoxy polymer. Many amorphous polymers would be expected to exhibit absorption and phase velocity behaviour that would change over a wider range of frequencies than the predictions of the anelastic solid. These could, in principle, be modelled by a distributed system of relaxation processes, to which many approximations exist.

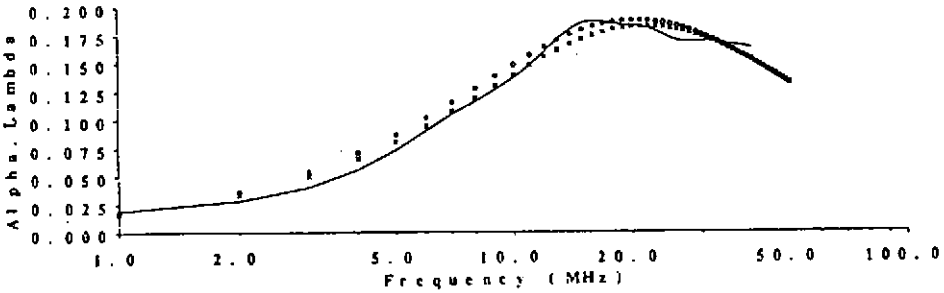


Fig. 3. LMS fits of anelastic solid model to measured absorption data to give ($\alpha\lambda$) versus frequency. Dotted curves are fits to phase velocity data, crossed curves are fits to absorption data. Solid line is measured data.

SCATTERING: FILLED POLYMERS

There are a large number of approaches to scattering in filled solids[8] and a review is beyond the scope of this paper. In order to explain excess absorption in filled adhesives we have adopted the approach of Ying and Truell[6] to solve the diffraction problem at a single spherical particle, from which scattered compression wave potentials take the form,

$$\phi_c = \sum_{n=0}^{\infty} A_n h_n(kr) P_n(\cos\theta) \tag{21}$$

where h_n are nth order spherical Hankel functions of the first kind and P_n are nth order Legendre polynomials. Solution of the wave equation at the particle boundary gives the coefficients A_n where n = 0, 1, 2 correspond to mono-, di-, and quadrapole scattered partial waves. For small (ka) A_n diminishes rapidly for $n > 2$. In the long wavelength limit the A_n are combined to give a complex wavenumber β for the filled material, as a function of the continuous phase wavenumber k, the particle radius R, and the volume fraction of dispersed particles, ϕ.

$$\left(\frac{\beta}{k}\right)^2 = 1 + \frac{3\phi}{jk^3R^3}(A_0 + 3A_1 + 5A_2) - \frac{27\phi^2}{k^6R^6}(A_0A_1 + 5A_1A_2) - \frac{54\phi^2}{k^6R^6}\left(A_1^2 + \frac{5}{3}A_0A_2 + 3A_1A_2 + \frac{115}{21}A_2^2\right) \tag{22}$$

The first bracketed term gives the contribution due to simple scattering (Foldy[9]), and the second and third bracketed terms give additional contributions due to multiple scattering following the formulations of Waterman and Truell[10] and Lloyd and Berry[11] respectively. We have extended eq 22 to incorporate distributions of particle size characteristic of real filled adhesives. In our implementation of this theory the code can input k as absorption and phase velocity data measured using a short pulse technique[12], or the anelastic solid model can be used.

EXPERIMENTS AND RESULTS

Test layers of epoxy adhesive (AY105 + HY2958, Ciba-Geigy Ltd) of thickness 200 μm were formed between float glass blocks. Samples were prepared with no filler particles, and also with increasing volume fractions of talc particles with a median Stokes radius of around 8 μm. Absorption per wavelength and phase velocity were measured[12] for the unfilled bond and input (k) to the scattering model which was then used to calculate the expected absorption and phase velocity for the composite material. The simulation was then compared to experimental measurements on the filled bonds, fig 4. All three implementations of eq 22[9,10,11] gave similar results to the one shown for ($\alpha\lambda$), whereas the Waterman and Truell[10] implementation gave the best match between predicted and measured phase velocity dispersion (not shown).

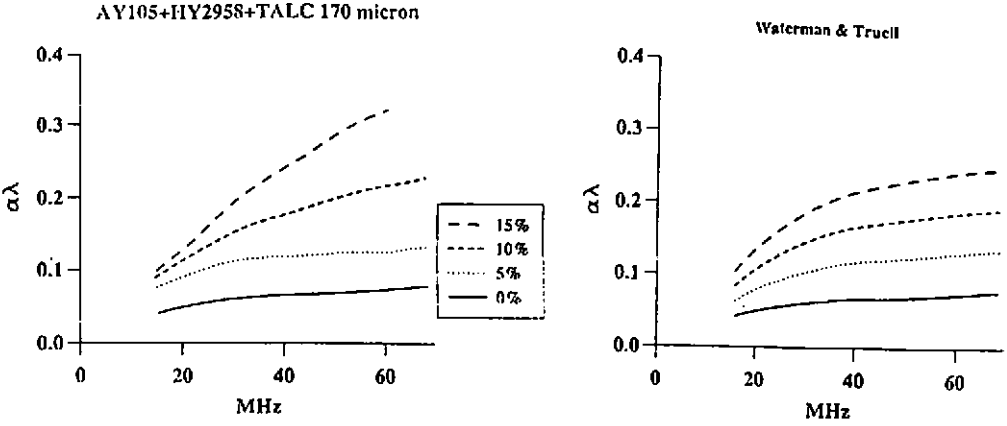


Fig. 4. Absorption per wavelength for talc in epoxy (a) experiments, and (b) simulation on the basis of[10].

CONCLUSIONS

In unfilled polymers compression wave absorption and phase velocity variation as functions of frequency cannot be simulated by the simple viscoelastic models of Maxwell and Kelvin-Voigt. A reasonable approximation can be made using the anelastic solid model. It is to be noted that this is merely a phenomenological model and that any broader scientific significance, and implications for the molecular phenomena underlying the observed wave propagation properties, should only be made with appropriate caution. More rigorous approaches, such as the correspondence principle[13], have greater universality. However, the model does provide a means to make estimates of wave phenomena in an engineering context.

Scattering at mineral fillers included in polymers greatly increases observed absorption, and the effect can be simulated quantitatively using conventional scattering theories for small (kR) and filler volume fractions up to 15%.

REFERENCES

1. Kinra, V.K. et al. J. Acoust. Soc. Am., **95**, 3059-3074, 1994.
2. Auld, B.A. *Acoustic Fields and Waves in Solids*, (2, 87-), Krieger, Florida, 1990.
3. Maxwell, J.C. Philos. Trans. Roy. Soc., **157**, 49- , 1867.

4a. Lord Kelvin (W.P. Thompson). Article on elasticity. Encyclopedia Britannica, 1875.

4b. Voigt, W. Ann. d. Phys., **47**, 671- , 1892.

5. Zener, C. *Elasticity and Anelasticity of Metals*. University of Chicago Press, Chicago, 1948.
6. Ying, C.F. and Truell, R. J. Appl. Phys., **27**, 1086-1097, 1956.
7. McSkimin, H.J. Ultrasonic methods for measuring the mechanical properties of liquids and solids. In *Physical Acoustics*, Part 1A, (ed. W.P. Mason). Academic Press, New York, 1964.
8. Anson, L.W. and Chivers, R.C. J. Phys. D: Appl. Phys., **26**, 1566-1575, 1993.
9. Foldy, L.L. Phys. Rev., **67**, 107-119, 1945.
10. Waterman, P.C. and Truell, R. J. Math. Phys., **2**, 512-537, 1961.
11. Lloyd, P. and Berry, M.V. Proc. Phys. Soc., **91**, 678-689, 1967.
12. Challis, R.E. et al. Meas. Sci. Technol., **2**, 59-68, 1991.
13. Beltzer, R.K. *Acoustics of Solids*, Springer-Verlag, 81-84, 1988.