THE CONSISTENCY OF PHENOMENOLOGICAL MODELS OF ULTRASONIC WAVE PROPAGATION IN A CURING THERMOSET

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ABSTRACT. This paper investigates the use of phenomenological models of viscoelasticity to simulate ultrasonic compression wave propagation in a curing thermoset. Kelvin-Voigt and Maxwell models do not give physical results whilst the anelastic solid (Debye) formulation and its Cole-Davidson (CD) extension provide a qualitative match to experiment, although with some inconsistencies. The CD model when fitted to experimental phase velocity data gave parameters that could be used to track molecular polydispersity in the curing thermoset.

INTRODUCTION

Thermosets and other polymers continue to find increasing use as parts of safety critical structures in the aerospace, automotive, marine and other product sectors. There are increasing requirements for quality assurance in the materials and the final structures as well as for non destructive evaluation of the product when in service. The formation of thermoset materials can be followed in the laboratory by a wide range of techniques such as DSC, IR, NMR, DMA, dielectric spectroscopy and ultrasound. Ultrasonic methods have the considerable advantage that they are non invasive and access to the thermoset material during formation is possible with appropriate modifications to tooling. As a thermoset cures its viscoelastic properties will develop from the liquid state, consisting of individual resin and hardener molecules, through an intermediate gel-like state, consisting of partially polymerised molecules, to a final cross linked solid which could be regarded as a single very large molecule. In principle, these states can be described in terms of the complex elastic modulus which governs ultrasonic wave propagation, or equivalently by functions related to the complex modulus. As a precursor to developing a process model for the formation of a thermoset it would be useful to identify a simple mechanical model which represents the viscoelastic state of the curing material; this would enable ultrasonic propagation data to be parameterized into a few variables that could be used to track the cure process. In this paper we consider classical phenomenological models of viscoelasticity and their applicability to tracking thermoset cure.
FIGURE 1. Phenomenological models of viscoelasticity: (a) Kelvin-Voigt, (b) Maxwell, and (c) the anelastic solid.

ULTRASONIC MEASUREMENTS

In a process context the most convenient measurements are compression wave attenuation coefficient $\alpha(\omega)$ and phase velocity $c(\omega)$ as functions of frequency. The attenuation shows a near linear dependence on frequency right through the cure cycle, the function rising to a maximum slope around the gel point of the material. Phase velocities increase as the elastic modulus governing propagation develops during the cure, and there is a small dispersion between low and high frequency values due to the viscoelastic nature of the material [1]. We seek a phenomenological model of viscoelasticity that would result in these propagation properties in the frequency domain.

PHENOMENOLOGICAL MODELS OF VISCOELASTICITY

Figure 1 shows three basic models of viscoelastic behaviour: Kelvin-Voigt, Maxwell, and the anelastic solid (Debye) arrangement, see McCrum [2]. Using the working of McSkimin [3] and ourselves [4] the Kelvin-Voigt model gives for phase velocity

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

where $\omega$ is radian frequency, $c_o$ is a notional low frequency velocity ($c_o^2 = M_o/\rho$ where $\rho$ is density) and the relaxation time $\tau$ is the ratio of the viscosity to the modulus of the material $\tau = \eta/M_o$. The phase velocity at high frequencies approximates to $c_o (2\omega\tau)^{1/2}$, a behavior not observed in thermoset materials. Whilst not included here, it can be shown that the attenuation per wavelength travelled by a wave at high frequency approaches $2\pi$ Nepers (54 dB) which is also not observed in practice [5]. The Maxwell model yields phase velocity of the form

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

This function tends to zero at low frequency ($\omega \tau << 1$) and reaches a high frequency value of $(c_o^2 = M_o/\rho)^{1/2}$ whilst the attenuation is highest at low frequency (6 Nepers per
wavelength) and approaches zero at high frequency [5]. Neither of these behaviors have been observed in thermosets. The anelastic solid model gives the phase velocity as

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

(3)

The low frequency velocity is \( c_0^2 = (M_0 / \rho)^{\frac{1}{2}} \), rising asymptotically to a high frequency value \( c_\infty = ac_0 \), where \( a \) is a relaxation strength parameter \( a^2 = (M_0 + \Delta M)/M_0 \). The relaxation time \( \tau = a \tau / \Delta M \). Experimental observations indicate similar but not identical behavior in curing thermoset materials, which we will investigate further in a later section. The attenuation coefficient predicted by the anelastic solid model for \( a \) close to but not equal to unity is

\[ \alpha(\omega) = \frac{(a^2 - 1)}{2c_0} \frac{\omega^2 \tau}{1 + \omega^2 \tau^2}. \]  

(4)

This follows \( \omega^2 \) at low frequency and rises to the high frequency asymptotic value

\[ a_\infty = \frac{a^2 - 1}{2c_0 \tau}. \]  

(5)

Between these two limits there is a region around \( \omega \tau = 1 \) where \( a \) is approximately a linear function of frequency. At any given frequency a plot of \( \alpha \) versus \( \tau \) reaches a peak value at \( \omega \tau = 1 \). During a cure reaction \( \tau \) is expected to increase with time into cure and so an \( \alpha \) versus time plot at a fixed frequency will peak at a time corresponding to \( \omega \tau = 1 \). The height of the peak will yield an estimate of \( a \) if \( c_0 \) is known whilst the tracking frequency will yield an estimate of \( \tau \) [6]. The parameters \( a \) and \( c_0 \) can also be obtained from the loss tangent \( (\tan \delta) \) which is the ratio of the imaginary to the real parts of the modulus governing propagation; it corresponds to the attenuation per wavelength traveled by the wave and can be shown to be

\[ \tan \delta = \frac{a^2 - 1}{\pi} \frac{\omega \tau}{1 + a^2 \omega^2 \tau^2}. \]  

(6)

The peak value on a frequency plot occurs when \( a \omega \tau = 1 \) and is given by

\[ \frac{1}{2} \left( \frac{a - 1}{a} \right) \left( \frac{c_\infty - c_0}{c_0} \right). \]  

(7)

EXPERIMENTS AND MODEL FITTING

The purpose of the experiments was to investigate the extent to which the wave propagation phenomena outlined above could be represented by the anelastic solid model. The thermoset was a commercial epoxy resin-hardener combination (Araldite 2011, Vantico Ltd.). It was cured in a 2.5mm thick slab mould at 30°C for 720 minutes.
Using a through-transmission goniometer rig [7] ultrasonic compression wave phase velocity, attenuation coefficient, and $\tan\delta$ as functions of frequency were recorded at two minute intervals during the cure cycle. For each record estimates of $a$ and $\tau$ were obtained by LMS fitting first equation 3 to measured phase velocity data and then equation 4 to attenuation data. Typical results are shown on figures 2 and 3.

It is clear from figures 2 and 3 that the fit to phase velocity data is reasonable whilst the fit to attenuation is poor. The two estimates for parameter $a$ were 1.06 and 1.05 for the velocity and attenuation data respectively, showing reasonable agreement. The corresponding estimates for $\tau$ were 47ns and 22ns respectively indicating considerable inconsistency. Fits involving $\tan\delta$ were similarly inconsistent and are not shown here. Given these inconsistencies in the derived parameters and the poor fit to the attenuation data on figure 3 we conclude that the simple anelastic solid formulation will not model observed behavior in a curing thermoset. We believe that the reason for this could derive from polydispersity in molecular types and arrangements in the curing material, which we consider next.
Molecular Polydispersity

The cure process begins with a relatively simple mixture of resin and hardener molecules which would be expected to respond fairly uniformly to an exciting acoustic field. As cure proceeds to gel there will be a continuously changing mixture of partially polymerized molecular segments whose size and local entanglements may vary considerably at any given time within the mixture. Towards solidification there will be many molecular sub species which may be physically entwined with each other in complex and varied ways. We would thus expect the mechanical responses of the polymerizing mixture to vary locally, from molecule to molecule or from molecular cluster to molecular cluster. Such molecular polydispersity would be expected to result in a broad distribution of relaxation processes throughout the material. Many different relaxation times would contribute to the overall material response to ultrasonic waves, and the outcome would be a broadening of the phase velocity and attenuation functions in the frequency domain. In the context of the phenomenological models described earlier such broadening can be achieved through adaptation of the Debye expression for material parameters, following ideas developed originally in the context of dielectric spectroscopy [2, 8, 9, 10]. We consider here the Cole-Davidson model [9]. The frequency domain expression for the elastic modulus underlying equation 3 is

\[ M(\omega) = M_0 \left[ \alpha^2 - (\alpha^2 - 1)H(\omega) \right] \]  

where

\[ H(\omega) = \frac{1}{1 + i\omega \tau} . \]  

The phase velocity is obtained from the real part of \( M(\omega) \) whilst the attenuation is obtained from both the real and the imaginary parts, through the expression for \( \tan \delta \), equation 6. The Cole-Davidson modified form for \( H(\omega) \) is

\[ H(\omega) = \frac{1}{(1 + i\omega \tau)^\beta} . \]  

It leads to modified expressions for the real and imaginary parts of \( M(\omega) \) and thence phase velocity and attenuation. The parameter \( \beta \) in equation 10 has the effect of broadening the frequency range over which phase velocity and attenuation change for a given relaxation strength \( \alpha \). It provides a crude method to invoke a distribution of relaxation times \( \tau \) and it has potential to give a quantifying index of molecular polydispersity in the material. In order to investigate the applicability of the Cole-Davidson model to ultrasonic data we have adapted equations 3 and 4 to incorporate the frequency function of equation 10 and have then carried out LMS fits to our measured data, figures 4 and 5. We note from figures 4 and 5 that the fits to the experimental data are greatly improved compared to the single time constant fits shown on figures 2 and 3. The two estimates for parameter \( \alpha \) are now 1.11 and 1.06 for the phase velocity and the attenuation data respectively. The corresponding values for the now notional central time constant were 61ns and 100ns respectively. The fitted values for \( \beta \) were 0.8 and 0.2. We conclude that the Cole-Davidson model provides a better representation of the viscoelasticity in a curing thermoset than does a simple single time constant formulation, but that the results remain inconsistent between phase velocity and attenuation data for the material and cure cycle used in these experiments. These inconsistencies will be discussed later in the paper.
FIGURE 4. LMS fit of the Cole-Davidson model (solid line) to measured phase velocity data (dotted line).

FIGURE 5. LMS fit of Cole-Davidson model (solid line) to measured attenuation data (dotted line).

TRACKING THERMOSET CURE

Notwithstanding the inconsistencies noted above we have investigated the possibility of using the fitted parameters for relaxation strength $\alpha$ and molecular polydispersity $\beta$ as a means to track cure. The two parameters were obtained from fits to the phase velocity data and are shown plotted on figures 6 and 7 versus time expressed as a percentage of the total cure cycle time of 720 minutes. From these figures we note that at the beginning of cure the relaxation strength is relatively low and that $\beta$ is close to unity with a value of 0.8. This implies relaxation mechanisms close to Debye, with limited degrees of freedom and is expected on the basis that only two relatively simple molecular types, resin and hardener, are present in the mixture. As the cure process approaches gel around 20% cure time the relaxation strength increases to a maximum and $\beta$ passes through a minimum value of 0.4. These changes correspond to the growth of longer molecular chains with minimal cross linking but significant entanglements.
FIGURE 6. Relaxation strength parameter $a$ as a function of cure time %.

FIGURE 7. Molecular dispersion parameter $\beta$ as a function of cure time %.

There may at this time be many different molecular sizes present in the curing mixture leading to a broad range of relaxation times and consequently a low value of $\beta$ and a high value of $a$. As cross linking begins and polymerisation proceeds the molecular structure ‘tightens up’ leading to fewer degrees of mechanical freedom on the molecular scale, reduced $a$ and increasing $\beta$. This process continues up to about 40% cure time when a new and interesting phenomenon occurs. A rise in $a$ and a new fall in $\beta$ to a minimum at around 50% cure imply significant structuring in the evolving molecules. This we attribute to secondary amine reactions associated with cross linking, again leading to polydispersity in molecular arrangements and the observed parameter changes. After 50% cure time $\beta$ steadily increases as cross linking proceeds indicating reducing molecular polydispersity. There are inflexions in both $a$ and $\beta$ at around 80% cure time that we cannot at present explain. At the end of cure (100%) we note that $\beta$ reaches its highest value of 0.86; the number of degrees of freedom in the molecular arrangements is low as the thermoset is now a rigid cross linked solid. We note that at 100% cure $\beta$ is still rising and it is possible that we would have observed further increases in its value had we allowed cure to proceed for a longer time. We have not shown a plot of relaxation time during the cure cycle. Values of $\tau$ obtained from the Cole-Davidson fits represent some notional central time within a distribution of relaxation times. All through cure we have observed that the fitted relaxation times range between 40 ns and 90 ns and probably represent $\beta$-relaxations associated with short molecular segments rather than the principal $\alpha$-relaxation time associated with very large macromolecules and which are generally too low to lie within the bandwidth of our measurements once the gel point is passed. The fitted values of $\tau$ varied approximately inversely with $\beta$ - as $\beta$ increased $\tau$ reduced and vice-versa. We offer no explanation for this at the present time.
DISCUSSION AND CONCLUDING REMARKS

This paper has sought phenomenological models of viscoelasticity that could be used as a basis to simulate ultrasonic wave propagation in a curing thermoset. We note here that whilst such models offer only limited scientific insight in the context of molecular physics they do have potential for macroscopic modeling of polymer forming processes in an engineering context. The Kelvin-Voigt and Maxwell models were shown to be inappropriate whilst the anelastic solid or Debye formulation, and its Cole-Davidson extension, have potential because their predictions approach observed behavior. When fitting these models to measured wave propagation data there were inconsistencies between phase velocity and attenuation fits. It is probable that these are due to the limited bandwidth available for our measurements (2MHz to 12MHz), given that the effects of a single relaxation process are expected to extend over more than one decade in frequency. Using parameters fitted to phase velocity data we have shown that the Cole-Davidson model has potential to track a cure process in terms of a relaxation strength parameter and a parameter representing molecular polydispersion.

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REFERENCES