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# Isothermal epoxy-cure monitoring using nonlinear ultrasonics

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ABSTRACT

Isothermal curing of LY 1564SP resin in an aluminium-adhesive-aluminium laminate is investigated, using a nonlinear ultrasonic immersion technique, to prove its applicability for this type of dynamic material transformation. For verification and comparison, epoxy-cure kinetics and rheological behavior are measured using differential scanning calorimetery (DSC) and dynamic mechanical analysis (DMA). Results reveal that the nonlinear ultrasonics, based on noncollinear wave mixing, can successfully be applied to in situ epoxy-cure monitoring—for example, to adhesive bonds—with reliable detection of gelation and vitrification time instants.



## 1. Introduction

Ultrasonic measurements are widely used to detect dynamic changes and transition points in polymer materials. For example, they are successfully employed to monitor solidification and shrinkage processes [1,2], polymerization [3], physical ageing [4], and epoxy cure [5–8]. The main advantages of the ultrasonic techniques include relatively low cost, high sensitivity, and in-line and real-time measurement possibilities. The curing processes inherent for epoxy resins are the practically important example, because measuring the cure characteristics helps to develop an optimal cure process, which would achieve the best material performance. The use of ultrasonics also enables real-time quality control. The reported results demonstrate that ultrasonic measurements, which employ longitudinal and/or shear waves, are applicable for monitoring of thin epoxy layers [8–14] and for detection of gelation time when a viscous epoxy transforms into an elastic gel [5,7,15–20].

Nonlinear ultrasonics can often be more sensitive to material properties than linear ultrasonics. Historically, nonlinear ultrasonics usually employs a multiple harmonic generation of a single monochromatic wave, rather than other nonlinear measurement techniques. These harmonic generation measurements are relatively easy to implement. However, data from such measurements can be difficult to interpret, because of similar nonlinearity effects occurring in an acoustic channel, electronics, or a surrounding medium that masks a target signal. Fortunately, one wave-mixing technique [21] is free of these disadvantages, allowing for easy frequency-domain separation of a target sum and/or difference frequencies generated in the specimen from the multiples generated by other sources. Moreover, this wave-mixing technique, in its noncollinear form (when the primary beams interact at non-zero angles), further improves detection of the target waves, because such waves are also separated in space from other signals.

Despite the high potential of noncollinear wave mixing for nondestructive testing applications, noncollinear wave mixing is still not verified well enough for epoxy-cure monitoring. Also, there is at this time insufficient information about ultrasonic detection of the vitrification time (i.e., when the mobility of reactive groups vanishes and the epoxy undergoes a rubber-glass transition, then quickly approaches a solid state [22]). In this paper, we present an experimental study aiming at a partial filling of this knowledge gap. The presented nonlinear elastic wave-mixing technique enables monitoring of the epoxy cure in a thin layer (about 0.2 mm thick), with a robust detection of the characteristic points (gelation and vitrification). The importance of this method is illustrated, showing that the nonlinear-elastic material response has a higher sensitivity to the epoxy rheology compared to the linear response. Independent verifications are performed, with commonly used rheometry (dynamic mechanical analysis, DMA) and differential scanning calorimetry (DSC) measurements of the isothermal epoxy cure. Finally, the advantages and disadvantages of the three methods are compared.

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## 2. Noncollinear ultrasonic wave mixing

In isotropic nonlinear materials (described with the third-order elastic constants *l,m,n* [21]), the *resonant conditions* might exist wherein two elastic waves could possibly interact to generate scattered waves with mixed (sum and difference) frequencies. These conditions are

$$\omega_r = \omega_1 \pm \omega_2, \tag{1}$$

$$\mathbf{k}_r = \mathbf{k}_1 \pm \mathbf{k}_2, \tag{2}$$

where frequencies $\omega_1$, $\omega_2$, and $\omega_r$ represent two initial waves and the resonant wave, respectively. The parameters $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_r$ are their wave vectors. Even if the resonant conditions were satisfied, the scattered wave amplitude can be zero for all parameter combinations (polarization restriction). In [21], it is shown that only 10 of 54 possible combinations of two initial compressional L, and/or shear SV, and/or shear SH waves generate scattered resonance waves.

Two wave interaction cases

$$\mathrm{SV}(\omega_1)+\mathrm{L}(\omega_2)\rightarrow \mathrm{L}(\omega_1+\omega_2), \tag{3}$$

$$\mathrm{SV}(\omega_1)+\mathrm{SV}(\omega_2)\rightarrow \mathrm{L}(\omega_1+\omega_2), \tag{4}$$

appear to be the most suitable for nondestructive testing purposes [23]. These interactions can be used in single-sided or double-sided-access measurement modes (see Fig. 1), using either contact or immersion ultrasonic measurement techniques. This property enables us to find incident angles of primary waves such that the generated longitudinal wave strikes the specimen/liquid interface perpendicularly. This perpendicular incidence also allows us to achieve the highest energy rate for the nonlinear wave and helps to simplify the acoustic channel, because there is no need to rotate the receiver at a specific angle.

Fig. 1 shows a submerged wave-mixing technique scheme with two modifications, using either reflected or transmitted scattered waves. For thick objects, the transmitted wave might be preferred, because the target scattered wave has a shorter path (i.e., less attenuation) and can be detected more readily. The advantage of the reflected wave scheme is in its single-side access to the specimen.

Interaction $\mathrm{SV}(\omega_1)+\mathrm{SV}(\omega_2)\rightarrow \mathrm{L}(\omega_1+\omega_2)$ between two shear waves appears most promising, because in this case it maintains a wave mode separation. However, this interaction requires a large angle between the two interacting waves (usually more than 120°). Therefore, it cannot be used for materials having low ultrasonic wave velocities; a conventional immersion measurement technique should be employed instead. This angle restriction can be overcome, however, by employing the interaction $\mathrm{SV}(\omega_1)+\mathrm{L}(\omega_2)\rightarrow \mathrm{L}(\omega_1+\omega_2)$ between shear and longitudinal waves. Note that

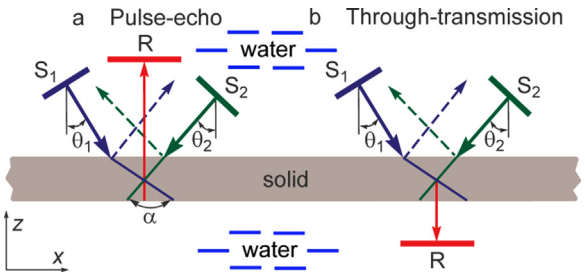


**Fig. 1.** Pulse-echo and through-transmission arrangement of transducers for single-side and double-side access measurements. Shown are the scattered wave receiver R, the pump wave sources $S_{1,2}$ having inclination angles $\theta_{1,2}$, respectively. $\alpha$ is the wave interaction angle. Red lines show propagation paths of the resonant wave. Dashed lines mark the specularly reflected pump waves. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

both chosen interactions are the functions of one third-order elastic constant $m$ only, as illustrated in Table 2 in [21]. Imaging and testing of two other elastic constants, $l$ and $n$, require other interactions.

The interaction (4) between two shear waves was employed for the epoxy-cure monitoring. The corresponding nonlinear wave amplitude coefficient (with dimension length$^{-3}$) is [21]

$$W = D_L\frac{1+d}{2\gamma^2}[C_1\ \cos\ 2\alpha + C_2\cos^2\alpha - C_3\sin^2\alpha] \approx D_L\frac{1+d}{2\gamma^2}m\ \cos\ 2\alpha, \tag{5}$$

where the following notations are used:

$$D_L = d/(4\pi c_L^2\rho)(\omega_1/c_r)^3, \tag{6}$$

$$\gamma = c_S/c_L, \tag{7}$$

$$d = \omega_2/\omega_1. \tag{8}$$

Parameter $\alpha$ is the wave interaction angle, $c_L$ and $c_S$ are the longitudinal and shear wave velocities in a medium, respectively, $\rho$ is the material density, and $c_r$ is the nonlinear wave velocity in a medium (in our case $c_r = c_L$). The constants $C_i$ have simple relations:

$$C_1 = \mu+\frac{A}{4},\quad C_2 = \lambda+\mu+\frac{A}{4}+B,\quad C_3 = \frac{A}{4}+B,\quad C_4 = B+2C,$$
$$C_5 = \lambda+B, \tag{9}$$

with third-order elastic constants and Lamé parameters $\lambda$ and $\mu$. Prediction of the nonlinear wave amplitude coefficient enables us to choose the measurement conditions under which the highest nonlinear wave amplitude is expected, and maintains the best signal-to-noise ratio. Note that the nonlinear wave amplitude coefficient has a dependence on the $\omega_1^3$ (see Eq. (5)), indicating that the noncollinear wave interaction is more strongly pronounced at higher frequencies.

An example of a nonlinear wave amplitude calculation is shown in Fig. 2 for aluminium studied in [24]; its properties are listed in Table 1.

Prediction of the nonlinear wave amplitude is carried out when attenuation is not taken into account and $\omega_1$ is 4 MHz. Fig. 2a shows the predicted nonlinear wave amplitude coefficient $W$ (red curve), the nonlinear wave scattering angle $\psi$ (blue curve), and the wave interaction angle $\alpha$ (black curve) over the entire allowed frequency range [21]. The scattering angle $\psi$ is calculated between the first pump-wave vector of frequency $\omega_1$ and the nonlinear wave vector [21]. When ultrasonic experiments are performed using the immersion technique, it is useful to employ a procedure that allows tuning an acoustical channel for noncollinear wave mixing [23]. The optimized parameters (the nonlinear wave amplitude coefficient $W_T$, and the inclination angles $\theta_1$ and $\theta_2$ for the pump-wave sources) when the nonlinear wave strikes the aluminium/water interface perpendicularly for the through-transmission mode are shown in Fig. 2b. $W_T$ is the nonlinear wave-amplitude coefficient when the energy-transmission coefficients between the liquid–solid ($T_1$ and $T_2$), and the solid–liquid ($T$) interfaces are taken into account. Therefore, the amplitude function is $W_T = W\times T_1\times T_2\times T$ — presented in [23] in detail.

As seen in Fig. 2, the predicted maximum of the nonlinear wave amplitude coefficient in the frequency ratio range 0.6–1.66 is shifted from the initial frequency ratio ($d=1.56$, Fig. 2a) to the frequency ratio $d=1.32$. This shift occurs because of the energy transmission and reflection coefficient between the water–aluminium and aluminium–water interfaces.

Since commercially available ultrasonic transducers of standard frequencies are available, it is practical to choose the frequency ratio of pump (primary) waves in such a way that both the performance of the transducers and the sensitivity of the receiver to the