Cure Monitoring of Epoxy Matrices for Composites by Ultrasonic Wave Propagation

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ABSTRACT: Although ultrasonic wave propagation is a well-known technique for nondestructive analysis, it can be also applied for dynamic mechanical characterization (DMA) of polymers and composites. Most of DMA characterizations at ultrasonic frequencies are performed on thermoplastics and only a few articles are available on the characterization of the reactive properties of thermosetting resins. Therefore, in this work a complete characterization of the cure of a model epoxy system is presented, by comparing isothermal and nonisothermal data. The propagation of ultrasonic waves acting as a dynamic mechanical deformation at high frequencies can be used for the calculation of complex longitudinal bulk moduli during the cure of the epoxy resin. The evolution of attenuation and velocity during reaction is related to the strong physical changes occurring during the cure process. Furthermore, a comparison between the degree of reaction measured by Differential Scanning Calorimetry and ultrasonic data is proposed. The ultrasonic velocity (or the bulk longitudinal modulus) can be considered the most interesting parameter for cure monitoring because it follows the growth and evolution of the mechanical stiffness of the resin during cure. In particular, the obtained results suggest that the measurement of longitudinal velocity or L' could be exploited for on-line measurements of post-gel properties. Finally, an immediate correlation is also proposed between the gel time and the end of cure and the ultrasonic data. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1969–1977, 1999

Key words: cure monitoring; ultrasonics; epoxy; DSC

INTRODUCTION

The large amount of experimental and theoretical information about the basic phenomena that accompany epoxy-based composite processing produced in past years[1–10] is responsible for more efficient processes and higher quality products, mainly obtained in the field of high performance composite materials for aerospace applications. This quality need has led to the development and implementation of "*in situ*" sensors capable of providing information that can be correlated to the fundamental process variables, such as degree of reaction and viscosity, during cure.[11–14]

The research devoted to this objective has led to the development and implementation of dielectric sensors.[11–13] However, intrinsic difficulties and unresolved issues related to the generation and interpretation of the data obtained from dielectric measurements are only partially re-

solved.[14,15] The "*in situ*" monitoring of dielectric properties currently is available through the utilization of several commercial instruments equipped with special micro-dielectric sensors operating up to 100 MHz. The preliminary results obtained with laboratory equipment operating in the microwave range indicate a strong potential for the high frequency dielectrometry.[16]

More recently, the use of fiber optic sensors for on-line Fourier transformed infrared spectroscopy operating in the near infrared is also proposed.[17–19] This approach involves the recording of Fourier transformed infrared spectroscopy spectra obtained by embedding the fiber optic in the resin. Breaks into the fiber or an uncoated portion of a fiber allow the near infrared radiation to penetrate into the resin detecting the change in the absorption of radiation occurring during reaction. However, all these techniques still need further development either for their technological applications or for quantitative correlation between measured properties and the main material properties evolving during cure, degree of reaction, and viscosity.

Although the ultrasonic wave propagation is a well-known technique for nondestructive analysis, its application as a thermal analysis technique for measurements of dynamic mechanical properties of polymers is limited to laboratory studies. In particular, most ultrasonic characterizations of polymers are performed on thermoplastics[20–23] and only a few articles are available on the characterization of the reactive properties of thermosetting resins.[24–32] On the other hand, the application of the ultrasonic wave propagation to cure monitoring has been devoted essentially to an analysis of the evolution of ultrasonic properties during cure. Only a comparison with the evolution of the more familiar shear properties obtained at low frequency is reported by Lairez et al.[24]

The aim of this study is to compare the evolution of ultrasonic properties (velocity, attenuation, and calculated complex moduli) with the degree of reaction during cure of an epoxy matrix for composites. This study is devoted to seeking immediate correlation with critical points such as the gelation and the end of the cure whereas further work will be devoted to the development of a quantitative correlation between ultrasonic and material properties. Moreover, the dynamic mechanical properties obtained by the longitudinal and shear ultrasonic measurements also are exploited for the characterization of cured resin sample. Finally, a sensitivity analysis of the longitudinal storage modulus changes as a function of the degree of reaction is presented.

BASIS OF ULTRASONIC WAVE PROPAGATION IN POLYMERS

The propagation of elastic waves at high frequency, as in the ultrasonic range, corresponds to a dynamic mechanical deformation imposed to the material. This deformation produces a displacement around the equilibrium position of atoms and chain segments in the nm range, so the information that can be obtained from the ultrasonic measurements is related to small-scale mobility of short segments between entanglements. On the other hand, the deformation rate is very high because the typical frequencies of analysis range from the hundreds of KHz to the tens of MHz. When an alternating time-dependent deformation at the ultrasonic frequencies is applied to a material, the velocity of propagation of elastic waves (called ultrasonic or acoustic velocity) and the attenuation of the amplitude of the waves (called ultrasonic or acoustic attenuation) can be measured. The measurements of these quantities can be performed only if the samples are sufficiently larger than the wavelength, typically higher then 0.17 mm for a polymer at a frequency of 10 Mhz, and sufficiently small to allow the detection of the wave traveling from the ultrasonic transducer to the receiver.[20,33,34] The longitudinal velocity, V_L, in the pulse-echo mode, is defined as the ratio between two times the sample thickness, d and time of flight, t, of the ultrasonic wave through the sample:

$$V_L = 2d/t \tag{1}$$

The attenuation or attenuation coefficient,[34] α, is defined from the decrease of the amplitude, A, of a plane wave across a thickness:

$$A = A_o \exp(-\alpha d) \tag{2}$$

where A_o is the amplitude of the incident wave. The coefficient α is measured in dB/mm according to:

$$\alpha = (1/d)20 \log(A_o/A) \tag{3}$$

or in Neper/mm = 8.686 dB/mm according to:

$$\alpha = (1/d)\ln(A_o/A) \tag{4}$$

From measurements of acoustic velocity and attenuation, the components of a complex longitudinal or shear modulus can be calculated if a longitudinal or shear wave propagates through the sample respectively. The propagation of shear waves is restricted by the very high damping properties of polymers often leading to a complete attenuation of the wave through the sample. On the other hand, the propagation of longitudinal elastic waves is easily observed in polymers as well as in reactive mixtures of monomers. When the sample dimension normal to the acoustic wave is large compared with respect to the wavelength, the wave propagation is governed by the complex bulk longitudinal modulus L^* given by:

$$L^* = L' + iL'' \tag{5}$$

The storage (L') and loss (L'') bulk longitudinal moduli are related to the bulk (K' and K'') and shear (G' and G'') moduli[20,33]:

$$L' = K' + 4/3G' \tag{6}$$

$$L'' = K'' + 4/3G'' \tag{7}$$

where L' corresponds to the stiffness of a system that is deformed changing its dimensions in one direction while in the other two directions the dimensions are constrained to be constant, as it occurs in samples where two dimensions are much larger than the third. For a liquid or a soft rubbery material $K' \gg G'$, and L' may be considered equal to the bulk modulus, whereas K'' and G'' may be of the same order of magnitude and the effect of G'' on L'' cannot be neglected.

The measurements of ultrasonic longitudinal velocity (V_L) and attenuation (α) may be used for the calculation of the storage (L') and loss (L'') bulk longitudinal moduli[20]:

$$L' = \frac{\rho V_L^2 \left[1 - \left(\dfrac{\alpha\lambda}{2\pi} \right)^2 \right]}{\left[1 + \left(\dfrac{\alpha\lambda}{2\pi} \right)^2 \right]^2} \tag{8}$$

$$L'' = \frac{2\rho V_L^2 \left(\dfrac{\alpha\lambda}{2\pi} \right)}{\left[1 + \left(\dfrac{\alpha\lambda}{2\pi} \right)^2 \right]^2} \tag{9}$$

where ρ is the material density and λ is the wavelength, given by $\lambda = V_L/\nu$ as a function of the frequency, ν. These expressions also may be applied to the calculation of the shear or Young moduli when a different type of wave or sample geometry is used.[20,33] For low damping solids, like metals or ceramics, the attenuation may be neglected and a single longitudinal modulus $L = \rho V_L^2$ can be calculated.

EXPERIMENTAL

The studied resin system was a mixture of a diglycidyl ether of bisphenol A based epoxy resin (Epon 828 from Shell, USA) and an aliphatic esaamine curing agent (HY 951 from Ciba, USA). The resin and the hardener were kindly provided by Salver (Italy) S.p.A. A ratio of 10.6 phr of amine by weight, corresponding to a molar ratio between the functional groups of epoxy and amine $r = 0.67$, was adopted.

The longitudinal velocity and the ultrasonic wave attenuation during the cure at different temperatures were measured by pulse-echo technique at the frequency of 10 MHz by means of a Panametrics 560A1–ST system connected with an oscilloscope Philips (Germany) PM3323. The setup is computer controlled through an HP-VEE software and the data concerning temperature, longitudinal velocity, and attenuation are collected every 5 s and stored on hard disk.

The ultrasonic measurements were performed in isothermal conditions by placing the resin sample, in the form of a thin sheet of thickness less than 2 mm, at constant temperature ($\pm1°C$), between a buffer rod, at the opposite end of which the transducer and a heated plate are placed. Also, nonisothermal experiments were performed by heating at 1°C/min either noncured or partially cured samples between 20 to 90°. The estimated relative error of the velocity measurements obtained by combining the relative errors on time and thickness measurements is about $\pm0.4\%$.

The attenuation was calculated from the ratio between amplitude of the first echo due to the reflection from the buffer rod-sample interface (A_o) and the second echo due to the reflection from the opposite surface of the sample (A_1) according to eq. (4).

The cure degree was monitored by using a differential scanning calorimeter (DSC) Perkin-Elmer DSC-7 operating in isothermal and nonisothermal conditions. Isothermal ultrasonic and

DSC measurements were obtained at the same temperatures.

The gel time in isothermal conditions was observed at the same temperatures used for ultrasonic and DSC measurements following the procedure indicated by the standard test method ASTM D 3532.

RESULTS AND DISCUSSION

DSC Measurements

DSC measurements may be used for the determination of the progress in the cure by assuming that the heat evolved during the reaction is proportional to the overall extent of reaction given by the fraction of reactive groups consumed. Following this approach the degree of reaction, w, is defined as[5,7]:

$$w = Q(t)/Q_{tot} \qquad (10)$$

where $Q(t)$ is the partial heat of reaction developed during an isothermal DSC experiment and Q_{tot} represents the maximum heat of reaction measured in nonisothermal experiments, taken as a reference value. The reaction rate, dw/dt, is thus obtained from the heat flow, dQ/dt, measured by DSC as:

$$dw/dt = 1/Q_{tot}(dQ/dt) \qquad (11)$$

A value of $Q_{tot} = 380$ J/g is assumed as an average of the heats of reaction measured in nonisothermal experiments. The heat developed during isothermal DSC experiments (Q_{is}) is lower than Q_{tot}, indicating that unreacted groups are still present. In fact, the glass transition temperature (T_g), continuously increasing during cure, may approach the isothermal cure temperature, strongly reducing the molecular mobility. In these conditions, the reaction becomes diffusion-controlled and the cure is arrested by this strong reduction in the molecular mobility determined by vitrification. When the cure temperature is higher than the T_g of the fully cured system ($T_{gmax} = 85°C$), a maximum degree of reaction, $w_m = 1$ is obtained. Therefore w_m is given by:

$$w_m = Q_{is}/Q_{tot} \qquad (12)$$

When T approaches the T_g of the fully cured system (T_{gmax}), w_m becomes close to 1. The tem-

Figure 1 Longitudinal velocity and attenuation measured during isothermal cure at 48°C. The indicated gel time is calculated according to ASTM D 3532.

perature dependence of w_m is widely reported in the literature[5,7,8] and it follows the dependence of the T_g from the degree of reaction in thermoset polymerization.[35] The evolution of the degree of reaction as a function of the cure time in isothermal condition will be shown below in comparison with the ultrasonic data, measured at the same temperature.

Ultrasonic Measurements

The ultrasonic velocity and attenuation measured during an isothermal cure at 48°C are reported in Figure 1. At the beginning of the cure, while the molecular weight is growing and the resins appear as a viscous liquid, the velocity shows a very limited increase. Then, close to the gel time, the velocity shows a significant increase, a true jump of its derivative, reflecting the buildup of bulk and shear modulus as a consequence of the incipient formation of a crosslinked structure. On the other hand, the attenuation shows a maximum in the first part of the cure. The ultrasonic attenuation may be considered as the equivalent of a damping factor in a dynamic-mechanical experiment,[33] representing a measure of the energy loss as the wave travels through the polymer. The glass transition is characterized by a peak in the loss modulus, in the loss factor, in the dielectric loss, and also in the acoustic attenuation.[33] As reported by Babayevsky and Gillham,[36] who analyzed the shear dynamic-mechanical properties of an epoxy system during cure at low frequency (1 Hz), two peaks in the damping factor are expected. The first (weaker) was attributed to gelation and the second (stronger) to the transition in the glassy state (vitrification). In the case of propagation of

Figure 2 Longitudinal storage modulus and loss factor calculated from the data of Figure 1.

acoustic waves, a much higher frequency is used and the peak due to vitrification is expected at a crosslinking degree corresponding to a looser network. During cure, the temperature is constant while the molecular weight, up to gelation, and the degree of crosslinking grow until a transition to the glassy state is observed. In a similar way, if a polymer is cooled from the rubbery state through its T_g, the observed maximum of acoustic attenuation is shifted significantly at higher temperatures as the frequency of the deformation is increased.[36] In dielectric measurements, performed at frequencies comparable with that used in ulltrasonic analysis, a maximum in tan δ also is detected at vitrification.[11,14] Therefore, the observed peak is attributed to a vitrification detected at MHz frequencies as also reported in other articles devoted to the ultrasonic analysis of thermosets cure.[24,27,28] In particular, for the isothermal cure at 48°C (Fig. 1), the attenuation peak occurs after about 40 min while a reduction of the rate of reaction, consequence of the diffusion effects determined by vitrification, appears after about 80 min (Fig. 6a).

The measurements of ultrasonic velocity and attenuation may be used for the calculation of the storage (L') and loss (L'') bulk longitudinal moduli and of the loss factor, tan δ, as the ratio L''/L'. A plot of L' and tan δ calculated from the velocity and attenuation reported in Figure 1 is shown in Figure 2. The changes of L' and tan δ as a function of the cure time can not be easily interpreted as a consequence of their complex nature arising from the combination of bulk and shear moduli. The time dependence of L' follows the same behavior shown by the velocity in Figure 1. The limited changes of L' observed at the beginning

may be associated with a slight increase of K' in the liquid resin while G' gives a significant contribution to L' only when a rubbery gel is formed. The maximum of tan δ is slightly delayed with respect to the attenuation peak.

The effect of residual reactivity on the ultrasonic velocity after an isothermal cure at 58°C is shown in Figure 3. An isothermal cure at 58°C leads to a maximum degree of reaction lower than 1 and to a T_g of about 65°C. The reaction may restart in conditions of enhanced molecular mobility by simply heating the sample at a temperature higher than the T_g developed during the former isothermal cure. As the temperature reaches the T_g of the sample (about 65°C), the ultrasonic velocity reaches a minimum. Then the residual unreacted groups in the rubbery polymer may further crosslink the resin leading to a stiffening of the network and consequently to a sharp increase of the velocity. When the sample temperature is higher than $T_{g\text{max}}$, the reactive groups are completely consumed and the effect of the temperature becomes dominant, determining a velocity decrease.

The ultrasonic velocity measured during the cure of the studied resin at five different cure temperatures (48, 53, 58, 64, and 70°C) is reported in Figure 4. A decrease of the initial velocity as the cure temperature increases may be attributed to a reduction of the bulk modulus and of the density of the unreacted resin with temperature. The characteristic time for the steep increase of velocity decreases as the cure temperature increases, indicating that this break, observed also in Figure 2 for L', is related to the

Figure 3 Longitudinal velocity evolution during a temperature scan on a sample cured in isothermal conditions at 58°C.

Figure 4 Comparison of longitudinal velocity measured in isothermal conditions at different cure temperatures.

increased rate of reaction occurring at higher temperatures.

Ultrasonic measurements may be used at room temperature for the determination of different maximum degrees of reaction obtained under different cure conditions. To induce different values of w_m, the ultrasonic velocity of samples cured at room temperature and then postcured at higher isothermal temperatures, is measured at room temperature. As shown in Table I, the ultrasonic velocity increases with the postcure temperature indicating that a stiffer crosslinked structure, corresponding to higher values of w_m, can be detected by using ultrasonic velocity measurements. Furthermore, the ultrasonic longitudinal and shear velocities can be used for the calculation of the Young (E), shear (G), bulk (K), and Poisson (ν) moduli of a cured resin.[34] In particular, the bulk modulus measured at room temperature on the samples postcured at 40 and 50°C, reported in Table II, is in agreement with the literature data.[37]

Table II Comparison Between Dynamic Moduli of Elasticity [Young Modulus (E), Shear Modulus (G), Bulk Modulus (K), and Poisson Ratio (ν)] of Samples Measured at Room Temperature after 6 h of Postcure at the Indicated Temperatures and Typical Static Mechanical Data for Epoxy Resin[37]

Cure Temperature (°C)	E (GPa)	G (GPa)	K (GPa)	ν
40	4.7	1.7	6.7	0.38
50	4.9	1.8	6.5	0.37
Data from ref. 37	2.5	0.9	6.4	0.40

Comparison Between Ultrasonic and DSC Data

The time corresponding to the attenuation peak, the characteristic time at which the ultrasonic longitudinal velocity rapidly starts increasing, calculated as an extrapolated onset, and the gel time, reported in Figure 5, suggest an immediate correlation between kinetic behavior and ultrasonic parameters. As shown in Figure 5, the gel time in each measurement occurs after the onset of velocity increase and before the peak of the loss modulus. These characteristic times, marking incipient and fully achieved gelation, may be exploited at least to predict the interval in which gelation occurs. Moreover, the position of the gel time along the velocity-time and the L'-time curves confirms that the observed steep increase of velocity can be associated with the development of elastic properties in the resin. The theoretical value of the degree of reaction at the gel point, w_g, may be calculated as a function of the molar ratio, r, between epoxy and amine functionals and of the functionality of epoxy F_e and amine, F_a, monomers[5]:

$$w_g^2 = 1/[r(F_a - 1)(F_e - 1)] \qquad (13)$$

Table I Longitudinal and Shear Velocity of the Samples Measured at Room Temperature

Cure Temperature (°C)	Longitudinal Velocity (m/s) 1 h Postcure	Longitudinal Velocity (m/s) 6 h Postcure	Shear Velocity (m/s) 6 h Postcure
40	2552	2727	1187
50	2625	2735	1214
60	2635	2740	—
70	2670	2742	—
80	2670	2752	—

Figure 5 Comparison of characteristic times observed during cure.

Equation (13) provides a value of $w_g = 0.55$ with $r = 0.67$, $F_a = 6$, and $F_e = 2$. This result is in agreement with the values measured by DSC in correspondence with the experimental gel time as reported in Table III. The degree of reaction measured in correspondence with the attenuation peak, w_p, and of the onset of velocity increase, w_v, are also listed in Table III for comparison. w_p, and w_v present values of about ± 0.1 with respect to w_g and therefore may be used as a measurement of incipient and fully achieved gelation.

The degree of reaction measured by DSC and the bulk longitudinal modulus are compared in Figure 6(a–d) at four different cure temperatures. At the beginning of the cure, the degree of reaction obtained by DSC grows more rapidly than the longitudinal velocity as a consequence of the high concentration of reactive groups in the liquid reactive mixture. On the other hand, the growth of molecular weight in the form of branched oligomers, scarcely affects the mechanical properties of the resin before the gel point. Close to gelation, the growing branched molecules are characterized by extensive entanglements capable of providing an elastic response measured as a significant growth of longitudinal velocity and L'. Then, the development of a crosslinked structure is responsible for the achievement of the final values of modulus. In the last part of the cure, a moderate or negligible increase of the degree of reaction is accompanied by a recognizable increase of L'. Therefore, L' shows a strong sensitivity to the last part of the reaction when the crosslinked structure is fully developed and the cure involves the reaction of a limited number of amine and epoxy groups in a glassy polymer. Al-

though the last part of the cure, occurring under the control of diffusion, cannot be observed by DSC, it is accompanied by a significant increase of the crosslinking density measured by the changes of the longitudinal modulus. Then, the ultrasonic technique may be exploited for the determination of the end of the cure showing a better sensitivity than DSC.

A further test on the sensitivity of the ultrasonic measurements to the last part of the cure process is shown in Figure 7, where a plot of L' as a function of the degree of reaction is presented for three cure temperatures. A simple expression cannot be applied to the quantitative correlation between L' and the degree of reaction measured by DSC. The reported data indicate that L' is mainly sensitive to the increasing crosslinking density occurring after gelation rather than to the number of reacted groups. Nevertheless, the evolution of mechanical properties after gelation is theoretically predicted by Flory[38] in the theory of rubber elasticity and may be computed, for example, applying the statistical approach of Macosko and Miller.[39,40] The correlation between degree of reaction and longitudinal modulus could be attempted accounting for the crosslinking density defined as the concentration of effective junction points in the infinite network. However, the results of Table III and of Figures 6 and 7 indicate that a mechanical response may be observed also before gelation when the velocity abruptly increases. This may be explained by accounting for mechanically effective crosslinks arising from trapped entanglements developed in the branched molecules of very high molecular weight.

CONCLUSIONS

In this work, a complete characterization of the cure of a model epoxy system is presented by

Table III   Degree of Reaction at the Gel Point, w_g, at the Time for Change of Slope of Velocity, w_v, and at the Attenuation Peak, w_p

Cure Temperature (°C)	w_g	w_v	w_p
48	0.52	0.45	0.62
53	0.54	0.41	0.64
58	0.57	0.45	0.64
63	0.56	0.50	0.68
70	0.55	0.47	0.69

Figure 6 Comparison of ultrasonic and DSC measurements at four different cure temperatures (a–d).

comparing isothermal and nonisothermal data. The propagation of ultrasonic waves acting as dynamic mechanical deformation at high frequen-

Figure 7 Cross plot of ultrasonic longitudinal storage modulus and degree of reaction measured by DSC data observed at the same cure times.

cies can be used for the calculation of complex longitudinal bulk moduli during the cure of the epoxy resin. The evolution of attenuation and velocity during reaction is related to the strong physical changes occurring during the cure process.

Furthermore, a comparison between the degree of reaction measured by DSC and ultrasonic data is proposed. The experimental data indicate that ultrasonic measurements show a limited sensitivity at the beginning of the cure whereas at the end of cure a recognizable increase of L' is observed in correspondence to small or negligible changes of the degree of reaction measured by DSC. The ultrasonic velocity (or L') can be considered as the most interesting parameter for cure monitoring since it follows the development of the mechanical properties of the reacting mixture. In particular, the obtained results suggest that the mea-

surement of the longitudinal velocity (or L') could be exploited for an on-line measurement of postgel properties. Finally, an immediate correlation is also proposed between the gel time and the end of cure and ultrasonic data. Conversely, a deeper theoretical analysis, based on a statistical approach is still needed to provide a quantitative correlation between L' (or ultrasonic velocity) and the degree of reaction.

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