Monitoring Thermoset Polymerization by Using Piezoelectric Measurements

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SYNOPSIS

The electric impedance of a piezoelectric element placed inside a polymeric system depends on the viscoelastic property of the polymer. Its measurement is a sensitive and nondestructive method for monitoring the curing of such materials. The validity of this new method is shown by comparison with traditional viscoelastic and ultrasonic techniques.

INTRODUCTION

The chemorheological transformations appearing during the polymerization of thermosets involve two main transitions: the gel point and the vitrification.

Gelation results from the structural transition from linear and branched molecules into the macromolecular network. During the reaction, a sudden increase in molecular weight is then observed, which induces an abrupt increase in the viscosity. The gel point occurs at a chemically given conversion rate and is independent of the determination method. The vitrification is a glass transition occurring in a reacting material. In this case, the main factor governing this transition remains the slowing down of the molecular motions due to the increase in the molecular weight before gelation or due to the cross-link density enhancement after gelation. Vitrification occurs over a large time domain that depends on the resin chemistry, on the temperature, and on the measurement conditions, and it occurs when the molecular motion frequency is in the same range as those of the investigation method itself.

Traditionally, studies of curing polymers use a chemical approach that consists of an analysis of the conversion rate of reactive groups by methods such as chemical analysis, sol–gel analysis, IR or RMN spectroscopy, and calorimetry. Chemical ti-

trations are useful for studying the kinetics of the cure reaction, but their sensitivity and capability decrease sharply in the late stage of cure. Theoretically, the gel point can be determined by sol–gel ratio measurements as the first appearance of the insoluble fraction. But this technique is laborious to perform and is often reserved for fundamental studies. By calorimetry, the rate of the exothermic chemical reactions can be measured through the heat generated during a scanning or isothermal run.[1,2] The vitrification can then be approached indirectly by the slowing down of the reaction kinetics. The glass transition temperature, T_g, is determined by calorimetry by specific heat measurements. Moreover, it is well known that an incomplete cure of a resin yields a network having a T_g lower than the T_g of the completely cured network.

Rheological measurement is the preferred method for gelation and vitrification observation. Gillham and co-workers developed an instrument using a self-oscillating torsion pendulum and a glass fiber braid impregnated with the resin for rheological studies.[3] By this method, the gel point and the vitrification are characterized by a damping peak. The results obtained are used to build the time–temperature–transformation cure diagram of the resin (TTT diagram). Gelation and vitrification of a polymeric material are often studied by using the results obtained at a fixed frequency with a viscoelastometer. Discussion still persists upon the criterion to be used to characterize these transitions. In the simple case where gelation occurs before the

onset of vitrification, the gel point might occur at the time at which G' and G'' cross each other (G': storage modulus; G'': loss modulus).[4] A more exact value of the gel point is then obtained by working in the frequency sweep mode. In this case, authors have agreed to define the gel point as the crossing point of the $\tan(\delta) = f(t)$ curves obtained with each frequency.[5] Concerning vitrification, the same criteria as those that are used for the study of the glass transition are found in the literature: The onset and the middle of vitrification are taken, respectively, at the minimum and at the maximum of the curve corresponding to the loss factor variation.

Dielectric analyses based on the study of dipole orientation in the resin are also very sensitive to the physical transformation occurring in the sample during its polymerization, although they may fail because of electrode or interface polarization. Recently, there has been new interest in dielectric analysis due to the improvement of the instruments such as a microdielectrometer insertable inside the material.[6]

The use of ultrasonic waves to monitor the cure of thermosets is very interesting because they are really nondestructive. This method is based on the measure of propagation velocity and attenuation inside the curing material and can be sensitive up to the late stage of the reaction. Although these methods obviously become inept when the properties of the material make it difficult to establish a good mechanical contact with the transducer or when the attenuation becomes so high that the ultrasonic waves cannot propagate inside the material. Nevertheless, these methods give interesting data concerning the resin cure since the acoustic properties of the material reflect its viscoelastic properties.[7,8]

We have developed a new ultrasonic technique based on the study of the deformations occurring in a piezoelectric ceramic placed inside the curing medium when it is electrically excited.

The aim of this study is to show the validity of our method by comparing the results we obtain with those resulting from traditional rheological and ultrasonic techniques.

PROCEDURE

Method Principle

This original method is based on the deformations of a piezoelectric ceramic inserted inside a curing resin. Thereby, when it is submitted to an electric

current, this element deforms. According to its geometry, different shapes may occur, each characterized by a natural resonant frequency and by the magnitude of the displacement. Indeed, a ceramic in the form of a thin disc undergoes two types of deformation: in its thickness (thickness mode) and in its radius (radial mode). In the case where its diameter is much larger than its thickness, the frequency of these two modes are quite different from each other, so they may be considered as independent and studied separately. It has been shown by another way that the electric impedance of a piezoelectric element describes its deformations. Vibration is characterized in the impedance curves by a resonant peak. The magnitude of the resonant peak associated with each vibration is connected both to its piezoelectric properties and to the viscoelastic properties of the surrounding medium. Precisely, the more similar the acoustic properties of this medium to those of the ceramic, the higher is the damping. Thus, the study of the electric impedance variation is an indirect tool for measuring the properties of the surrounding medium and also can be used for gelation and vitrification detection.

Parameters

The vibration phenomenon is characterized in the frequency spectrum by a peak whose magnitude and frequency bandwidth are connected to the magnitude of the vibration. Damping of this vibration produces a decrease in the peak magnitude and an increase in its frequency bandwidth. Therefore, the magnitude and bandwidth variation are connected to the resin viscoelastic property changes, and the study of their evolution is an original way to monitor the cure reaction.

EXPERIMENTAL

Materials

We have used two model epoxy–amine resin systems. The first one is a stoichiometric mixture of diglycidylether butanediol (DGEBD) with diamino dioxadodecane (DADODD), which at temperatures above 5°C exhibits only gelation. The second one is a stoichiometric mixture of NN'-dimethylhexanediamine (DMHDA) with diglycidylether of bisphenol A (DGEBA). These prepolymers and hardeners have only two reactive groups, which is why

they can only yield linear macromolecules. Thus, with such a mixture, gelation cannot occur, and only vitrification appears.

Experimental Setup

Piezoelectric Method

The experimental setup includes a piezoelectric ceramic and an impedancemeter driven by a computer. The piezoelectric ceramics used are thin PZT discs having 0.45 mm thickness and 5 and 10 mm diameters. In these conditions, the first three radial resonances are 235, 535, and 835 KHz and 414, 945, and 1500 KHz, respectively, for the 10 and 5 mm-diameter elements. The first resonance of the thickness mode is at 5 MHz for each type of ceramic. It is interesting to use different frequencies for better understanding of the effects of gelation and vitrification.

The resin and the ceramic are introduced in a metallic container that is introduced in a temperature-controlled water bath, and a thermocouple placed inside the container measures the resin temperature throughout the reaction. The piezoelectric element is connected by a wire to the impedancemeter, which directly gives the complex value of its impedance. The computer linked to the impedancemeter initiates the tests and stores and processes the signals.

Viscoelastic Method

The viscoelastometer used for this study is a Rheometrics RDA 700 model, with two parallel plates between which the sample is inserted. The lower plate is driven by an oscillating strain with an assigned magnitude and frequency. The induced deformation is transmitted through the sample to the upper plate, which is connected to a sensor. This sensor measures the resulting torque and the phase between the strain and the stress.

Ultrasonic Propagation Method

The other technique used is an ultrasonic method based on the velocity and attenuation measurements inside the curing materials. A bandwidth transducer centered at 5 MHz is introduced in the resin. When it is submitted to a pulse excitation, it emits longitudinal waves that propagate inside the resin and are reflected by the bottom of the container and then collected by the same transducer. An oscilloscope is used for the signal visualization, which is then stored and processed by a computer.

RESULTS AND DISCUSSION

Gelation Characterization

This study was performed with a stoichiometric mixture of BDDGE–DADODD that at 25°C exhibits only gelation.

#### A. Piezoelectric Measurements

The transformation of the resin from a liquid to a solid state induces a constant and regular evolution of the real part of the ceramic electric impedance. The variations in the relative magnitude and in the relative frequency bandwidth of each radial vibrating mode and of each ceramic diameter are similar (Fig. 1). The radial resonances shear the resin, which is why they are very sensitive to the resin gelation. The sensitivity of the 10 mm-diameter ceramics is better than that of the 5 mm-diameter ones, because they induce greater shearing of the resin.

As can be seen in Figure 2, the variation in the same parameters measured on the thickness resonance is weak. The thickness resonance induces simple pressure waves; thus, it is less sensitive to the resin gelation than to the radial one.

First, the variation in the resonance peak magnitude prevails as a consequence of the changes in
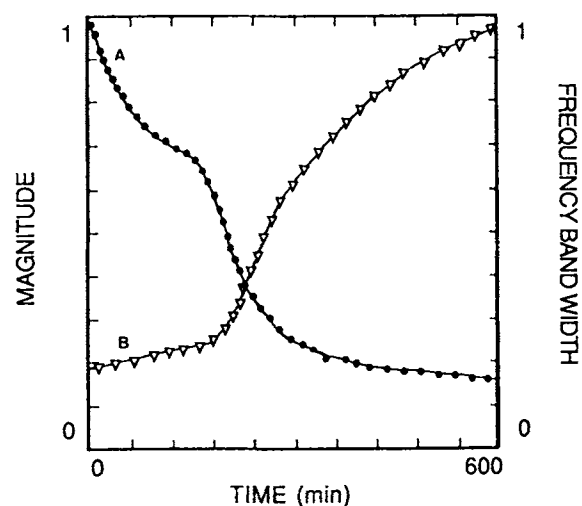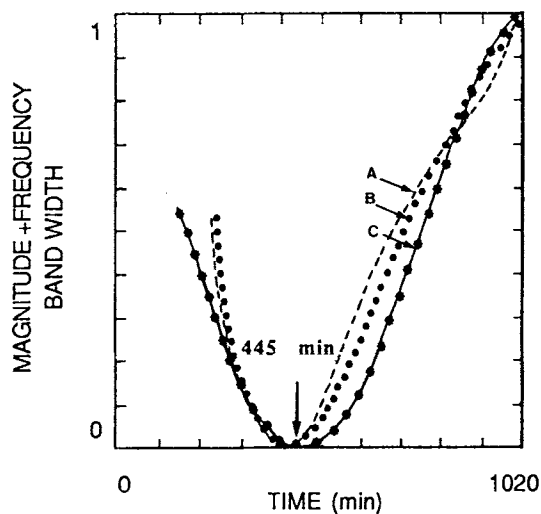

Figure 1 Variation (A) in the relative magnitude and (B) in the relative frequency bandwidth of the first radial resonance (f = 235 KHz) of the 10 mm-diameter ceramic during gelation.
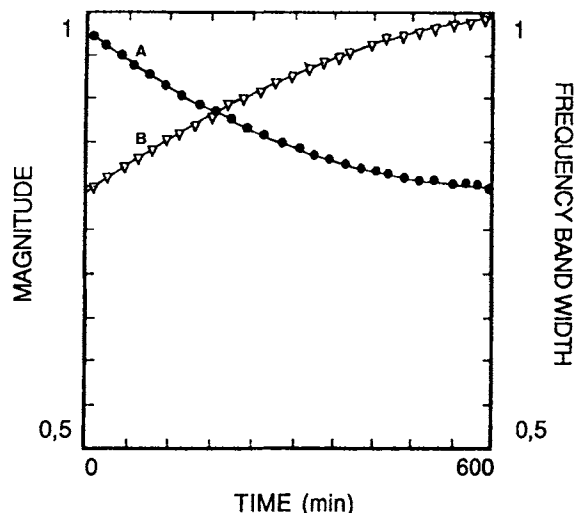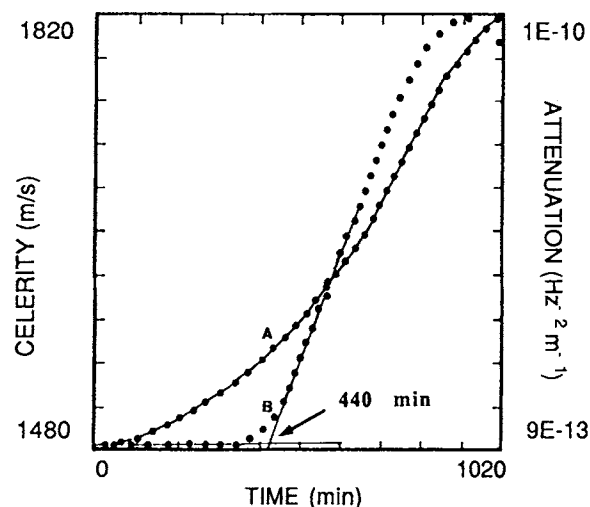
Figure 2 Variation (A) in the relative magnitude and (B) in the relative frequency bandwidth of the thickness resonance (f = 5 MHz) of the 10 mm-diameter ceramic during gelation.

Figure 4 Variation in the (A) ultrasonic celerity and (B) attenuation during gelation. Transducer bandwidth = 5 MHz.

the coupling between the ceramic and the resin. Then, when the resin becomes elastic, the bandwidth variation becomes dominant. So a very sensitive parameter is obtained by adding the respective variation in these two damping parameters. As can be

seen in Figure 3, this new parameter undergoes the same variation at each radial frequency (the variation of the damping parameters of the thickness resonance is too weak to be used). At the intersection of the curves obtained at the different frequencies, the gel point can be determined because this phenomenon must be independent of the test frequency.[2] Using the curves obtained with each ceramic diameter, we determine the gel point to be at 445 ± 10 min.
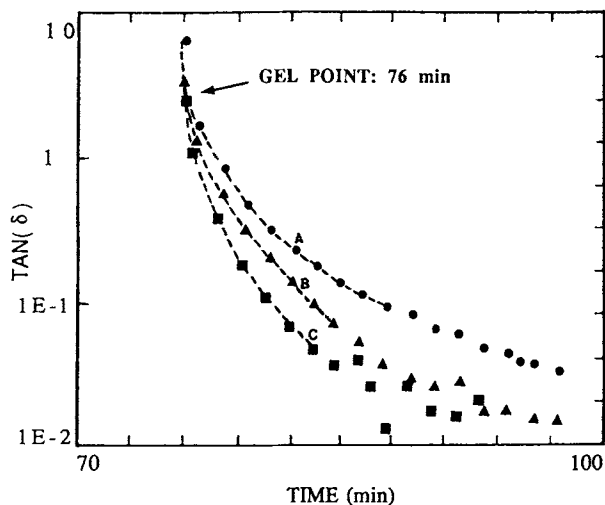

Figure 3 Plots resulting from the addition of the respective variation in the relative magnitude and in the relative frequency bandwidth of the radial resonance during gelation. (A, B) First and second radial resonances (f = 235 KHz, f = 535 KHz) of the 10 mm-diameter ceramic. (C) First radial resonance (f = 414 KHz) of the 5 mm-diameter ceramic.
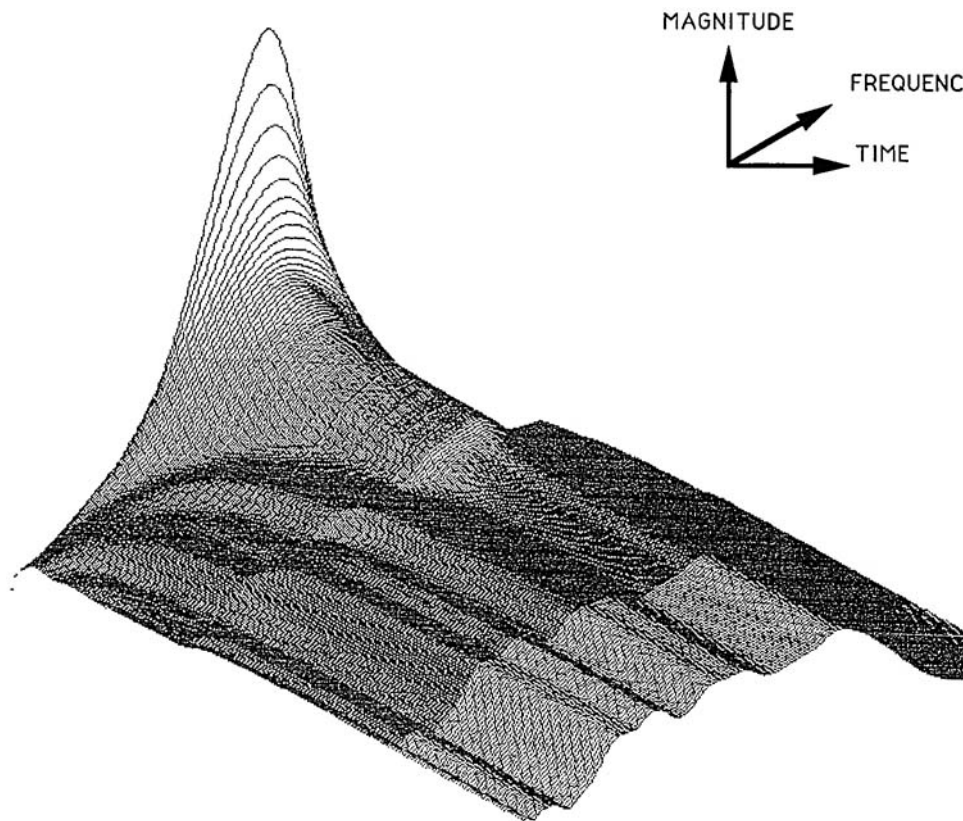

Figure 5 Variation in the viscoelastic property tan δ during gelation. Temperature, 60°C. Frequency: (A) 0.32 Hz; (B) 3.18 Hz; (C) 31.83 Hz.

Figure 6 Deformation of the first radial resonance peak appearing during vitrification.

B. Comparison with Classical Methods

The gel point may be characterized by classical methods by using ultrasonic wave propagation inside the curing material. The resulting curves (Fig. 4) present the classical appearance of celerity and attenuation variation curves in a gelling resin.[8] The gel point is determined at the first curvature point observed on these curves and was found to be at 440 ± 10 min.

Viscoelastic measurements, performed in the frequency sweep mode at 60°C, were also used to determine the gel point of this resin. The loss factor variation obtained at each frequency is given in Figure 5. The gel point is measured at the crossing point of all these curves. At 60°C, the gel point is equal to 76 min. As the activated energy of the resin is known (10 kcal/mol), we are able to predict the gel time at any isothermal temperature.[5] At 25°C, the gel time is predicted to be 450 min.

The gel point measured by piezoelectric measurements is equal to 450 ± 10 min. This is in good
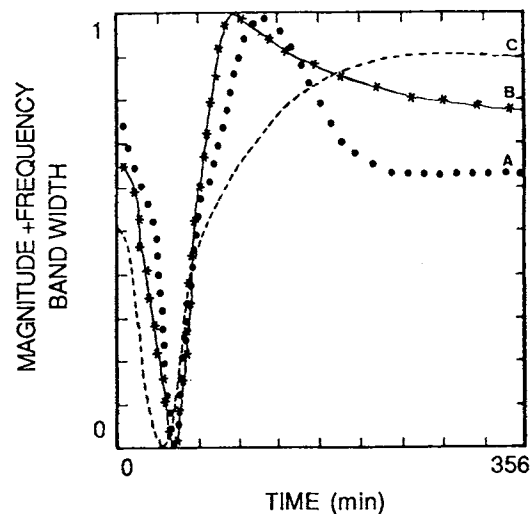
Figure 7 Plots resulting from the addition of the respective variation in the relative magnitude and in the relative frequency bandwidth of the radial and axial resonance during gelation. (A, B) second and third radial resonances (f = 535 KHz; f = 835 KHz); (C) thickness resonance (f = 5 MHz) of the 10 mm-diameter ceramic.
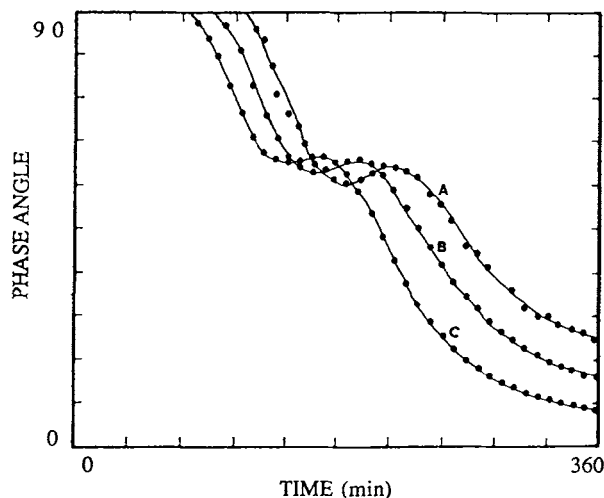
Figure 8 Variation in the viscoelastic property δ during vitrification. Temperature, 35°C. Frequency: (A) 39.8 Hz; (B) 4 Hz; (C) 0.4 Hz.

agreement with those determined by classical methods.

Vitrification Characterization

This study was performed at 35°C, with a stoichiometric DMHDA–DGEBA mixture that exhibits at this temperature only vitrification.

A. Piezoelectric Measurements

During vitrification, deformation of the first radial resonant peak is observed for the regular evolution of the resonance damping (Fig. 6). The same evolution is noted for both diameters of the ceramic. This could be due to a stress field around the sensor. Indeed, the variation of temperature during the polymerization process induces thermal shrinkage, which can be seen by photoelasticimetry. Furthermore, a thermal treatment at a temperature above the cure temperature makes this stress field disappear. The other radial resonances are as less disturbed as their frequency is high, and the thickness resonance is not perturbed at all. Each resonance can then be exploited.

The curves resulting from the addition of the respective variation in the relative magnitude and in the relative frequency bandwidth are given in Figure 7. It is interesting to note that the first part of these curves is frequency-dependent (up to the minimum of the curves, $0 < t < 45$ mn). The radial curves then undergo an unexpected evolution due to the

stress effects. The axial resonance, which is not disturbed by such stresses, gives supplementary information concerning the end of the reaction.

B. Comparison with Viscoelastic Measurements

Variations in the resonance damping are induced by changes in the resin viscoelastic properties. Subsequently, it is interesting to compare the results obtained with those resulting from the viscoelastic study, even if the frequencies used are very different from each other.

Figure 8 gives the variation of the loss factor at 0.4, 4, and 39.8 Hz. In Table I, the values corresponding to the beginning and to the middle of the vitrification are regrouped.

A rough linear and logarithmic extrapolation of these values to the ultrasonic frequency range would lead to the time given in Table II.

By comparing these values with the values measured at the minimum of the curves, it seems that the latter characterizes a point close to the onset of the vitrification. This point is now under study, in parallel to dielectric measurements in the same frequency range.

CONCLUSION

The cure of thermosetting resins can be studied indirectly by measuring the variation in the electric impedance of a piezoelectric sensor inserted inside the curing medium. As a matter of fact, the electric impedance of the ceramic expresses its deformations that are connected to the resin viscoelastic properties.

Using different resonance modes (thickness and radial), different sets of frequencies can be exploited (from 230 KHz to 5 MHz). Their processing can then be used for the study of polymer gelation and vitrification.

In particular, the radial resonances are very sensitive to the viscosity of the surrounding medium

Table I Characteristic Points of the Viscoelastic Curves

Frequencies (Hz)	t_{onset} (min)	t_{middle} (min)
0.4	121	219
4	102	197
39.8	81.5	172

**Table II   Values Resulting from the Extrapolation
of the Viscoelastic Measures to the Ultrasonic Frequencies**

Frequencies	Linear Extrapolation (min)		Logarithmic Extrapolation (min)	
	t_{onset}	t_{middle}	t_{onset}	t_{middle}
535 KHz (2nd radial mode)	24	75	75	108
835 KHz (3rd radial mode)	—	71	62	106
5 MHz (thickness mode)	—	52	45	97

and lead to a good determination of the gel point. Moreover, the gel point is found to be independent of the frequency, as it is well known.

On the other hand, vitrification is found to be dependent on the frequency range, as expected. But this phenomenon is complicated to study because of the stresses that affect the sensor as the resin vitrifies. These effects are now under study.

This original method is promising, because it offers an easy to use technique for the "*in situ*" monitoring of composite structures during manufacturing.

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