Monitoring of resin curing and hardening by ultrasound

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ABSTRACT

A major aspect regarding the attainment of the desired properties for epoxy composite materials, bonded repair as well as repaired structural components via resin infusion is the control of the curing of the employed thermoset. This is required in order to distinguish the different stages of the structural formation and to provide adequate conditions for proper epoxy impregnation. In this study, ultrasonics was employed for the monitoring of the polymerization of a typical epoxy system. A wave generator was connected to a sensitive acoustic emission transducer in order to transmit elastic waves through the thickness of setting and hardening epoxy. The acquisition was conducted by another sensor of the same type acting as receiver. Different parameters like the wave velocity and attenuation are monitored in order to examine the rate of hardening. Results show that the changes in viscosity and elastic modulus with time can be monitored by the changes in the wave parameters. The effect of temperature is also discussed.

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1. Introduction

The curing efficiency of thermosets in structural components is of the utmost importance, particularly when the polymer acts as the means for the attainment of structural integrity, for environmental protection as well as for structural rehabilitation. This is the typical case for polymer composite materials, for bonded structural repair of civil, naval or aerospace components, or for repair via resin infusion for cementitious structures. Fundamental to the achievement of optimal properties is the monitoring of curing in order (i) to provide necessary conditions for proper epoxy wetting or impregnation, (ii) to distinguish the different stages of the structural formation in order to define the process time window and (iii) to be able to identify the degree of curing that satisfies the minimum requirements. Ultrasonics is one of the most widely used nondestructive testing (NDT) techniques for monitoring the behavior of time dependent materials, and as such is ideal for the detailed study of the curing of thermosets. It utilizes elastic waves, the propagation characteristics of which depend strongly on the mechanical properties and the general condition of the testing material. The velocity of the wave depends among other properties on the elastic modulus and density of the material while the transmitted amplitude is indicative of the attenuation and thus scattering and viscous components of the material. The monitoring of the setting and hardening behavior of cementitious materials using ultrasonics has been extensively studied [1–4]. Ultrasound supplies continuous information on the development of elastic modulus and the point at which a certain standard of rigidity has been

obtained [5,6]. Besides the vast literature in the field of concrete, studies have been published for the monitoring of curing of melamine thermosets [7] as well as in the dairy industry concerning the monitoring of yogurt fermentation [8,9]. Shear ultrasonic waves have also been used to assess the stiffness of bond layers in relation to the curing process of the adhesive [10]. Ultrasonic waves exhibit sensitivity to properties of the liquid such as density, compressibility and concentration of salt or other substances [11]. In the present study, longitudinal waves are employed for the continuous monitoring of curing of epoxy resin.

Epoxy systems are widely used for repair purposes in concrete industry. They can be applied by injection or gravity filling in order to bond the crack and restore the structural integrity of the material [12,13]. In other cases epoxy adhesives are used to bond between the concrete surface and fiber reinforced plastic (FRP) strips which improve the tensile loading capacity [14]. For any such application, the time dependent behavior of the epoxy material is of paramount importance [15]. The initial liquid characteristics enable the proper impregnation between the interfaces (either sides of the crack or between concrete surface and FRP panel), while as the polymerization reaction proceeds the material is transformed into a rigid solid with considerable strength. Therefore, as stated above, monitoring of the efficiency of the curing process is essential. This is particularly important since the environmental temperature strongly influences the initial viscosity and the rate of epoxy curing and hardening [12,14].

Concerning curing monitoring of resins, different techniques have been applied, including near infrared chemometrics (NIR) [16], Raman spectroscopy [17], dynamic mechanical thermal analysis (DMTA) [18] and dielectric properties [19]. In all cases the identification of the characteristic points of structural formation

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is attempted based on the transient changes of the monitored properties.

In the current work, ultrasonic waves were transmitted through the thickness of a typical epoxy system during standard curing cycles that lead to the vitrification of the epoxy system. Due to the fact that transmission of ultrasound can be applied indirectly, the contact between the resin and the sensors is not necessary, providing a truly non-intrusive and economic way to measure the degree of reaction completion in real time [20]. The different phases of the epoxy curing process were found to correspond to the time evolution of distinct parameters that characterize the propagated wave. The degree of completion of the curing process could be determined via the asymptotic behavior of the characteristics of the propagated wave. The measurements were repeated for different temperatures in order to examine the effect of temperature on curing rate and degree. As is well known, typical epoxy systems (resin and hardener) are viscous liquids in room temperature. The mixture is thinning with temperature increase until polymerization reverses the effect and induces a rapid viscosity increase due to the increase in macromolecule size. Mobility is further reduced at the "gel" point, where the material obtains some rigidity, acquiring elastic properties while retaining a viscous component. As the reaction continues, molecular mobility is further reduced and the material gains stiffness rapidly with a continuously reducing rate. The viscous component is gradually reduced and the material is typically "frozen" to a glassy state. Ultrasound propagation depends directly on the specific properties of the material. In particular, stiffness is directly linked to the velocity of the wave and viscosity relates directly to the propagated energy. This work aims at using ultrasonics to efficiently monitor and evaluate the curing of epoxy systems, a field where detailed ultrasonic studies are scarce.

2. Experimental details

The experimental setup was designed for through-transmission propagation. The liquid resin was poured between two 5 mm thick PMMA plates, see Fig 1. The distance between the plates was accurately measured to be 20.6 mm, as defined by a U-shaped Teflon spacer placed in between the PMMA plates. The plates were held together using through thickness bolts at all four corners. In order to avoid any variation of the thickness of the resin specimen for different experiments, two spring clamping devices were employed so that the same pressure was applied during joining of the plates ensuring repeatability of the thickness of the Teflon spacer. This was particularly significant as even slight changes in the small specimen thickness, would lead to erroneous measurements. One sensor acting as pulser was mounted on one side (see Fig. 1), while the receiving transducer was placed on the exactly opposite position. The employed piezoelectric sensors (Pico, by Physical Acoustics Corporation) were sensitive to a quite broad band of frequencies, i.e. from 50 kHz to 800 kHz. The pulser was connected to a waveform generator (AFG3102, by Tektronix) which introduced one cycle of 500 kHz, at a constant time interval
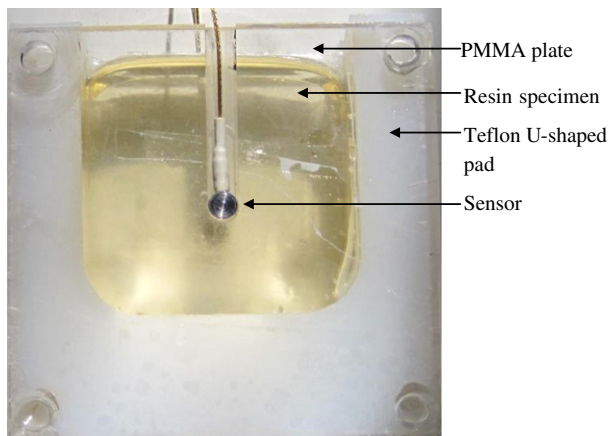
of 90 s. This time interval was selected in order to adequately monitor the evolution of the polymerization reaction at all rates. The electric signal was transformed to an elastic wave by the transducer (pulser). The transducer was acoustically coupled to the PMMA plates using ultrasonic gel. Thus, the ultrasonic waves were propagated through the plates to the curing epoxy. When reaching the opposite transducer (receiver), the signal was again transformed to an electric waveform via the receiver which was acoustically coupled to the opposite plate in the exactly same manner. Signals above a threshold of 40 dB were digitized and stored through a two channel PCI-2 acquisition board (by Physical Acoustics Corporation) with a sampling time of 0.1 μs. For a typical transit time of 10 μs for the sound to travel through the curing epoxy, the typical error associated with the measurement was around 1%. The electric signal of the wave generator was also directly fed to the other acquisition channel. The two channels were synchronized so that when the acquisition was triggered in one channel, the other channel simultaneously started recording. This allowed the measurement of the time delay between the excited and the received signals (Fig. 2). For the specific setup, the delay between the two pulses (excited and received) was mainly due to the travel time of the propagated wave through the epoxy. Some delay was also due to the propagation through the PMMA plates (see Fig. 3a), as well as to sensor delay effects. The latter accounted for the time necessary (i) for the transformation from electric to mechanical energy (and vice versa) on the piezoelectric disc of the transducers and (ii) for the propagation through the cover plate of the transducers. The total transit time that corresponded to the aforementioned delays could be of the order of 1–2 μs and could result in significant error if not accounted for [4]. As the pure transit time through the resin t_{resin} was the wanted part, from the measured total time delay the rest should be subtracted (see Fig. 3a, left). In order to measure the delay due to factors other than the resin, measurements under identical conditions were conducted with the plates in direct contact in all employed curing temperatures, i.e. from 20 to 40 °C (see Fig. 3a right). The transit time was 4.0 μs for 25 °C and 30 °C, 4.1 μs for 35 °C and 4.2 μs for 40 °C. These values were subtracted from the measurements at the corresponding temperatures. At the onset of each experiment and before filling the epoxy in the mould, excitation from the pulser did not lead to the transmission of any signal, indicating that any leakage of energy through the PMMA and Teflon plates of the container was negligible and could not interfere with the direct transmission through the resin specimen.

At the end of the measurement protocol which lasted for 800 min (approximately 14 h) the recorded waveforms were saved as separate files, and treated using a simple custom-made algorithm in Matlab environment in order to extract the transit time and the amplitude of the waveform automatically and reliably. The amplitude was defined as the voltage of the peak of the maximum cycle of the waveform. The results are presented normalized to the initial value for comparative purposes. The transit time measurement was based on a threshold crossing algorithm; the threshold was set equal to 1.5 times the maximum noise level exhibited during the pre-trigger period of 50 μs (see Fig. 4a). The first threshold crossing was considered as the onset of the received waveform. As should be mentioned, the recorded noise was at a very low level, allowing for a low threshold value and thus accurate determination of the waveform onset point. The signal-to-noise ratio was typically over 3000 and therefore no waveform stacking was employed.

Apart from the longitudinal wave measurements, surface wave measurements were also conducted in a thick epoxy specimen after the recommended high temperature curing cycle. These enabled the measurement of both longitudinal and Rayleigh velocities and consequently the determination of the Poisson's ratio which cannot be measured by through thickness longitudinal waves. The two receivers were placed in 30 mm distance and a pencil lead break excitation was conducted 10 mm away from the first receiver, see Fig. 3b. The distance of the receivers over the delay between the onsets of the two waveforms was used to calculate the longitudinal wave velocity, while the velocity of the Rayleigh was calculated by the delay between the strong characteristic Rayleigh peaks that can be easily identified after the initial weak longitudinal arrivals, as seen in Fig. 4b [21,22].

The resin and hardener (HT2) were of R&G Faserverbundwerkstoffe GmbH. According to manufacturer values, the density of the epoxy resin and the hardener was 1.14 g/ml and 0.98 g/ml respectively. With the recommended mixing ratio of resin and hardener of 100:48, the density of the final mixture could be estimated
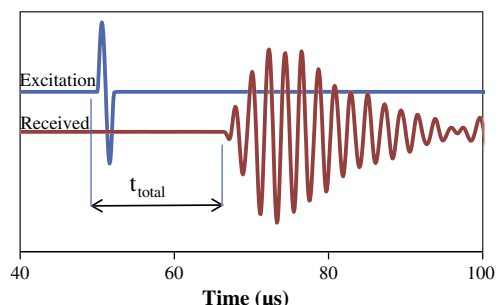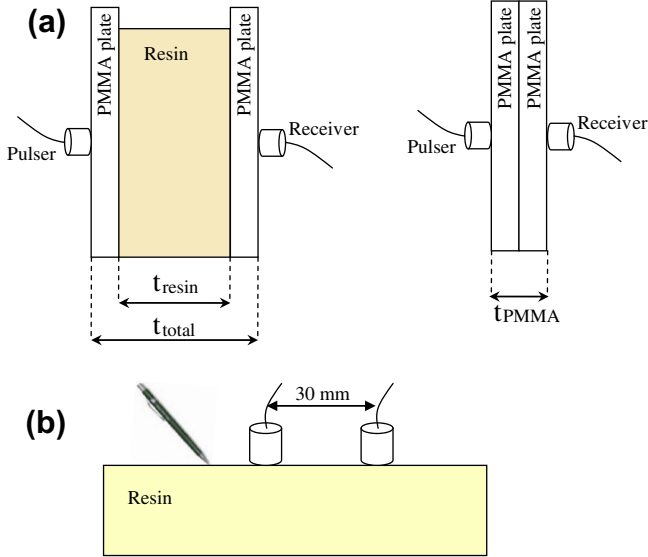

Fig. 1. Photograph of the experimental setup.

PMMA plate

Resin specimen

Teflon U-shaped pad

Sensor

**Fig. 2.** Delay between excitation and received signal.

Fig. 3. Schematic representation of ultrasonic through the thickness (a) and surface measurements (b).

to be 1.088 g/ml. The constituent materials (epoxy and hardener) were put under vacuum in a vacuum oven at the predefined experiment temperature for 1 h before mixing. After mixing, the epoxy system was immediately poured in the mould and placed in the oven under constant temperature and the ultrasonic monitoring commenced. Measurements were conducted in different temperatures (25, 32 and 40 °C) in order to assess the influence of temperature on the curing behavior.

3. Results

3.1. Pulse velocity

Immediately after mixing, the physical state of the epoxy system can be defined as viscous liquid. Liquids support longitudinal
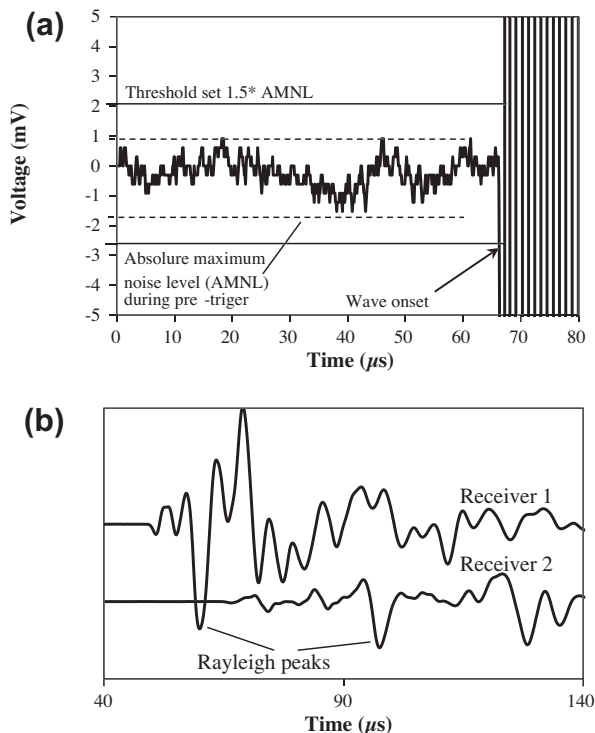
Fig. 4. (a) Noise level and threshold for automatic waveform onset picking, (b) typical surface waveforms.

waves due to their compressibility (inverse of bulk modulus). The propagation velocity V_L, is given by:

$$V_L = \sqrt{\frac{K}{\rho}} \qquad (1)$$

where ρ is the density and K the bulk modulus of the medium.

In its final state, resin has been transformed to a glassy solid. As a result, the longitudinal wave velocity is given by

$$V_L = \sqrt{\frac{E(1-v)}{\rho(1+v)(1-2v)}} \qquad (2)$$

where ρ is the density, E is the dynamic modulus of elasticity, and v is the Poisson's ratio of the medium.

Fig. 5 depicts the development of pulse velocity with time for three specimens cured in different temperatures. For all specimens an initial velocity decrease is recorded for the first minutes after mixing, which is followed by a rapid velocity increase, with progressively reducing rate. The velocity converges asymptotically to a value that may be regarded as corresponding to "complete" polymerization for the employed stoichiometry. The initial velocity value was approximately 1700 m/s for all specimens, while the asymptotic final velocity was approximately 2700 m/s. The effect of temperature was evident on the shape of the curves. The specimen cured at 40 °C, exhibited the initial drop, as well as the consequent rise of velocity much earlier than the specimens cured at 25 °C. Additionally, the level of the initial drop was also temperature related since it was less prominent for 25 °C lying at 50 m/s, while for the 40 °C specimen, at about 250 m/s. The point at which the velocity gained 95% of the final value was 140 min for 40 °C, 210 min for 32 °C and 350 min for 25 °C, indicating that "complete" curing was achieved earlier with increasing temperature, as is expected. The specimens were also measured by contact ultrasonic transducers of 5 MHz, in a pulse-echo mode after seven days at room temperature. The velocities for all specimens were between 2600 and 2700 m/s. This indicated that the stiffness of the polymer did not change significantly after the monitoring experiment.

As mentioned earlier, surface measurements on a cured polymer plate were also performed aiming at a typical Poisson's ratio determination for epoxy. The Rayleigh wave velocity was measured to be 1060 m/s. Through (3) the Poisson's ratio, v, was calculated at 0.39:

$$\frac{V_L}{V_R} = \frac{1+v}{0.87+1.12v}\sqrt{\frac{2(1-v)}{(1-2v)}} \qquad (3)$$

From Eq. (2), the final dynamic modulus of elasticity for all three monitored systems was calculated at approximately 3.8 GPa.

From Eq. (1), the bulk modulus of the initial liquid was calculated at 3.1 GPa, while the final elastic modulus and Poisson's ratio lead to a bulk modulus value for the cured resin of 4.8 GPa. The main structural change in the polymerization process in terms of elastic properties is the acquisition of shear rigidity with the shear modulus starting from zero in the liquid state and reaching a value of 1.4 GPa at the fully polymerized state.

3.2. Amplitude

Apart from the information derived from velocity measurements, the amplitude of the received wave is a measure of the transmitted wave energy. During monitoring of time dependent materials, energy related parameters such as amplitude can be very useful, since changes in the microstructure of the material are normally directly related to transmission efficiency. Fig. 6 depicts the amplitude vs. time curves for the three different
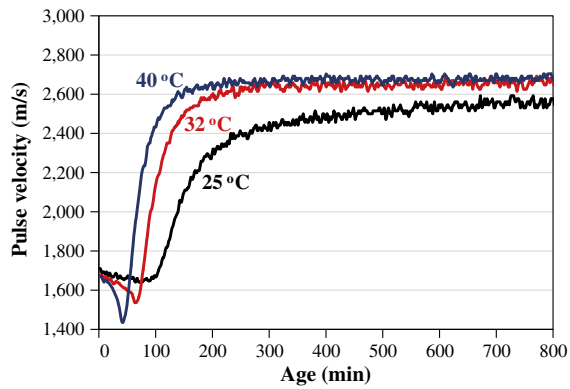
Fig. 5. Pulse velocity vs. curing age.

Fig. 6. Amplitude vs. curing age.

specimens. All curves were similar in that they exhibited a quick increase of amplitude, followed by a sharp decrease. Thereafter the transmission is partially restored to an asymptotic value. As in the case of velocity, the process was directly related to the applied temperature. The local amplitude minimum occured at 52.5 min for 40 °C and at 135 min for 25 °C. The wave amplitude decrease is a direct result of the increase of material attenuation. In a general case this could be attributed to scattering and damping. However, the specific material does not contain distinct constituent phases that could act like scatterers (especially for the applied wavelength of approximately 4 mm). As can be postulated, this decrease can be directly attributed to the increase of viscosity. One interesting phenomenon which was consistently observed was the initial increase of relative amplitude immediately after mixing. This can be attributed to the exotherm of the polymerization process which increased the temperature temporarily and rendered the liquid less viscous at the initial nucleation phase of the polymerization. This phenomenon was more pronounced at low temperature (25 °C), since in that case, the exotherm led to the thinning of the high viscosity epoxy system at room temperature. As the polymerization rate increased rapidly after nucleation, the viscosity also increased leading to increased energy loss of the propagated signal, as manifested by the increased attenuation of the wave amplitude. This was manifested by the strong decrease in transmitted amplitude for all studied epoxy specimens. In the final phase, where the polymer was vitrified or frozen to a glassy state, the transmission efficiency was again improved reaching an asymptotic value that was expected to characterize the final state of the cured polymer.

Fig. 7a and b depict the velocity and amplitude curves focusing on the first 200 min. The local minima of the curves were clearly translated to earlier times and lower values with the increase in temperature. Interestingly enough, the minima of velocity were exhibited earlier in time than those of amplitude for each specimen. In similar monitoring studies during vulcanization of elastomers the initial velocity decrease was attributed to the "softening" due to transient temperature rise [23]. According to the aforementioned rationale, the minima were indicative of two counteracting mechanisms. The initial temperature increase due to the exotherm at the early reaction stages decreased the initial viscosity and changed the bulk modulus of the liquid system leading to an increase in transmission efficiency and a decrease in velocity respectively. On the other hand, the ongoing polymerization reaction increased the viscosity and "thickened" the liquid with a corresponding delay and attenuation of the stress waves. At later curing stages the rate of the reaction dropped with the material reaching the gel state and after a certain time the polymer vitrified or obtained structural rigidity. The gel state can be regarded as the state
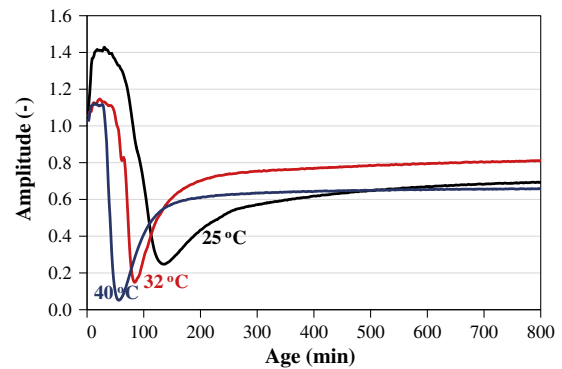
where the material reached maximum viscosity which as postulated was accompanied by the maximum energy loss or the minimum wave amplitude. The onset of vitrification had the opposite effect as it led to increased transmission efficiency and higher propagation velocities. The minima of the two curves (velocity and amplitude) did not coincide as the material already acquired a degree of extensional and shear rigidity from the gel state while the viscosity had not yet reached its maximum. As a result, the velocity minimum preceded the amplitude minimum.

3.3. Pulse duration

In order to monitor any time dependent behavior of a material, the parameters that exhibit the most pronounced changes throughout the process are most valuable. Apart from the wave parameters that are typically monitored in wave propagation experiments, other parameters that relate to the shape of the pulse may reveal interesting information, particularly with respect to the dispersive character of the propagated wave. In a homogeneous, non viscous fluid, a propagating pulse will not suffer any change in shape. In the time domain, this is equivalent to a constant duration of the propagated pulse, no matter how long the pulse will propagate. However, in inhomogeneous or viscous media the duration of the pulse usually increases and generally its shape is distorted [24,25]. In Fig. 8, two pulses recorded at two different ages of the same resin specimen are depicted. The two waveforms are translated in order for their first negative peak to coincide. However, it can clearly be observed that the next peaks do not coincide. The duration of ten full cycles differs by approximately 1.4 μs. Although correlating pulse duration to a physical property of the medium is not straightforward, the duration exhibits strong variations throughout the polymerization process and therefore, it is a descriptor that enhances the characterization of curing. The effect of viscosity damping is not constant for all frequencies. Therefore, for any pulse, even for narrow-band, there is a differential influence on the transmission and transit time of different frequency components. This creates a slight elongation of the pulse. Fig. 9 shows full waveforms recorded through the same specimen (25 °C) at different times. The shortest signal corresponded to the condition close to "complete" curing (200 min), while the longest was exhibited at 50 min. In this waveform the successive reflections could also be seen, with a delay between successive maxima of approximately 30 μs. This delay corresponded to twice the thickness of the specimen (2 ∗ 20.6 mm) with a corresponding pulse velocity of approximately 1400 m/s, as was measured for curing time of 50 min. In order to measure a duration-related parameter of the pulse and its development with time, a threshold crossing algorithm was again applied. The duration was defined by the delay between the first and the last threshold crossings. Due to
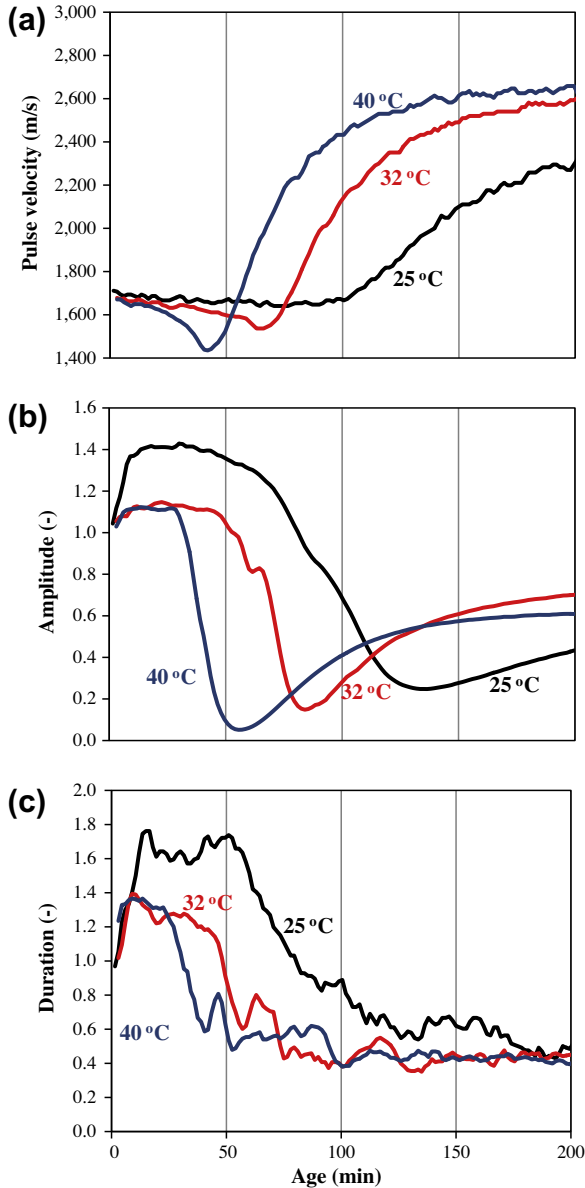
Fig. 7. (a) Pulse velocity, (b) amplitude, (c) pulse duration vs. curing age.

Fig. 8. Typical received waveforms at different ages of resin (50 min, dashed line and 200 min, solid).

in the duration of the pulse ceases earlier than changes in amplitude or velocity. This observation implies that pulse duration did not depend on the acquisition of structural rigidity which continued until later times. Table 1 summarizes the characteristic points of the velocity, amplitude and duration curves vs. time.

As can be seen in Table 1, the final velocity was attained faster than the final amplitude. Additionally, the amplitude was more sensitive to microstructural changes since it continued to change even after velocity had ceased to increase. This indicated that although the elastic properties are fully attained, transmission efficiency is further enhanced by the decrease of damping properties which follows the vitrification stage.

Additionally, Table 2 shows the relative change of the three wave parameters studied herein normalized by their initial value. Pulse velocity exhibited a strong change (eventual increase), but it was always within 51% of its initial value. Amplitude was very sensitive for the initial stage of curing as it exhibited a rise to 144% and a decrease to less than 25% before reaching a value close to 70% of the initial. Finally, duration seems to be the most sensitive parameter for the initial stage just after mixing with an increase to 176%, while later it reduces to 41% of the initial value, although it exhibits the highest "noise" of all studied parameters. It is mentioned that the pulse duration measured with the threshold of 1/50th of the maximum amplitude, proved the most sensitive descriptor not only due to the dispersion of the pulse, but also because when the amplitude is high, several reflections (up to three, see Fig. 9) are included into the pulse, while when the amplitude is lower, the reflections vanish and the duration becomes shorter.

the severe changes in amplitude during the experiment, a fixed threshold would produce biased results, especially for the times where the amplitude of the waveform was very low. Therefore, it was deemed necessary to introduce a variable threshold dependent on the peak amplitude for each waveform. More specifically, an optimum variable threshold of 1/50 of the maximum amplitude of each waveform was chosen in order to define the pulse duration. The duration of the pulse vs. curing time can be seen in Fig. 7c for the three different specimens. The application of different variable thresholds led to similar behavior for pulse duration with varying effect on the noise of the graph. Initially, a sharp increase in duration was observed leading to a wide plateau which lasted until approximately 50 min. Higher temperature led to a less sharp increase as well as a plateau of shorter duration. It is reasonable to assume that at this point the dispersion of the medium was maximum. Afterwards, the pulse duration decreased to reach to a value less than 50% of the initial for all studied temperatures. For 25 °C, the time to reach the minimum value was approximately 180 min, whereas for higher temperatures the final value was reached in approximately 90 min. As was observed, any change
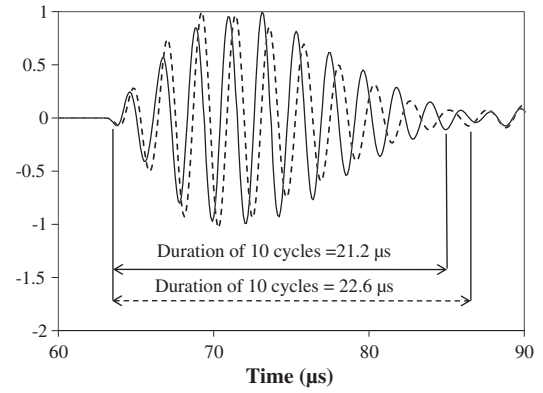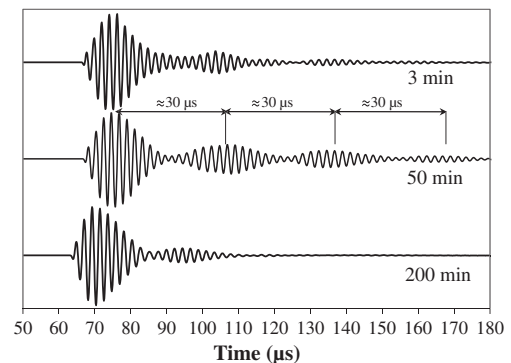

Fig. 9. Typical waveforms received at different ages of a resin cured at 25 °C.

Table 1
Characteristic times of wave parameters.

Curing temperature (°C)	Time of local minimum in velocity	Time of local minimum in amplitude	Time of final velocity[a]	Time of final amplitude[a]	Time of final duration[a]
25	88	135	350	550	260
32	65	82	210	440	140
40	42	55	140	250	100

[a] (Reaching within 5% of final value). Time is in min.

Table 2
Relative changes of wave parameters for the specimen of 25 °C.

Wave parameter	Minimum (%)	Maximum (%)	Final (%)	Range (%)
Pulse velocity	96	151	151	55
Wave amplitude	25	144	70	119
Pulse duration	41	176	70	135

4. Conclusion

The scope of this study was the ultrasonic monitoring of curing of epoxy systems. Ultrasonic longitudinal waves were propagated through the thickness of a typical epoxy system during polymerization and parameters such as pulse velocity, wave amplitude and pulse duration were continuously monitored. The complex time-dependent behavior of the material was reflected in the time evolution of the wave parameters. Pulse velocity exhibited a minor decrease at the early polymerization stages, before rapidly increasing due to the attainment of elastic rigidity. Wave amplitude on the other hand, which is a measure of the attenuation, was directly influenced by the viscosity, highlighting the point of the highest viscosity, which as postulated corresponded to the gelation of the epoxy system. The duration of the transmitted pulse, which is a sign of dispersion exhibited a sharp initial increase, as it was influenced by the viscosity but stabilized to a lower value shortly thereafter, earlier than the other wave parameters. The ultrasonic measurements allowed for the continuous nondestructive monitoring of the process, enabling the characterization of the state of polymerization, as well as the measurement of the mechanical properties of the mixture in real time. As was expected, the effect of temperature was particularly important as for higher temperatures all the fluctuations in the time history of the wave parameters occur much earlier as a result of the increased reaction rates. Summarizing, continuous ultrasonic monitoring was successful in identifying key elements in the polymerization process such as the temperature/polymerization dependent viscosity changes, the gradual attainment of structural rigidity, the evolution of the damping properties of the curing polymer and at the same time provided a measure of the degree of curing as manifested by the asymptotic behavior of all studied parameters.

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