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Nacef Ghodhbani, Pierre Maréchal, Hugues Duflo. Real-time polymerization monitoring of a thermosetting resin around its glassy transition temperature. 171st Meeting of the Acoustical Society of America, May 2016, Salt Lake City, United States. <10.1121/2.0000363>. <hal-03777982>

HAL Id: hal-03777982

<https://normandie-univ.hal.science/hal-03777982v1>

Submitted on 15 Sep 2022

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Citation: *Proc. Mtgs. Acoust.* **26**, 045004 (2016); doi: 10.1121/2.0000363

View online: <https://doi.org/10.1121/2.0000363>

View Table of Contents: <https://asa.scitation.org/toc/pma/26/1>

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Real-time polymerization monitoring of a thermosetting resin around its glassy transition temperature

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Real-time ultrasonic monitoring is investigated to quantify changes in physical and mechanical properties during the manufacture of composite structures. In this context, an experimental transmission was developed with the aim of characterizing a high temperature polymerization reaction and post-curing properties using an ultrasonic method. First, the monitoring of ultrasonic parameters of a thermosetting resin is carried out in an isothermal polymerization process at 160°C. During this curing, the resin is changing from its initial viscous liquid state to its final viscous solid state. Between those states, a glassy transition stage is observed, during which the physical properties are strongly changing, i.e. an increase of the ultrasonic velocity up to its steady value and a transient increase of the ultrasonic attenuation. Secondly, the ultrasonic inspection of the thermosetting resin is performed during a heating and cooling process to study the temperature sensitivity after curing. This type of characterization lead to identifying the ultrasonic properties dependence before, during and after the glassy transition temperature T_g . This study is composed of two complementary parts: the first is useful for the curing optimization, while the second one is fruitful for the post-processing characterization in a temperature range including the glassy transition temperature.



1. INTRODUCTION

The ultrasound monitoring of elastic properties of resins has been investigated by various authors [1-7]. These experimental studies showed the feasibility of measurements during the polymerization process. In a study for the reflection mode [8], an experimental setup has been developed for the monitoring of ultrasonic parameters within the context of composite plate production. The ultrasonic wave velocity and attenuation are successfully monitored at low temperature for the curing and the post curing processes. For this configuration in reflection, the use of ultrasonic echoes from composite plates elaborated with the Resin Transfer Molding (RTM) method requires some conditions: the thickness of the mold and that of the composite sheet are to be chosen carefully to avoid overlapping of echoes during the manufacturing, the signal-to-noise-ratio (SNR) of the second round-trip echo in the mold and the epoxy is to be considered with regard to the first one, and eventually the use of high temperature transducers. In the present work, the ultrasonic properties are monitored in the transmission mode at high temperature. Viscoelastic properties are deduced from pulse-echo measurements and dispersive properties are identified from FFT processed signals. These methods are described and the associated results are discussed.

2. EXPERIMENT

A. CONTEXT

Ultrasonic instrumentation of RTM fabrication process and ultrasound monitoring is still under research and development. The basic principles are well known, but *in situ* operating instrumentation is subjected to difficulties such as echo recovering, conversion modes, high attenuation, high temperature, repeatability, *etc.* Nevertheless, the information which can be extracted from such ultrasonic probes is of interest for manufacturing monitoring. Moreover, ultrasonic monitoring can be helpful for the improvement of the RTM process in terms of quality and production rate through the optimization of temperature and pressure cycles during the fabrication. The extracted ultrasonic signals give information on the viscoelastic properties and their temperature and frequency dependences. Particularly, the longitudinal velocity gives information on the elastic properties and the attenuation is related to viscosity. These properties are significantly evolving during the polymerization of a thermosetting resin.

B. EXPERIMENTAL SETUP

The RTM process is shown in Figure 1. The fiber fabrics are placed between the mold and backing mold. It is then impregnated by the flow of a fluid resin. As illustrated, the ultrasound monitoring can be integrated externally to the mold and provide information on the inside viscoelastic properties and reaction kinetics. Basically, a single ultrasonic transducer can be used in pulse-echo mode (Figure 1 (a)). An alternative setup consists in a transmission setup (Figure 1 (b)), which can improve signal-to-noise ratio and the real conditions imposed by the process, but brings additional constraints in terms of implementation.

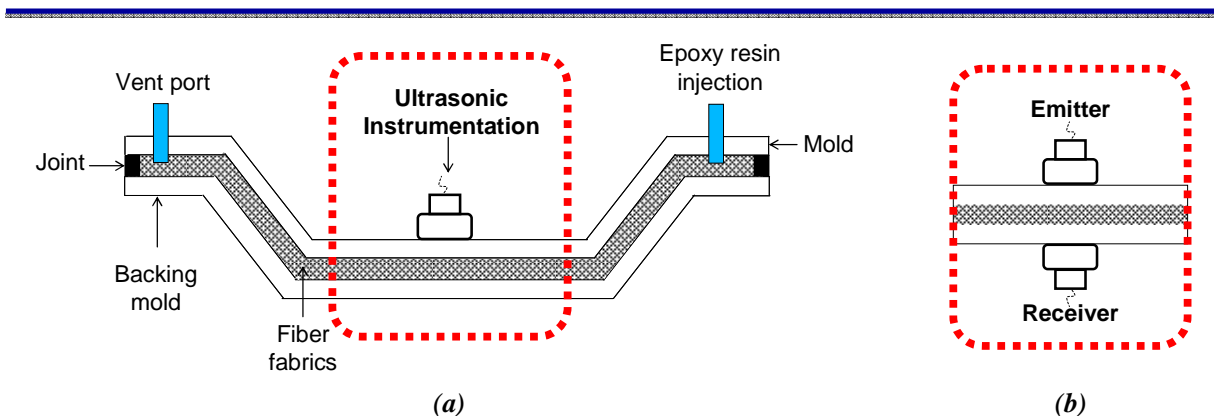


Figure 1. Scheme of the Resin Transfer Molding (RTM) fabrication process and associated ultrasonic instrumentation: (a) reflection mode and (b) transmission mode.

On the basis of the RTM process, an experimental setup was developed. A three-layer structure is obtained: Mold / Fiber-resin composite / Backing mold. The experimental setup was developed using aluminum blocks as mold and counter-mold, and dimensioned to avoid echo-recovering during the polymerization [9, 10].

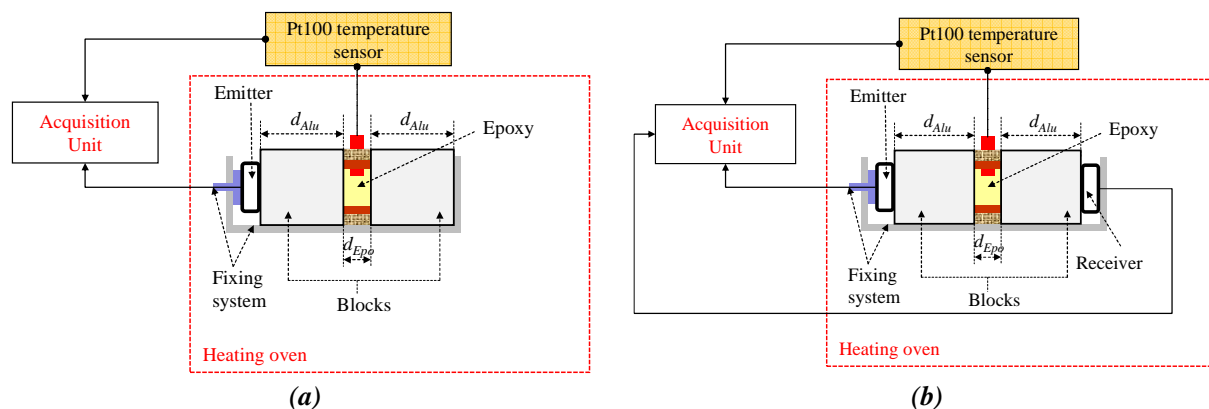


Figure 2. Experimental setup for the ultrasonic monitoring: (a) reflection mode and (b) transmission mode.

An acquisition unit was developed, with pre-processing for the on-line monitoring. The viscoelastic properties and their temperature and frequency dependences are then extracted by adapted post-processing. In the reflection mode [9-10] configuration (Figure 2 (a)), the experimental setup for the ultrasound polymerization monitoring was made up of a longitudinal transducer used in pulse-echo mode. As a result, the wave velocity was fitted using a Weibull distribution and was investigated by the Debye series modeling (DSM) [11], in order to compare experiment and modeling. The monitoring of the cured epoxy was also performed after curing in order to study the thermal transformation compared with DSC measurements. As a result, an approximated frequency temperature (f, T) model is proposed for frequency and temperature dispersions of attenuation and velocity. The use of transducers designed for high temperature environment *i.e.* integrating delay lines, imposes transmission mode measurements (Figure 2 (b)) to avoid overlapping echoes during the RTM process.

In this configuration, the ultrasonic wave velocity and attenuation are measured from the directly transmitted echoes at the beginning of polymerization (reference state) and during the process (instantaneous state) by means of an iterative optimization method [12].

3. RESULTS

The monitoring of ultrasonic properties can lead to identification of phase and thermal transformations in an epoxy resin and to establishing the relationship between ultrasound and rheological methods. In pulse-echo mode, the polymerization is studied through the transfer function between the reference state and the instantaneous state. In the following study, the polymerization is performed in transmission mode using classical longitudinal transducer at low temperature ($T < 60^\circ\text{C}$) and using the integrated delay lines transducers at high temperature ($T > 120^\circ\text{C}$).

A. LOW TEMPERATURE MONITORING

For the low temperature monitoring, the structure is a three layers Alu/Epo/Alu (Figure 3). The reference ultrasonic wave velocity and attenuation of the constitutive layers (*i.e.* in epoxy $\{c_{Epo,ref}(f), \alpha_{Epo,ref}(f)\}$ and in aluminum $\{c_{Alu,ref}(f), \alpha_{Alu,ref}(f)\}$) are calculated from the transfer function $\underline{T}_{21,ET}(f) = \underline{S}_{2,ET}(f) / \underline{S}_{1,ET}(f)$ and $\underline{T}_{31,ET}(f) = \underline{S}_{3,ET}(f) / \underline{S}_{1,ET}(f)$:

$$\begin{cases} \underline{S}_{1,ET}(f) = \underline{S}_0(f) e^{-2jk_{Alu}d_{Alu}} e^{-jk_{Epo}d_{Epo}} \underline{T}_{Alu/Epo} \underline{T}_{Epo/Alu} \\ \underline{S}_{2,ET}(f) = \underline{S}_0(f) e^{-2jk_{Alu}d_{Alu}} e^{-3jk_{Epo}d_{Epo}} \underline{T}_{Alu/Epo} \underline{T}_{Epo/Alu} \underline{R}_{Epo/Alu} \underline{R}_{Epo/Alu} \\ \underline{S}_{3,ET}(f) = \underline{S}_0(f) e^{-4jk_{Alu}d_{Alu}} e^{-jk_{Epo}d_{Epo}} \underline{T}_{Alu/Epo} \underline{T}_{Epo/Alu} \underline{R}_{Alu/Epo} \end{cases} \quad (1)$$

where $\underline{S}_{1,ET}(f)$, $\underline{S}_{2,ET}(f)$ and $\underline{S}_{3,ET}(f)$ are the spectra of the transmitted signals $s_{1,ET}(t)$, $s_{2,ET}(t)$ and $s_{3,ET}(t)$, respectively (Figure 3).

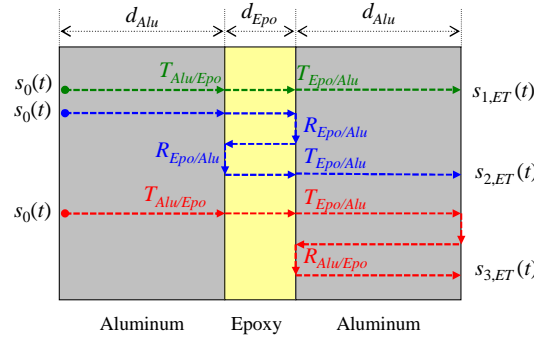


Figure 3. Experimental configuration for the ultrasonic monitoring at low temperature.

The ultrasonic properties are thus extracted from recorded echoes in the reference state ($\underline{S}_{1,ref,ET}(f)$) and the instantaneous state ($\underline{S}_{1,ET}(f)$) described in equation (1), and using the resulting transfer function $\underline{T}_{11,ET}(f) = \underline{S}_{1,ET}(f) / \underline{S}_{1,ref,ET}(f)$. Then, the instantaneous ($c_{Epo}(f)$, $\alpha_{Epo}(f)$) properties of the epoxy resin are deduced using the following equations:

$$\begin{cases} c_{Epo}(f) = \frac{d_{Epo}}{\frac{d_{Epo}}{c_{Epo,ref}(f)} - 2d_{Alu} \left(\frac{1}{c_{Alu}(f)} - \frac{1}{c_{Alu,ref}(f)} \right) - \frac{Arg(\underline{T}_{11,ET}(f))}{2\pi f} + \frac{Arg(\underline{T}(f))}{2\pi f}} \\ \alpha_{Epo}(f) = \alpha_{Epo,ref}(f) - \frac{1}{d_{Epo}} \ln \left(\left| \frac{\underline{T}_{11,ET}(f)}{\underline{T}(f)} \right| \right) + 2 \frac{d_{Alu}}{d_{Epo}} (\alpha_{Alu,ref}(f) - \alpha_{Alu}(f)) \end{cases} \quad (2)$$

The global transfer coefficient $\underline{T}(f)$ is calculated for each acquisition date using an iterative procedure involving the instantaneous properties of aluminum ($c_{Alu}(f)$, $\alpha_{Alu}(f)$) and epoxy ($c_{Epo}(f)$, $\alpha_{Epo}(f)$):

$$\underline{T}(f) = \frac{\underline{T}_{Alu/Epo}(f)\underline{T}_{Epo/Alu}(f)}{\underline{T}_{Alu/Epo,ref}(f)\underline{T}_{Epo/Alu,ref}(f)} \quad (3)$$

As illustrated by Figure 4, the polymerization of the epoxy resin can be identified and characterized through the ultrasonic parameters and their time and frequency dependencies.

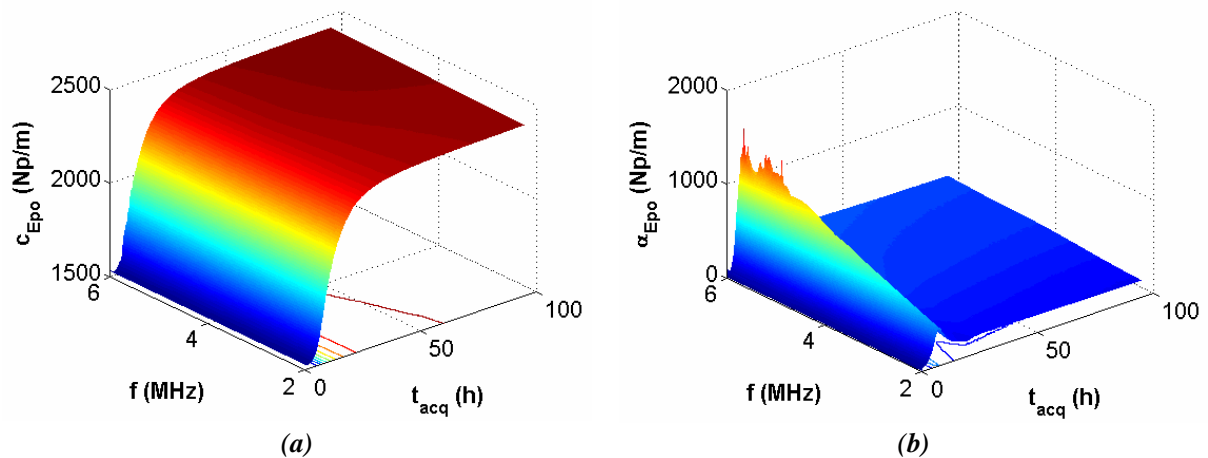


Figure 4. Longitudinal ultrasonic properties of the studied epoxy resin: (a) wave velocity $c_{Epo}(f)$ and (b) attenuation $\alpha_{Epo}(f)$, both characteristics depending on the acquisition time t_{acq} and frequency f .

B. HIGH TEMPERATURE MONITORING

For the high temperature monitoring, specific high temperature transducers integrating delay lines were used. Therefore, the signal processing method has to be adapted to the resulting five-layer configuration, including temperature sensitivity of the delay lines, as well as those of the aluminum blocks (Figure (5)).

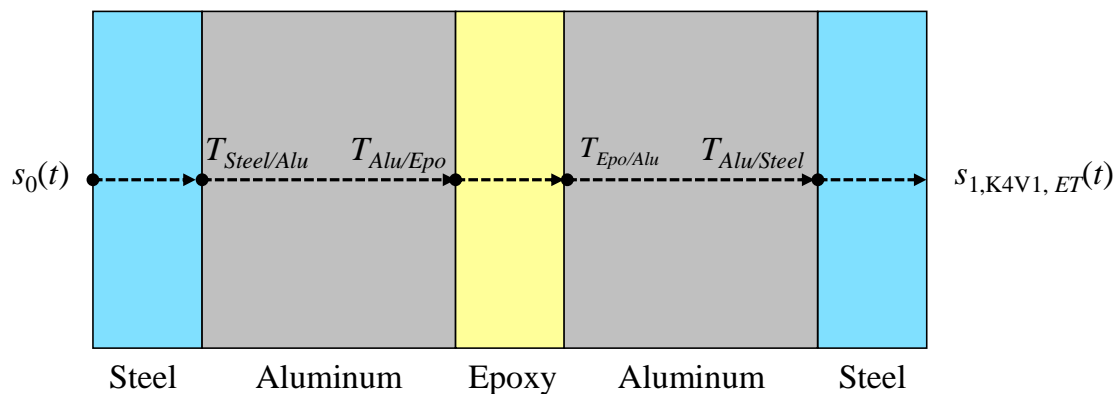


Figure 5. Experimental configuration for the ultrasonic monitoring at high temperature.

On the basis of this configuration, significant changes in terms of propagation time and amplitudes can be observed, not only due to the epoxy layer itself but also due to the surrounding metal layers, i.e. aluminum and steel. These external deviations to the problem of polymerization monitoring are therefore corrected in order to extract the proper epoxy resin properties during the polymerization (Figure (6)).

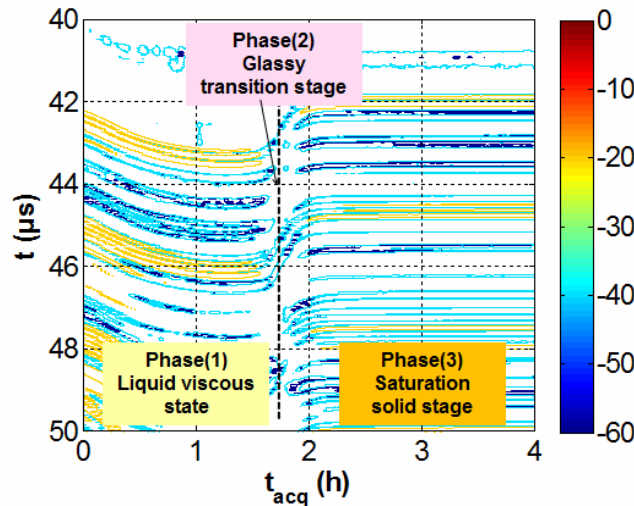


Figure 6. Ultrasonic monitoring of a high temperature polymerization.

An accurate analysis of each of the layers leads to the targeted result: the ultrasonic properties of the epoxy layer as a function of time and temperature.

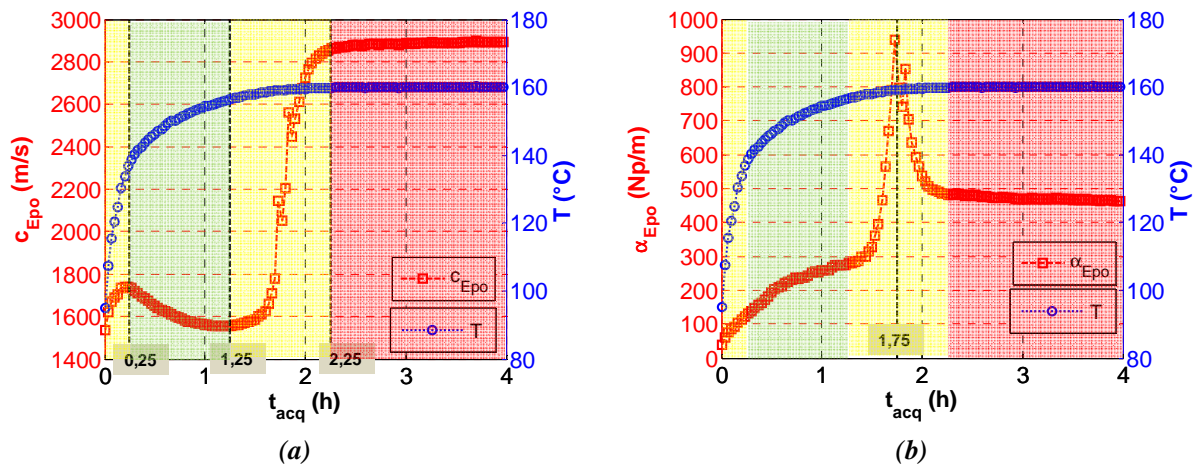


Figure 7. Longitudinal ultrasonic properties of the epoxy resin: (a) wave velocity $c_{Epo}(f)$ and (b) attenuation $\alpha_{Epo}(f)$, both characteristics depending on the acquisition time t_{acq} .

In Figure 7, the change in ultrasonic properties during polymerization is illustrated. Both temperature effect and polymerization are clearly observable. In Figure 7 (a), the wave velocity increases from $t_{acq} = 0$ to 0.25 h. In this region, the reaction begins and the temperature effect is negligible. Between $t_{acq} = 0.25$ and 1.25 h, the temperature varies between 140 and 160°C; in this

region the temperature effect is dominant, resulting in a decrease of the velocity. From $t_{acq} = 1.25$ to 2.25 h, the polymerization kinetics reaches its maximum and the wave velocity increases greatly. This time range, around the inflexion of wave velocity indicates the glass transition phase. Finally from $t_{acq} = 2.25$ h, the wave velocity is nearly constant as a function of the acquisition time. The reaction rate therefore tends to zero, and the resin has reached its steady state which indicates the end of polymerization. In Figure 7 (b), the wave attenuation increases with temperature. In the glass transition region the attenuation shows a peak at 1.75 hours. Finally from 2.25 h its evolution is nearly zero, corresponding to the end of polymerization.

4. CONCLUSION

In the framework of the RTM process, an experimental study was conducted to integrate a real-time monitoring of the viscoelastic properties of a polymerizing material. Phase and thermal transformations of a thermosetting resin were monitored and studied at low and high temperature. The ultrasonic properties of a resin and their time and temperature dependences were identified. The frequency dependence was also investigated as significant parameter for the viscoelastic properties.

ACKNOWLEDGMENTS

The authors would like to thank as well as Paul Benard, Henri Cahingt and Francis Duhamel for their technical support.

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