Polymerization Monitoring Using Ultrasound

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Abstract

The polymerization of a resin is the main interest during the fabrication of a composite material. In the case of a Resin Transfer Molding (RTM) process, the monitoring of resin polymerization can inform about the evolution of the process parameters. In this work, ultrasonic velocity and attenuation in the resin are monitored using a broadband ultrasonic transducer. Using this method, the time dependence of the characterized parameters allows determining the polymerization characteristics such as the beginning, the end or the inflexion point of the studied parameter. Through these measurements, the evolution of polymerization could be related to the process and environmental conditions (such as temperature) in order to consider improvements to the RTM technique.

Keywords: polymerization, epoxy resin, material properties, ultrasound, monitoring.

1. Introduction

The ultrasonic evaluation of material properties is classically used for the characterization of static materials. In the case of quasi-static evolution of material properties, such a method can advantageously be calibrated. Broadband ultrasonic transducers allow us to determine the ultrasonic spectral properties of materials, with a high sensitivity [1, 2]. In the case of a polymerization, the reaction is exothermic, and the temperature must also be monitored. In this paper, the monitoring of the polymerization of an epoxy resin is investigated in view of applications on the resin transfer molding (RTM) process [3]. Using a 2.25 MHz broadband ultrasonic transducer, an experimental setup is proposed for polymerization monitoring purpose, taking into account non-recovering conditions of roundtrip echoes [4]. As a result, the spectral ultrasonic properties of the polymerizing epoxy resin layer are deduced. From the acoustical properties point of view, based on the chemical reaction principle [5, 6, 7], a modeling approach of the polymerization is proposed. The high temperature sensitivity is highlighted and an Arrhenius compensation is fitted on the experimental data.

2. Theory

2.1 Velocity and attenuation

According to Figure 1, the spectra of useful roundtrip signals $s_{1r}(t)$ and $s_{2r}(t)$, denoted $S_{1r}(f)$ and $S_{2r}(f)$ are given by [1]:

$$S_{1r}(f) = A_1 e^{i k_L 2 d_2 j} T_{12} R_{23} R_{21}$$ (1)
$$S_{2r}(f) = A_2 e^{i k_L 4 d_2 j} T_{12} R_{23} R_{21}$$ (2)

where $A$ is the amplitude of the signal, $d_2$ is the thickness of the medium indexed 2, $k_L = \omega c_{L}(f)/c_{L}(f)$ is the complex longitudinal wavenumber associated to the medium indexed 2, where $c_{L}(f)$ and $\alpha_{L}(f)$ are the ultrasonic longitudinal velocity and attenuation, respectively. The coefficients $T_{pq}$ and $R_{pq}$ are the transmission and reflection coefficients respectively, when the beam is incident from medium indexed $p$ to the medium indexed $q$:

$$T_{pq} = \frac{2 Z_q}{Z_q + Z_p}$$
$$R_{pq} = \frac{Z_q - Z_p}{Z_q + Z_p}$$ (3)

where $Z_i = \rho_i c_{L,i}$ is the acoustic impedance with $\rho_i$ the density and $c_{L,i}$, is the longitudinal velocity of the medium of index $i$, considered constant in the useful frequency range.
2.2 Material characterization

The ultrasonic velocity $c_L(f)$ and attenuation $\alpha_L(f)$ are deduced from the spectral method [2], i.e. transfer function $\tilde{T}(f) = \tilde{S}_2(f) / \tilde{S}_1(f)$:

$$c_L(f) = 2\pi f \frac{2d_2}{\text{Arg} \left( \tilde{T}(f) \right)}$$

(4)

and

$$\alpha_L(f) = - \frac{1}{2d_2} \ln \left( \frac{T(f)}{R_{21} \cdot R_{23}} \right)$$

(5)

A study on the diffraction of the ultrasound beam was performed and its effect is averred negligible [2]. Thus, in the following work, the diffraction effect is not taken into account.

The longitudinal wave velocity is nearly constant in the bandwidth of the transducer. Therefore, the value of the longitudinal wave velocity is averaged in the bandwidth of the transducer and is noted $c_L(f) = c_L$. Concerning the longitudinal attenuation, it is considered linear with the frequency in the bandwidth of the transducer $\alpha_L(f) = \alpha_0 f / f_0$, where $f_0$ is the reference frequency.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\rho$ (kg/m$^3$)</th>
<th>$c_L$ (m/s)</th>
<th>$\alpha_0$ (Np/(m.MHz))</th>
<th>$Z$ (MRa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>2700</td>
<td>6375</td>
<td>1</td>
<td>17.2</td>
</tr>
<tr>
<td>Liquid resin</td>
<td>1000</td>
<td>1645</td>
<td>15</td>
<td>1.64</td>
</tr>
<tr>
<td>Solid resin</td>
<td>1000</td>
<td>2730</td>
<td>40</td>
<td>2.73</td>
</tr>
</tbody>
</table>

$\rho$: density; $c_L$: longitudinal wave velocity at $f_0 = 2.25$ MHz; $\alpha_0$: linear frequency dependence of the longitudinal attenuation at $f_0 = 2.25$ MHz; $Z = \rho c_L$; acoustic impedance.

3. Experiment

3.1 Setup

The experimental device (Figure 1) consists of two aluminum blocks of $d_1 = 120$ mm thick, between which a mixture of epoxy resin and hardener Inclupox® of thickness $d_2 = 11$ mm is introduced (Figure 2 (a)). A $f_0 = 2.25$ MHz center frequency single element transducer is used for the characterization of the resin. Acquisitions of ultrasonic signals and temperature are saved every 5 min for a total duration of 180 h. In order to take into account the effect of temperature on the velocity and attenuation, the temperature was saved for each acquisition.
through a Pt 100 temperature sensor immersed in the resin during polymerization (Figure 2 (b)). The probe is connected to a Wheatstone bridge and a differential amplifier (Figure 2 (c)) representing the heating of the resin temperature.

![Image](image1.png)

Figure 2: (a) Experimental set up, (b) Pt 100 temperature sensor, (c) Wheatstone bridge and differential amplifier.

### 3.2 Measurement results

The velocity is measured using the spectral method (equation (4)) but also using time of flight (TOF) method where the velocity is written as:

\[
C_{TOF} = \frac{2d_2}{t_{1,rt} - t_{1,Al}},
\]

where \(t_{1,Al}\) is the date of the first round-trip in the first aluminium plate and \(t_{1,rt}\) is the date of the first round-trip in the resin and in the first aluminium plate (Figure 3 (a) and (b)). Practical precautions relative to the tri-layer thicknesses were taken into account to avoid overlapping of the useful echoes and are detailed in previous work [4]. The variation of the velocity according to the frequency in the resin in the liquid state is very small and is of the order of 0.06%, while in the solid state the material becomes dispersive and velocity increases with the frequency is of the order of 0.72%. Comparing the results of these two methods in terms of velocity shows a very good agreement (Figure 4).

![Image](image2.png)

Figure 3: Experimental pulse-echo response, with resin round-trip echoes obtained for polymerization dates (a) \(t = 0\) (liquid resin) and (b) \(t = 180\ h\) (solid resin).
4. Results

4.1 Velocity measurements

Upon polymerization of the resin, the appearance of a cloud of bubbles due to the chemical reaction between the resin and the curing agent were observed. The observation of these bubbles can be observed between the dates from 12 h to 40 h (Figure 4). Indeed, the appearance of bubbles disturbs the propagation of ultrasonic waves in the resin and thus distorts the measurement results. The TOF method gives more points since it is based on the first roundtrip echo in the aluminum and the first roundtrip in the resin while the spectral method requires the first and the second roundtrip echoes in resin. If bubbles are present, attenuation becomes very important and the second roundtrip in the resin is completely buried in the noise.

![Figure 4: Comparison of two methods of velocity measurements: spectral (black dots) according to equation (4) and TOF (red dots) according to equation (6).](image)

A basic approach of the polymerization reaction consists in a first order differential equation describing the polymer concentration \[ P \]. It involves a polymerization kinetic constant \( k_P \), here noted as the classical time constant \( \tau = 1/k_P \):

\[
[P] = 1 - e^{-\frac{t}{\tau}} \quad (7)
\]

Nevertheless, due to the complexity of the reaction and diffusion process, the variable \( k_P \) is not constant [5, 6, 7]. When taken into account, these considerations lead to a variation of the corresponding time constant. Moreover, it is observed experimentally that the polymerization kinetic starts slowly (\( \frac{\partial c}{\partial t_{acq}}|_{t_{acq}=0} = 0 \)). Various models were developed [5, 6, 7], but their numerous parameter inputs is not always convenient. Based on these remarks, we chose to model the polymerization process using empirical laws. Here, the velocity curve can be fitted by the following hyperbolic tangent law (Figure 5 (a)):

\[
c_{th}(t_{acq}) = c_{th,l} + \frac{c_{th,s} - c_{th,l}}{2} \left( 1 + \tanh \left( \frac{t_{acq} - t_{th}}{t_m} \right) \right) \quad (8)
\]

where \( c_{th,l} \) is the initial velocity at \( t_{acq} = 0 \) (liquid state) and \( c_{th,s} \) the end velocity at \( t_{acq} = 180 \) h (solid state), \( t_{th} = 27 \) h is the inflexion date (Figure 5 (b)), i.e. for \( c_{th}(t_l) = (c_{th,l} + c_{th,s})/2 \) and \( t_m \) is a dilatation time constant. A closer approach to the first order solution (equation (7)) leads to consider dissymmetry of the polymerization reaction, using the Weibull distribution:

\[
c_w(t_{acq}) = c_{w,l} + \left( c_{w,s} - c_{w,l} \right) \left( 1 - e^{-\frac{(t_{acq} - t_{w})^2}{\lambda^2}} \right) \quad (9)
\]
where $\lambda$ and $k$ are the Weibull distribution parameters, fitted to model the polymerization reaction, in accordance with the canonical solution to the first order differential equation (7). The identification was performed with consideration to the half polymerization duration $t_{50}$, previously defined as $t_{50} = \lambda (\log(2))^{1/k}$, and a second identification point, i.e. $t_{95} = \lambda 3^{1/k}$. It leads to $\lambda = 32$ and $k = 2$ Weibull parameters.

### 4.2 Temperature compensation

This first fitting does not take into account the velocity fluctuations due to temperature variation. The temperature dependence of the sound velocity of an epoxy resin was measured by Wada [8]. By extrapolation of the measurements made on the Young’s modulus [9, 10, 11], the temperature compensation is given by the form of an exponential type $e^{B_{T}T/T}$ [12], where $T_{0}$ and $B$ are two constants. Indeed, this temperature correction derives from the classical Arrhenius law (equation (10)), describing the variation of the velocity of chemical reaction as a function of the temperature. Thus, the temperature correction constant $B$ depends on the considered physical state, either before the inflection point (liquid state) or after the inflection point (solid state), i.e. $B_{l}$ and $B_{s}$, respectively:

$$
 c_{th}(T) = c_{th,\lambda}(T) e^{B_{l} \left( \frac{T - T_{0}}{T_{0}} \right)}
$$

where $T_{m} = 296 \, ^{\circ}K$ is the average temperature, $B_{l} = 579\, ^{\circ}K$ is a fitting constant at the liquid state and $B_{s} = 174\, ^{\circ}K$ is a fitting constant at the solid state. Indeed, the liquid state is more sensitive to temperature (before inflection point) than the solid state (after the inflection point). As a result, the theoretical velocity curves $c_{th}$ (equation (8)) and $c_{W}$ (equation (9)) can be corrected in temperature and noted $c_{th,T}(T)$ and $c_{W,T}(T)$. The fitting procedure allows to follow the experimental profile of the velocity $c_{ep}$ and permits us to observe more clearly the effect of temperature (Figure 5).

![Figure 5](image_url)

**Figure 5**: (a) Experimental velocity calculated according to TOF method $c_{ep}$ (black points), temperature corrected velocity fitting $c_{th,T}(T)$ (solid red) and $c_{W,T}(T)$ (blue) (equations (8), (9) and (10)). (b) Time derivative of the experimental velocity $dc_{ep}/dt_{acq}$, theoretical models $dc_{th,T}/dt_{acq}$ and $dc_{W,T}/dt_{acq}$ and related inflexion points.

After 72 h, the resin is fully cured. However, local variations of velocity are recorded. These changes are related to temperature change in the resin. Changes are recorded around the ambient temperature $T = 297 \pm \Delta T \, ^{\circ}K$, this means that the chemical reaction due to the polymerization is not exothermic and changes in ultrasound velocity reveal the sensitivity of the ultrasound to the temperature. From this fitting (Figure 5 (a)), the velocity fluctuations due to the temperature are shown with a slight delay with respect to the theoretical curve. This delay time corresponds to the thermal diffusion in the material to the Pt 100 temperature...
sensor. Sensitivities to temperature for both liquid and solid cases can be written and approximated as follows:

\[
s_{c,l,s}(\%) = 100 \left( e^{B_{1,l,s} \left( \frac{1}{T} - \frac{1}{T_0} \right)} - 1 \right) = B_{1,l,s} \left( \frac{1}{T} - \frac{1}{T_m} \right) \approx -\frac{B_{1,l,s}}{T_m^2} \delta T
\]  

(11)

Rigorously, the velocity sensitivity \( s_c \) is decreasing as a function of the temperature (equation (11)). However, it can be linearized and approximated by a constant i.e. an increase \( \delta T = 1 \text{ °K} \) causes lowering of \( s_{c,l} = 0.65\% \) from the velocity in the liquid and \( s_{c,s} = 0.2\% \) in the solid case.

### 4.3 Attenuation measurements

The longitudinal attenuation is well fitted by a power law function [13, 2]:

\[
\alpha_l(f) = \alpha_0 f^n
\]  

(12)

The power parameter is \( n_s = 0.98 \), i.e. close to \( n = 1 \) when the propagation medium is solid (Figure 6 (a)). It is \( n_f = 1.81 \) close to \( n = 2 \) when the it is liquid (Figure 6 (b)).

![Figure 6](image1.png)

Figure 6: Attenuation measurement and fitting parameters (a) liquid state for \( \alpha_0 = 10^{-10} \) and \( n_f = 1.81 \) (b) solid state for \( \alpha_0 = 4 \times 10^{-5} \) and \( n_s = 0.98 \).

In the liquid case, adjustment parameters \( \alpha_l(f) \), \( \alpha_0 \) and \( n \) evolve as expected, i.e. \( \alpha_0 \) drastically increases, up to \( 10^{15} \) in the beginning of the polymerization, while the power parameter \( n \) decreases from nearly 2 down to nearly −1. When reaching solid state, the parameter \( \alpha_0 \) tends to \( 10^{-5} \) (Figure 7 (a)) and \( n \) tends to 1 (Figure 7 (b)) [2].

![Figure 7](image2.png)

Figure 7: Evolution of the fitting parameters (a) \( \alpha_0 \) and (b) \( n \) as a function of polymerization time.
The mean attenuation $\alpha_m$ is given by the average value on the bandwidth of the transducer for each acquisition and its evolution over time is given by Figure 8 (a). The attenuation increases with the polymerization until the appearance of bubbles where the attenuation becomes very high and non-significant before leveling off when the material is fully polymerized (Figure 8 (a)). On this level, fluctuations due to temperature changes are also observed with a small delay time. The average attenuation in the bandwidth of the transducer $\alpha_m$ is calculated by the spectral method (equation (4)). It shows a growth in the beginning from $\alpha_m \approx 50 \text{ Np/m}$, but it is strongly disturbed by the bubble cloud observed for $t_{acq} \in [8; 41] \text{ h}$. This phenomenon is also observed on the derivative of the average attenuation (Figure 8 (b)). The end date of polymerization can thus be observed when $(\partial \alpha_m / \partial t_{acq}) \approx 0$, i.e. $\alpha_m(t_{acq} \geq 72 \text{ h}) \approx 90 \text{ Np/m}$.

![Figure 8](image)

**Figure 8**: Evolution of attenuation over the time: (a) mean attenuation $\alpha_m$ calculated by spectral method and (b) derivative of the attenuation $d\alpha_m / dt_{acq}$.

### 4. Conclusion

In this paper, the ultrasonic monitoring of polymerization of an epoxy resin at ambient temperature was performed. Ultrasonic properties, such as velocity and attenuation in the resin layer, were determined during the polymerization time, using a single element transducer. The continuous evolution of the longitudinal wave velocity is nearly constant within the bandwidth of the transducer. It allows us to monitor the state changing, from liquid to solid, in agreement with classical polymerization reactions kinetics. A temperature dependence was observed and the velocity sensitivity to temperature was investigated around the ambient temperature. The identification of parameters corresponding to the longitudinal attenuation are frequency dependent. These attenuation parameters show strong variations and allow a precise monitoring of the polymerization reaction. As a perspective, the presented setup is able to monitor the polymerization reaction including the fiber matrix, constituting the future fiber composite material.

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References


