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Abstract. In this study, the 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 a device reproducing the experimental conditions for manufacturing a composite material with a process known as RTM, that is to say an isothermal polymerization at $T = 160°C$. 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. Second, 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 leads to identifying the ultrasonic properties dependence before, during and after the glassy transition temperature T_g. Eventually, 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 T_g.

1. Introduction

The polymerization kinetics is of interest for the thermochemical research community [1]. In the recent decades, the monitoring of viscoelastic parameters of polymers and composite structures from the manufacturing phase to the aging phase has been investigated using various methods: DSC [2], rheology [3], IR [4] or ultrasound [5]. The ultrasound monitoring of resins [6-12] can operate during the fabrication process. In a previous study in reflection mode [13-16], the ultrasonic characteristics were directly related to the reaction kinetics and the reaction conversion. A transmission mode setup would enable to avoid overlapping of echoes during the manufacturing. In the present work, the ultrasonic properties are monitored at high temperature [17-20] in the transmission mode [21-25]. Here, the transmission characterization method is based on the direct transmission of a pulse at the beginning of polymerization (reference state) and enables the monitoring of the ultrasonic properties (instantaneous state) by means of an iterative optimization method [21,22,15]. This paper is divided into two parts: the first describes the theoretical equations and the general approach of the proposed method. The second part presents the experimental setup and associated results with an application of

this approach with the high temperature transducer and the RTM6 epoxy resin.

2. Monitoring of the ultrasonic properties

2.1. Low temperature monitoring

As illustrated, Figure 1 shows the different echoes used to the monitoring of the ultrasonic proprieties of an epoxy resin during its polymerization with the transmission method. The structure is composed of two identical aluminum blocks between which the resin liquid is introduced. Multiple echoes can be recorded after various transmission and reflections in the constituting layers. First, the complex spectrum $\underline{S}_1(f)$ corresponds to the direct transmitted echo $s_1(t)$ through the three-layer structure composed of the first aluminum block, the epoxy layer and the second aluminum block (*Alu/Epo/Alu*). Second, the complex spectrum $\underline{S}_2(f)$ corresponds to the direct transmitted echo $s_2(t)$ through the three-layer structure with a round-trip echo in the epoxy. Third, the complex spectrum $\underline{S}_3(f)$ corresponds to the direct transmitted echo $s_3(t)$ through the structure with a round-trip echo in one of the aluminum blocks. These spectra $\underline{S}_1(f)$, $\underline{S}_2(f)$ and $\underline{S}_3(f)$ are written in the following form:

$$\begin{cases} \underline{S}_1(f) = \underline{S}_0(f)e^{-2j\underline{k}_{Alu}d_{Alu}}e^{-j\underline{k}_{Epo}d_{Epo}}\underline{T}_{Alu/Epo}\underline{T}_{Epo/Alu} \\ \underline{S}_2(f) = \underline{S}_0(f)e^{-2j\underline{k}_{Alu}d_{Alu}}e^{-3j\underline{k}_{Epo}d_{Epo}}\underline{T}_{Alu/Epo}\underline{R}_{Epo/Alu}\underline{R}_{Alu/Epo}\underline{T}_{Epo/Alu} \\ \underline{S}_3(f) = \underline{S}_0(f)e^{-4j\underline{k}_{Alu}d_{Alu}}e^{-j\underline{k}_{Epo}d_{Epo}}\underline{T}_{Alu/Epo}\underline{T}_{Epo/Alu}\underline{R}_{Alu/Epo} \end{cases} \quad (1)$$

where $\underline{S}_0(f)$ is the emission signal; $k_{Alu} = \omega/c_{Alu}(f) + j\alpha_{Alu}(f)$ and $k_{Epo} = \omega/c_{Epo}(f) + j\alpha_{Epo}(f)$ are the longitudinal complex wavenumbers, in aluminum and epoxy resin respectively; d_{Alu} and d_{Epo} are the thicknesses of aluminum and resin layer, respectively; $\underline{T}_{\{Alu/Epo, Epo/Alu\}}$ and $\underline{R}_{\{Alu/Epo, Epo/Alu\}}$ are the complex transmission and reflection coefficients from aluminum to epoxy (*Alu/Epo*) or reversely, from epoxy to aluminum (*Epo/Alu*), respectively.

Figure 1. Paths of the transmission signal in three-layer structure composed by a first aluminum block, an epoxy layer and a second aluminum block (Alu/Epo/Alu).

The transfer function $\underline{T}_{21}(f) = \underline{S}_2(f)/\underline{S}_1(f)$ contains information on the longitudinal properties of the epoxy resin layer, i.e. the velocity $c_{Epo}(f)$ and attenuation $\alpha_{Epo}(f)$. Consequently, the argument of the transfer function Arg($\underline{T}_{21}(f)$) and its modulus $|\underline{T}_{21}(f)|$ give the following frequency dependencies:

$$\begin{cases} c_{Epo}(f) = \dfrac{-4\pi f d_{Epo}}{Arg(\underline{T}_{21}(f))} \\[4mm] \alpha_{Epo}(f) = \dfrac{-1}{2d_{Epo}} \ln\left(\left| \dfrac{\underline{T}_{21}(f)}{\underline{R}_{Epo/Alu}^2} \right| \right) \end{cases} \tag{2}$$

Similarly, the transfer function $\underline{T}_{31}(f) = \underline{S}_3(f)/\underline{S}_1(f)$ contains information on the longitudinal ultrasonic properties of the aluminum blocks, i.e. the expressions of the velocity $c_{Alu}(f)$ and attenuation $\alpha_{Alu}(f)$ in the aluminum layer.

The transmission technique consists in calculating the ultrasonic properties of the epoxy relatively to a reference state of the epoxy at the beginning of polymerization. At the reference state, the spectrum $\underline{S}_{1,ref}(f)$, corresponds to the first transmitted echo $s_{1,ref}(t)$:

$$\underline{S}_{1,ref}(f) = \underline{S}_0(f) e^{-2j\underline{k}_{Alu,ref} d_{Alu}} e^{-j\underline{k}_{Epo,ref} d_{Epo}} \underline{T}_{Alu/Epo,ref} \underline{T}_{Epo/Alu,ref} \tag{3}$$

where $\underline{k}_{Alu,ref} = \omega/c_{Alu,ref}(f) + j\alpha_{Alu,ref}(f)$ and $\underline{k}_{Epo,ref} = \omega/c_{Epo,ref}(f) + j\alpha_{Epo,ref}(f)$ correspond to the complex wavenumbers at a reference state, $\underline{T}_{\{Alu/Epo,ref, Epo/Alu,ref\}}$ and $\underline{R}_{\{Alu/Epo,ref, Epo/Alu,ref\}}$ are the complex transmission and reflection coefficients from aluminum to epoxy (*A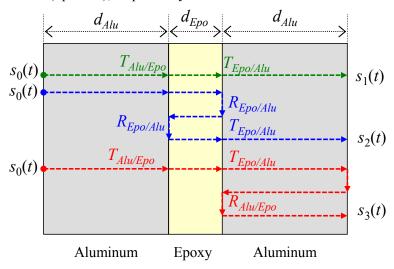lu/Epo*) or reversely, from epoxy to aluminum (*Epo/Alu*) fro the reference state, respectively. The transfer function $\underline{T}_{11}(f) = \underline{S}_1(f)/\underline{S}_{1,ref}(f)$ contains information on instantaneous ultrasonic properties in epoxy. The expression of the velocity $c_{Epo}(f)$ and attenuation $\alpha_{Epo}(f)$ in the epoxy are written as a function of the argument of the transfer function $Arg(\underline{T}_{11}(f))$ and the modulus $|\underline{T}_{11}(f)|$ in the following form:

$$\begin{cases} c_{Epo}(f) = \dfrac{d_{Epo}}{\dfrac{d_{Epo}}{c_{Epo,ref}(f)} - \dfrac{1}{2\pi f} Arg\left(\dfrac{\underline{T}_{11}(f)}{\underline{T}}\right) + 2d_{Alu}\left(\dfrac{1}{c_{Alu,ref}(f)} - \dfrac{1}{c_{Alu}(f)}\right)} \\[6mm] \alpha_{Epo}(f) = \alpha_{Epo,ref}(f) - \dfrac{1}{d_{Epo}} \ln\left(\left|\dfrac{\underline{T}_{11}(f)}{\underline{T}}\right|\right) + 2\dfrac{d_{Alu}}{d_{Epo}}\left(\alpha_{Alu,ref}(f) - \alpha_{Alu}(f)\right) \end{cases} \tag{4}$$

where $\underline{T}$ is a transfer coefficient which is written in the following form:

$$\underline{T} = \dfrac{\underline{T}_{Alu/Epo} \underline{T}_{Epo/Alu}}{\underline{T}_{Alu/Epo,ref} \underline{T}_{Epo/Alu,ref}} \tag{5}$$

The calculation of the ultrasonic properties during polymerization is summarized by the algorithm procedure in Figure 2. At the beginning of the polymerization reaction, the reference ultrasonic properties in epoxy are calculated from equation (2). These initial properties at the reference state are used to calculate the instantaneous properties in the epoxy resin as a function of time, according to equation (4), including the iterative calculation of transfer coefficient $\underline{T}$ (equation (5)).

2.2. High temperature monitoring

As illustrated by Figure 3, the high temperature transducers with delay lines lead to a five layers structure (*Stl/Alu/Epo/Alu/Stl*), corresponding to the steel delay line of the emission transducer (*Stl*), the aluminum block (*Alu*), the epoxy layer (*Epo*), the aluminum block (*Alu*) and then the delay line of the receiving transducer (*Stl*). The instantaneous signal transmitted through the five layer structure is denoted $s_{1,HT}(t)$ results from the direct transmission transfer function $\underline{T}_d = \underline{T}_{Stl/Alu} \cdot \underline{T}_{Alu/Epo} \cdot \underline{T}_{Epo/Alu} \cdot \underline{T}_{Alu/Stl}$.

The spectra $\underline{S}_{1,HT}(f)$ corresponding to the transmitted echo $s_{1,HT}(t)$ can be written as:

$$\underline{S}_{1,HT}(f) = \underline{S}_0 e^{-2j\underline{k}_{Alu} d_{Alu}} e^{-2j\underline{k}_{Stl} d_{Stl}} e^{-j\underline{k}_{Epo} d_{Epo}} \underline{T}_d \tag{6}$$
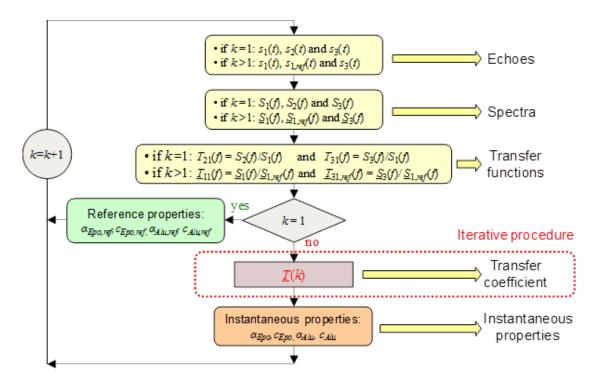
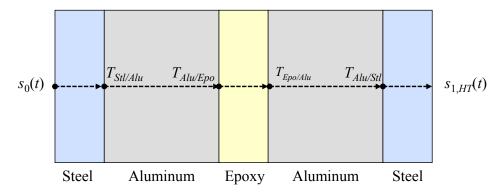**Figure 2.** Algorithm for calculating ultrasonic properties.

Figure 3. Direct transmission path in a five layer structure (*Stl*/*Alu*/*Epo*/*Alu*/*Stl*) and associated instantaneous signal $s_{1,HT}(t)$.

Using the procedure described in Figure 2, the ultrasonic velocity c_{Epo} can be written as a function of the time shift between the reference and the instantaneous echo $\Delta t_{11,HT}$, of the time shift in the molds δt_{Alu} and in the delay lines δt_{Stl}. The attenuation α_{Epo} is expressed as a function of the of the ratio between the maximum amplitude of the instantaneous echo $\max(s_{1,HT}(t))$ and that of the reference echo $\max(s_{1,HT,ref}(t))$, and the attenuation variation in the molds $\delta\alpha_{Alu}$ and in the delay lines $\delta\alpha_{Stl}$:

$$
\begin{cases}
c_{Epo} = \dfrac{d_{Epo}}{\dfrac{d_{Epo}}{c_{Epo,ref}} - \Delta t_{11,HT} + \delta t_{Alu} + \delta t_{Stl}} \\[4ex]
\alpha_{Epo} = \alpha_{Epo,ref} - \dfrac{1}{d_{Epo}} \ln\left(\dfrac{\max(s_{1,HT}(t))}{\max(s_{1,HT,ref}(t))} \dfrac{1}{\left|\underline{T}_{HT}\right|} \right) + \delta\alpha_{Alu} + \delta\alpha_{Stl}
\end{cases}
\tag{7}
$$

where $\underline{T}_{HT}$ is a transfer coefficient describing the evolution of the direct transmission coefficient $\underline{T}_d$:

$$\underline{T}_{HT} = \frac{\underline{T}_d}{\underline{T}_{d,ref}} = \frac{\underline{T}_{Stl/Alu}\underline{T}_{Alu/Epo}\underline{T}_{Epo/Alu}\underline{T}_{Alu/Stl}}{\underline{T}_{Stl/Alu,ref}\underline{T}_{Alu/Epo,ref}\underline{T}_{Epo/Alu,ref}\underline{T}_{Alu/Stl,ref}} \tag{8}$$

3. Experiment

3.1. Experimental setup

The experimental setup is composed of two contact transducers, one emitter and the other receiver, placed in contact with mold (
(a)). The procedure for preparing the epoxy resin (Resoltech or RTM6) and the instrumentation is detailed in a previous work [13]. The transducer emits longitudinal waves using a pulse generator. The second transducer receives the echoes (
(b)) then acquired using a digital oscilloscope. The temperature is programmed and regulated by a heating oven. A Pt100 temperature sensor is immersed in the epoxy resin in order to record the temperature changes during the polymerization. The acoustic signals and the temperature are automatically recorded and processed with an acquisition period of 10 minutes, using an acquisition program on Matlab.
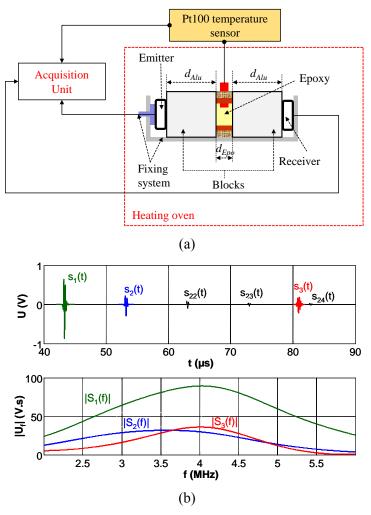

(a)

(b)

Figure 4. Experimental setup and associated signals: (a) experimental setup for the ultrasonic monitoring; (b) processed transmitted echoes $s_1(t)$, $s_2(t)$ and $s_3(t)$, including round-trip echoes $s_{22}(t)$, $s_{23}(t)$ and $s_{24}(t)$ in the epoxy layer, and associated spectra in the three-layer structure (*Alu/Epo/Alu*).

3.2. Low temperature processing

As illustrated Figure 5, the ultrasonic properties of the epoxy layer were evaluated while the polymerization was monitored as a function of the acquisition time t_{acq}, at a setpoint temperature $T = 40°C$. These results are illustrated in Figure 5(a) for the velocity $c_{Epo}(t_{acq})$ and in Figure 5(b) for the attenuation $\alpha_{Epo}(t_{acq})$.
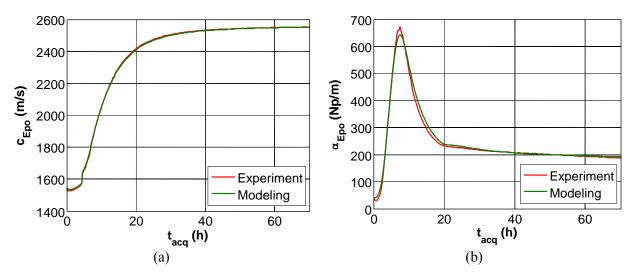

(a)   (b)

Figure 5. Ultrasonic properties of the epoxy resin: (a) velocity $c_{Epo}(t_{acq})$, and (b) attenuation $\alpha_{Epo}(t_{acq})$, while the polymerization was monitored at a setpoint temperature $T = 40°C$.

3.3. High temperature processing

A high temperature (HT) piezoelectric transducer (GE Measurement and Control) is specifically used for continuous high-temperature transmission measurements (up to 180°C). The center frequency of the transducer is $f_0 = 4$ MHz. This type of transducer has an integrated steel (*Stl*) delay line used for the protection of the piezoelectric material, and as illustrated in Figure 3, it results in multiple round-trip echoes in the delay line. These delay lines make the emission-reflection configuration complicated by the echoes overlap. The chosen method consists in working with the first transmitted echo provided that we know the ultrasonic properties in the aluminum molds and the integrated steel delay lines as well as their evolutions as a function of the temperature. This is what was done with what we called the reference state.

The polymerization monitoring at high temperature of the RTM6 resin was carried out according a precise protocol. The resin was degassed during 30 minutes. Meanwhile, the molds were heated at 80°C, and once the resin was flowed in the mold, the setpoint temperature was set at 160°C. At that time $t_{acq} = 0$, the polymerization monitoring started and the transmitted signals through the five layer structure were recorded periodically. As illustrated by

(a), the liquid viscoelastic phase ranges from $t_{acq} = 0$ and 1.25 h and shows a small variation, mainly due to the temperature increase of the resin. The second phase ranging from $t_{acq} = 1.25$ to 2.25 h is that of the glassy transition, characterized by a strong variation of the echoes amplitude and time-of-flight. The third phase defined by $t_{acq} > 2.25$ h, corresponds to the stabilization of the echoes properties, i.e. solidification of the epoxy. As a result, in

(b), the associated wave velocity c_{Epo} (m/s) and attenuation α_{Epo} (Np/m) in the epoxy layer were extracted using the previously described algorithm. These deduced properties of the epoxy layer clearly show the glassy transition around 1.75 h.
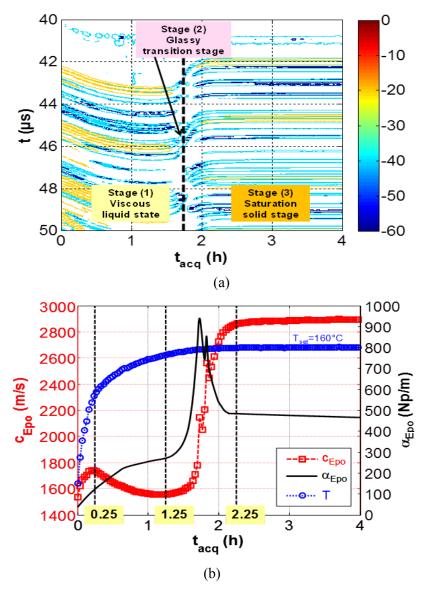
(a)

(b)

Figure 6. (a) Ultrasound monitoring of the transmitted signals through the five layers studied configuration, in the case of a RTM6 epoxy resin with a couple of high temperature transducers and (b) associated velocity c_{Epo} (m/s) and attenuation α_{Epo} (Np/m) in the epoxy layer.

4. Conclusion

The reference properties were estimated using different spectral and temporal methods. The transfer coefficient $\underline{T}$ has been determined in an analytical form and via an iterative optimization based on an inverse approach. Since the processing method has been described and validated, then the ultrasonic properties can be studied at high temperature with transducers integrating delay lines. In this five layer configuration, the ultrasonic properties of the epoxy resin $\{c_{Epo}, \alpha_{Epo}\}$ can be calculated from those evaluated at the reference state $\{c_{Epo,ref}, \alpha_{Epo,ref}\}$, including also those of the aluminum molds $\{c_{Alu}, \alpha_{Alu}\}$ and delay lines $\{c_{Stl}, \alpha_{Stl}\}$ and the appropriate temperature compensations through the transfer coefficient $\underline{T}$. Polymerization monitoring of a RTM6 epoxy resin was carried out at high temperature, leading to the determination of the thermal and phase transformations through ultrasound.

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