CHEMICAL SHRINKAGE AND THERMOMECHANICAL CHARACTERIZATION OF DIFFERENT RESIN SYSTEMS AND PREPREGS DURING CURE BY A NOVEL IN SITU MEASUREMENT METHOD

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1 General Introduction
As the composite industry grows, the use of thick parts and pieces of complex shape is increasingly in demand notably for structural applications requiring larger cross-sections to respond to mechanical stresses. The curing of thick parts remains a challenge because of their low thermal conductivity and the high heat of reaction generated during the cross-linking polymerization. This combination of low conductivity and high heat sources in the part can induce large temperature gradients and thus generate residual stresses and possible polymer degradation. Internal stresses can generate defects in the part affecting its mechanical performance and inducing geometrical distortions. The resin cure and the chemical shrinkage have to be characterized in order to predict the geometrical variations of the part during processing and use. For this, several techniques have been developed in the past, implying notably the coupled use of different equipment. Recently, a novel in-situ technique has been developed [1-3] which allows simultaneous characterization of resin cure as well as dimensional and rheological change during polymerization. This innovative technique presents the great advantage of reducing the sources of error such as the time lag or difference in sample size by the use of a single device. These measures are performed with a thermal flux cell combined with a Dynamical Mechanical thermal Analyzer (DMA).

The design of the novel thermal cell enables direct injection of the liquid resin into a closed cavity. The temperature control is ensured by the thermal enclosure of the DMA. The resin is contained in a mold where the upper and lower surfaces act as heat flux sensors. Changes in temperature and thermal flux are directly monitored as well as the dynamical displacement and the stiffness during the curing process.

First tests carried out on a Di-Glycidyl Ether of Bisphenol A (DGEBA) epoxy –anhydride cured resin system were very promising [1,2]. The heat of reaction measured was very close to DSC measurements. Moreover shrinkage and stiffness showed consistent results. This new measurement technique opened a new window for process optimization leading to better understanding of combined phenomena that take place during polymerization process. The purpose of this study is to extend this approach to different resin systems and prepregs in order to demonstrate its capabilities.

2 Experimental
2.1 Thermal flux cell method
The thermal shrinkage and mechanical measurements were carried out with the new thermal cell HFC-200 installed in a DMA 450+ from 01dB Metravib. The thermal cell (see Figure 1) possesses area heat flux sensors specially designed by Thermoflux located beneath each side of the sample. The temperature control is ensured by the thermal enclosure of the DMA instrument. A Teflon ring covers the two plates to provide insulation of the sample to its surrounding to minimize side thermal effects. The heat flux and temperature are monitored by these flux sensors. The sample shrinkage and stiffness are respectively measured by the static displacement and dynamic response of the DMA.
2.2 Material and experimental set up

In this work, several resin systems are studied as well as prepregs. For tests on liquid resin, the material is directly injected into the closed cavity whereas for prepregs it is insertion between the upper and lower plates. For tests on liquid resins, the temperature is stabilized in the thermal enclosure before the material injection into the sample holder. For tests on prepregs, the temperature stabilization is done with the sample already in place at room temperature. Then the temperature is raised at a rate between 0.5 to 3°C/min to the isothermal plateau, in order to simulate the autoclave curing. The DMA is activated applying a dynamic force to the sample with a low displacement.

For comparison purpose, differential scanning calorimetry experiments were conducted using TA Instruments DSC Q2000 under similar conditions as the DMA tests. Heat of reaction was calculated from the total heat flow curve. Gel point determination was also carried out using Anton-Paar MCR501 rheometer. Experiments were run under Small Amplitude Oscillatory Shear (SAOS) at strain and frequency in the linear viscoelastic (LVE) region.

3 Results and discussion

On each system studied, and particularly for liquid resins given the high isothermal temperatures, optimization of testing parameters is necessary. This optimization takes into account the thermal effect due to sample mass and the dynamic signal of the DMA as well. For liquid resin, a sample mass of 1 g was fixed based on these analyses which corresponds to the volume of a cylindrical sample of 20 mm diameter and 2 mm thick. For prepregs, pre-compaction of the layers is necessary in order to ensure good contact with the upper plate along the polymerization reaction.

Figure 2 shows an example of the evolution of the heat flux generated by the cross linking reaction of a DGEBA-anhydride resin at 120°C in the DMA. The sudden drop of heat at the beginning of the curve (i.e. values below zero) is due to the thermal shock created by the injection of the liquid resin at room temperature. During cross-linking, the two heat sensors record a positive change of the heat flux with a maximum peak reached around 300 seconds. The polymerization is completed after 1000 seconds as illustrated by the ending plateau. In order to get...
comparative basis between the samples, the measured heat flux is divided by the sample mass.

The heat of reaction during the polymer curing is determined from the measurement of heat flux by the heat flux sensors which are in close contact with the sample. The reaction rate is assumed to be a unique function of the degree of conversion \( \alpha \) and temperature \( T \), neglecting the diffusion of chemical species:

\[
\frac{d\alpha}{dt} = f(T, \alpha) \quad \text{and} \quad \alpha = \int_0^t \frac{d\alpha}{dt} \, dt \quad (1)
\]

In this novel characterization cell, the heat flow was measured with the heat flux sensors in close contact with the sample. The heat of reaction was computed as the total heat flow measured at the upper and lower plate of the cell. In previous work on DGEBA-anhydride resin [1, 2], an average heat of reaction of 337 J/g was measured with the DMA resulting of 40 experiments. This value was very similar as DSC’s value of 321 J/g. Figure 3 shows the evolution of the resin heat of reaction during cure at 120°C. This heat of reaction was obtained by integration of curves in Figure 2 following equation (1). A nearly full cure is obtained after 600 seconds although some heat still released until 1000 seconds.

![Fig. 3. Evolution of the heat of reaction with time during isothermal cure of DGEBA-anhydride resin at 120°C with the DMA HFC200 cell.](image)

Figure 4 shows the thermal history and cure evolution during an isothermal test on the DMA cell. Initially, the cell is kept isothermal at 120°C. The resin is then injected at room temperature at 0 seconds, which is denoted by a drop of 1°C in the temperature of the cell. The temperature of the system then increases due to the exothermic reaction of the resin. At 300 seconds, the reaction of the resin is enough to release sufficient heat to increase the temperature locally up to 124°C. At the exothermic peak, the resin undergoes a degree of cure of 70%, meaning that gelation has already occurred prior to 300 seconds. A full cure is observed after 1000 seconds.

![Fig. 4. Thermal history and cure evolution during isothermal test at 120°C.](image)

Figure 5 illustrates the evolution of degree of cure with time using both DMA cell and DSC methods. The degree of cure evaluated with the DSC technique (full line) arises before the DMA. There is a time shift as illustrated in Figure 5. This time shift is not negligible and should therefore be compensated in the case of coupling measurements from different devices [4].

In Figure 5, the DMA and DSC curves show a similar slope during most of the curing process. It is known that during isothermal cure experiments, variability may occur because of the temperature instabilities [5] and large difference in sample mass between these two devices. Given that the sample mass is three orders of magnitude larger for the DMA test (1 g) than the DSC (8 mg), temperature gradients are expected to be a source of cure differences. As the cure reaction progresses, the resin becomes more solid reducing the mobility of the polymer chains. After 90% cure, the polymerization is mainly controlled by diffusion. At this point, the differences in sample mass between DSC and DMA will have an important impact on the cure process. This effect can be seen in Figure 2 by
the differences in slopes near the plateau at the end of cure.

Fig. 5 Comparison between degree of cure measured with DSC and the DMA HFC200 cell for DGEBA-anhydride resin.

The upper plate of the DMA cell oscillates at amplitude of 20 microns and frequency of 10 Hz. The instrument applies a controlled force to induce such oscillation to the resin sample. As the liquid resin undergoes polymerization, the dynamic force required to apply a constant amplitude oscillation will increase from gelation to full cure. Then, knowing the variation on dynamic force, the change in mechanical properties of the resin can be followed during polymerization. On the other hand, when the resin shrinks during cure, the instrument adjusts the position of the upper plate so that it is in continuous contact with the sample (see Figure 1). Measuring the static position of the upper plate is then a direct evaluation of the volume changes occurred during resin polymerization.

Figure 6a illustrates the evolution of sample stiffness during resin cure on the DMA cell. At the early beginning of the test, the liquid resin has no dynamical mechanical properties and a stiffness of 10 N/m is measured by the DMA cell. This small stiffness is due to the moving liquid under dynamic compaction. The stiffness slowly increases linearly the first 200 seconds up to 50 N/m corresponding to 20% of cure. At this stage the polymer chains start to form an inter-connected tridimensional network resulting in a quick increment of mechanical properties shown by sudden change to a steeper slope in stiffness.

Figure 6a also shows the evolution of Tan δ which is the ratio between the storage and loss modulus of the dynamic stiffness. It can be seen that a maximum of Tan δ is observed at 230 seconds, representing a maximum of the dissipating energy in the sample. The peak in Tan δ can be associated to the initiation of resin gelation [6] and the time value from DMA test is quite close to the gel time of 245 seconds from rheology data as illustrated in Figure 6b, considering the point that the instruments principle is quite different and cannot be compared on an absolute basis. This time of 245 seconds corresponds to the cross-over of the storage (G') and loss modulus (G'') and at this point the complex viscosity (η*) starts to increase to infinity. Rheology gel point determination was verified for different
frequencies from 5 to 100 rad/s and the gel time was found to be independent to frequency \([7, 8]\). The difference of 15 seconds in the gel point detection between DMA and rheology can be associated to the difference in the measurement principle and sample mass inertia. As illustrated in Figure 3a, at gel, the material changes from a liquid-like to a gel-like state and since it is no longer flowing, it reveals a pseudo-elastic behavior similar as a solid when compacted. The sample’s mechanical properties grow logarithmically from this gelation point until reaching a plateau of \(10^7\, \text{N/m}\) at the end of cure.

In a previous work, Ruiz and Trochu \([4, 9]\) have model this nonlinear behavior with a log-log function of degree of cure. They have shown that the evolution of mechanical properties starts just after gelation and increases, following a logarithmic function, until the sample is fully cured. This nonlinear function of cure is assumed to be related to the increment of glass transition temperature \((T_g)\) from the monomer to the polymer. The increment of \(T_g\) is a power law function of cure as described by Di Benedetto equation \([10]\). In this study, a new model is proposed to predict the evolution of mechanical properties with degree of cure as presented in equation (2).

\[
\frac{\log K}{\log \alpha} \cong B \quad \text{and} \quad \log K = B \left[ \frac{(1-\alpha_{gel})\log \alpha + 1}{1-\alpha_{gel}} \right] \quad (2)
\]

where \(K\) is the stiffness of the sample, \(\alpha\) the degree of cure, \(B\) a fitting constant obtained from the experimental results and \(\alpha_{gel}\) is the degree of cure at gelation (ie. peak of \(\tan \delta\) in Figure 6a). The first equation on the left represents the general trend by a log-log function, while the equation on the right is the particular model proposed for the epoxy-anhydride resin been studied. The parameters of this model are reported in Table 1.

![Figure 7. Stiffness as a function of degree of cure and proposed model. Isothermal cure at 120°C of DGEBA-anhydride resin for various samples.](image)

Figure 7 illustrates the evolution of stiffness during polymerization for series of tests with DMA carried out at different amplitudes and frequencies. Stiffness found to be nonlinear from the same degree of cure of 33% which corresponds to the gelation point. Although there are differences in stiffness before gelation, the data overlapped after gelation. This nonlinear relation was also reported by previous studies of Ruiz et al. \([4, 9]\) for polyester resins and more recently Abou Msallem et al. \([11]\) for epoxy resins. These approaches take into account the transition from viscoelastic to elastic behaviour and the glass transition temperature as well.

Along the polymerization, the upper plate of the sample-holder dynamically stimulates the resin with strain amplitude of 20 microns and frequency of 10 Hz. The position of the sample holder \(z(t)\) is defined as the average value of the oscillation and a controller ensures that the dynamic displacement around this value is maintained at constant predefined amplitude. The variation in time of linear change of the polymer \(Lch(t)\) can then be defined as follows:

\[
L_{ch}(t) = \frac{z(t)-z_{init}}{th_{init}} 
\]

where \(z_{init}\) is the initial position of the upper plate of the sample holder (see Figure 1), \(z(t)\) is the varying position in time of the upper plate, and \(th_{init}\) is the initial thickness of the liquid sample.

<table>
<thead>
<tr>
<th>Stiffness model</th>
<th>Shrinkage model</th>
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<tbody>
<tr>
<td>Equation (2)</td>
<td>Equation (7)</td>
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<tr>
<td>(B)</td>
<td>(C)</td>
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<tr>
<td>11.225</td>
<td>5.050</td>
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<tr>
<td>(\alpha_{gel})</td>
<td>(\alpha_c)</td>
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<tr>
<td>0.332</td>
<td>0.535</td>
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Previous experimental studies have been conducted by several researchers relating the volumetric changes that occur during thermoset processing. Hill et al. [12] proposed that the overall volumetric changes of a thermoset resin during cure can be considered as a combination between thermal expansion/contraction and polymerization shrinkage as follows:

\[
\left(\frac{1}{V_0}\frac{dV}{dt}\right)_{\text{overall}} = \left(\frac{1}{V_0}\frac{dV}{dt}\right)_{\text{Thermal contribution}} - \left(\frac{1}{V_0}\frac{dV}{dt}\right)_{\text{Polymerization shrinkage}}
\]

(4)

where the first term on the right-hand of equation (4) represents the bulk thermal expansion and contraction contribution and is expressed as follows:

\[
\left(\frac{1}{V_0}\frac{dV}{dt}\right)_{\text{Thermal contribution}} = CTE \frac{dT}{dt} = CTE_m (1 - \alpha) + CTE_p \alpha \frac{dT}{dt}
\]

(5)

where \( CTE \) is the coefficient of volumetric thermal expansion with \( m \) and \( p \) suffixes referring to the monomer and polymer states [12].

In this work, dimensional change was measured by the static displacement of the upper plate of the DMA cell during sample cure. For DGEBA-anhydride resin, illustrated in Figure 8, shrinkage is noticeable from 280 seconds, where the minimum stiffness of 100 N/m is reached. At this moment, the sample has already gellified and is seen to have noticeable shrinkage. It can be noticed that a delay appears between the gelation and the detection of mechanical properties and the beginning of the shrinkage at 280 seconds. This time difference is associated with the stage of the material between the beginning of gelation at 33% of cure and the rubbery-like material at 54% of cure when shrinkage is noticeable.

During cure, the exothermic chemical reaction increases the sample temperature from 1 to 4°C (see Figure 4). As a consequence, the sample will expand and compensate shrinkage. The thermal expansion of liquid polymers is in the order of 35 x 10^-5 m/m°C [4]. For a 5°C increment, the expansion of the sample would be below 0.2%. This quantity is much lower than the polymer shrinkage varying from 3 to 10% [14], thermal gradients can then be neglected on this study.

In this study, for liquid resin systems only, since tests were carried out under isothermal conditions, the volume changes due to thermal expansion were neglected to simplify. The second term of equation (5) represents the shrinkage associated to the chemical cure reaction. This latter was expressed by a simple linear relation between the shrinkage and the conversion and is assumed to be proportional to the reaction rate:

\[
\left(\frac{1}{V_0}\frac{dV}{dt}\right)_{\text{Polymerization shrinkage}} = C \frac{d\alpha}{dt}
\]

(6)

where \( C \) is a constant determined from the experimental results.

However for prepregs, given the temperature ramp at the beginning of the tests, thermal contribution will have to be considered. Thermal phenomena related to prepregs will be detailed latter.

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Fig. 8. Evolution of resin shrinkage with time during isothermal cure at 120°C of DGEBA-anhydride resin.

Figure 9 shows the measured shrinkage as a function of degree of cure. The beginning of shrinkage is observed at 54% of cure. From this polymerization degree, the linear shrinkage increases proportionally until nearly full cure. This behaviour is consistent with previous observations on thermoset resins [4, 12].
and can be modelled by the following equation:

\[ l = C(\alpha - \alpha_c) \]  

(7)

where \( l \) is the linear shrinkage, \( \alpha \) the degree of cure at beginning of shrinkage and \( \alpha_c \) is a constant determined from the experimental results.

Fig. 9. Resin shrinkage as function of degree of cure and proposed model during isothermal cure at 120°C of DGEBA-anhydride resin.

The value of these model parameters for the epoxy-anhydride resin is reported in Table 1. This linear shrinkage behavior is observed until the polymerization reaches a DoC of 90%. At this point the cure reaction is controlled by thermal diffusivity and the deviation of the experimental points from the linear behavior can be associated to the non-negligible sample mass. Similar observations were reported in the past for a similar aeronautical epoxy resin [14]. However, no much explanation of this phenomenon is given. The maximum shrinkage attainable by the resin studied in this work is around 3% which is in the usual range of epoxies.

Figure 10 illustrates the evolution of heat flux during the cure of a carbon-epoxy prepreg for tests carried out at different dynamic amplitudes of 10 and 20 microns but same frequency of 10 Hz. Each sample consists into 10 plies of prepreg aligned in same direction. Pre-compaction was done in order to ensure homogeneous thickness of around 2 mm along the sample disk. Layers were stamped in disk of 25 mm diameter using cutting press.

Pre-compaction is necessary before testing in order to avoid delamination during the thermal process and keep the contact between the upper sensor of the DMA HFC200 cell and the sample during dynamic stimulation.

Sample is placed into the DMA before the beginning of the test. The first plateau at 25°C illustrated on Figure 10 corresponds to the stabilization period of 1 hour required for the dynamic response being homogeneous with the signal. This stabilization period is not illustrated for tests on liquid resin since it happens prior to resin injection. Thereafter, heat flux starts to increase following the heating rate of 1.5°C/min until the temperature reaches the set point of 177°C. The maximum exothermic peak is attainable when this temperature is reached. The polymerization undergoes and ends around 225 minutes, which corresponds to an exothermic maintain of about 1 hour. The heat flow curve behavior shows similar results whatever the dynamic amplitude is.

Figure 11 shows the dimensional change that happens during cure of the carbon-epoxy prepreg. This is calculated using equation (3). During the heating ramp, there is an increase of the sample thickness that can be associated to the thermal expansion. This increase is linear and follows the curing rate. Chemical shrinkage starts being visible around 175 minutes, which corresponds to the maximum of the exothermic peak. At this point, there is a thermal stabilization and chemical
shrinkage becomes predominant and reaches a plateau value around 300 minutes. The final dimensional change is around 1.7% with a part associated directly to chemical shrinkage of 0.50%. This value is quite similar to literature for unidirectional carbon-epoxy [17, 18].

4 Conclusion

A novel in-situ method allowing combined measurement of dimensional changes and mechanical properties during cure was presented in this work. These measurements were carried out in a single device called a thermal flux cell combined with a DMA. Tests were performed on both liquid resin and prepreg, demonstrating the flexibility of the heat flux device. Sample is contained into a mold where its base and cover include heat flux sensors. This allows the monitoring of changes in temperature and thermal flux as well as the dynamical displacement and stiffness during cure.

An epoxy DGEBA resin was used in this work first to demonstrate the capability of this new approach. Different vibration frequencies and amplitude were used in order to optimize results as well as the quantity of resin. Optimum results were found for a mass of 1g and application of 10 Hz frequency and 20 microns dynamical amplitude. The heat of reaction was found to be 337 J/g which is very close to the DSC value of 326 J/g. The averaged chemical linear shrinkage of the cured resin was of 3% and its stiffness reached a plateau of $10^7$ N/m at the end of cure. The evolution of stiffness with the degree of cure was found to be nonlinear from the gelation point of 33%. The time corresponding to gelation was confirmed using rheological method. The evolution of shrinkage with degree of cure was found to be linear from 54% cure up to 90% where the reaction starts being mostly controlled by diffusion.

Phenomenological models were also proposed to describe the shrinkage and stiffness behaviour as a function of degree of cure. The shrinkage of the epoxy resin was modeled using a linear function of degree of cure. However, the initial cure at which shrinkage is noticeable was found to be higher than gelation point. The stiffness evolution was modeled using a log-log function that describes the increment of the dynamic mechanical properties with degree of cure. The proposed model and experimental data are in line with chemo and thermo-mechanical models found in the literature.

Analyses were also performed on carbon-epoxy prepreg with 10 Hz frequency and 10 and 20 microns dynamical amplitude. Sample consisting into 10 plies aligned and pre-compacted is introduced into the heat flux cell device at room temperature. The testing procedure follows the autoclave process starting with a ramp of 1.5°C/min and stabilization at 177°C. The heat flow follows the heating ramp and the thermal expansion as well. The chemical shrinkage is visible when there is no longer thermal effect due to expansion and its final value is around 0.50%.

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