ACTIVE CURING MONITORING BY MEANS OF DEA

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Abstract
Active monitoring of the curing process by means of Dielectric Analysis (DEA) sensors is proposed with the aim of gaining knowledge about the curing process, and of optimizing the curing cycles. For instance, monitoring the mold filling and resin cure level by means of DEAs will enable to determine the optimal time for de-molding allowing shortening the cure cycle, or identify the event of the material gelification which would be useful for semicuring processes, cure cycle nonconformities, etcetera.
This work aims to provide a reliable and robust method to monitor and control curing processes, being able to show in real time glass transition temperature and degree of cure in the part by correlating the dielectric response of the thermosetting resin during cure to the material phase transitions. The reliability and accuracy of the proposed sensor system for on-line monitoring of curing processes is presented for the case of resin transfer moulding (RTM) materials.

1. Introduction

The continous growth of the composite materials industry together with the use of new emerging advanced materials and the increasing complexity of parts shape and structures, cause added difficulties in design and production. Detailed knowledge of reactivity at every step of the process is fundamental to achieve fully-cured composite parts with a minimum cycle time. The little knowledge about the cure kinetics and about the structural health of the composites during the production phase sometimes results in some imperfectly cured or degradated/aged composite parts, that will lead to structural failure. Therefore, on-line monitoring of the curing process of thermosetting resin matrix composite materials is key for the improvement of quality and productivity.

There are several cure monitoring methods, thermo-physical analysis in postprocess measurements such as differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), infrared spectroscopy (IRS), and real-time sensors for flow and cure monitoring to measure the real-time behavior of the polymer during processing [1-11]. From these methods, dielectric analysis (DEA) is known to be the most promisisng technique to monitor the cure of thermosetting materials during a production moulding operation [12, 13] since it is rather flexible in terms of experimental setup and conditions, and can monitor continuously the change of resin cure state throughout the process going from monomeric liquid to cross-linked solid. Previous studies have already shown that the dielectric response of thermoseeting resins during cure can be correlated to the resin phase transitions [14].

Since the change in the dielectric properties of composites during the curing is mainly contributed by the matrix material, current work concentrates on the study of a pure epoxy resin, as first step to fiber reinforced composite. Specifically, this work shows preliminary results of the on-line curing monitoring of an epoxy Resin Transfer Molding (RTM) process, since RTM is commonly used to manufacture advanced composite materials. In this process, a fabric preform is placed in a mold cavity and thermosetting resin is injected into the mold to fill the empty spaces between the fibers of the fabric. After complete filling, the mold is kept closed until the resin cures to a certain level so that enough strength and rigidity of the part are achieved. Complete mold filling may not be repeatable due to the variations in the fabric preform preparation, compaction and nesting. These variations affect the permeability distribution of the fabric preform, the resin flow pattern may significantly derivate from the originally designed pattern, and macro size voids may remain in the part. This is why DEA is particularly interesting for this process.

This study focuses on the correlation of DSC and dielectric measurements on RTM epoxy using a coupled setup of both techniques.

2. Experimental

2.1. Material

The epoxy matrix used in this work is a standard RTM material for aeronautic applications, a monocomponent system, as the resin and amine hardener are already premixed and degassed, of 180 ºC curing. This material needs to be stored in a freezer at -18 ºC to prevent chain motion and suppress curing. The resin was taken out of the fridge to be tempered before the curing trials. All trials were performed with resin from the same batch and with identical conditioning.

2.1. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) and Modulated differential scanning calorimetry (MDSC) were carried out on a TA Instruments DSC Q2000 equipment under nitrogen atmosphere using samples of around 10 mg sealed in aluminum pans, in order to determinate the curing enthaply (ΔH_A) and glass transition temperature (Tg), following standard ASTM E2602

2.2. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) have been performed with a TA Instruments DMA Q800 equipment to determine glass transition temperature (Tg) following standard AITM 1-0003. Test parameters were 15 µm amplitude, 1 Hz frequency, and 5 ºC/min heating rate.

2.3. Dielectric analysis measurement (DEA)

When applying an electric field to a polymer, the reaction given by electrical conductance and polarization can be detected, it can be understood as the movement of charge carriers and deflection of dipoles, respectively. If mechanical or dielectric stress is applied in the viscoelasic range of a polymer, every transition to another equilibrium state is translated as a relaxation process. In contrast to mechanical stresses, where the linkage of whole-chain segments will be observed, the dielectric response is sensitive to the motion of independent dipoles of single groups. It was found that the time-dependent macroscopic relaxation processes are related to the underlying microscopic dynamics [15]. While observing the temperature dependence, it coud be found that dielectric and mechanical α-

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relaxation originate from the same processes regardless of the molecular weight of the poymer. In consideration of diffusion processes of ions through a medium,Einstein-Smoluchowski relation, and ionic mobility due to an outer electric field, the reciprocal dielectric conductivity σ is proportional to the viscosity η:

$$1/\sigma \sim \eta \qquad (1)$$

Equation (1) is only valid in the range below the gel-point where the polymer behaviou is dominated by the viscous response (G' < G") [16].

Dielectric measurements were conducted in multifrequency mode with an alternating current (AC) excitation in the range from 1 Hz to 100kHz. Four frequencies per decade in equidistant spacing on a logarithmic scale were recorded. Usually, two main magnitudes comprise the entire information about the specimen uder test: relative permittivity (ε') and dielectric loss (ε"). Relative permittivity is a measure for the polarizability of a material, if the dipoles are induced or permanently present. Dielectric loss contains information about the energy loss due to relaxation of the deflected dipoles and the level of direct current (DC) conductivity. The uncured resin must be in contact with a dielectric sensor consisting of two electrodes. A sinusoidal electrical voltage (excitation) is applied to the electrodes and the resulting current and corresponding phase shift (φ) are measured (see Fig.1).
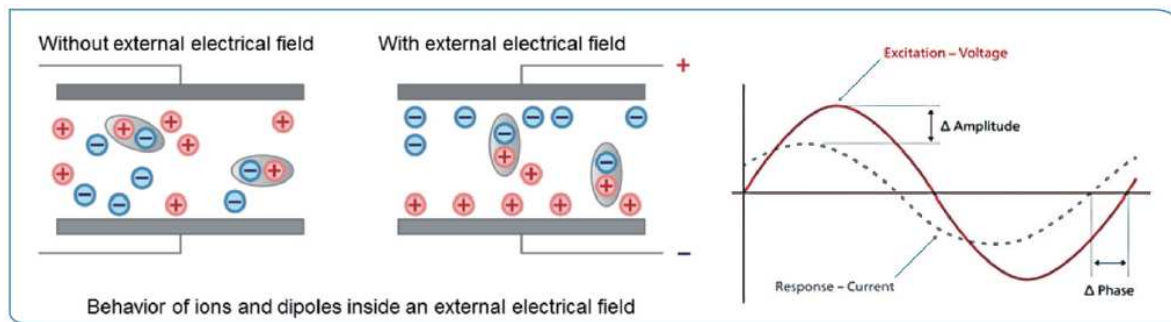

Figure 1. Dipoles and ions in the resin are stimulated by an electrical field generated by a sinusoidal voltage; the response signal is a phase-shifted sinusoidal current.

The dielectric properties of the resin, monitored by DEA change during the curing. By analyzing the dielectric data (ε' and ε"), the degree of the cure (α(%)) can be understood. The response signal correlates with the ion mobility of the resin and the alignment of dipoles. As the curing reaction progresses, the resin becomes increasingly viscous, the mobility of the charge carriers decreases, followed by a corresponding attenuation of the amplitude and an increased phase shift. The dielectric coefficient (εr) describes the resulting signal (comprising ε' –real part- and ε" –imaginary part). In addition ε" is proportional to the ion conductivity (σ) which is the reciprocal value of the ion viscosity (η). Since ion viscosity changes as a function of the degree of curing, DEA is the ideal tool for in-situ monitoring of the cross-linking progress of any thermosetting resin.

Figure 2 shows the typical cure monitoring measurement at 1 KHz for an epoxy resin. The logarithmic ion viscosity exhibits a significant decrease as the sample temperature increases from room temperature, which enhances the mobility of ions in the uncured resin. The sharp increase in ion viscosity indicates the beginning of network formation by cross-linking of the epoxy, which hinders the ion mobility.
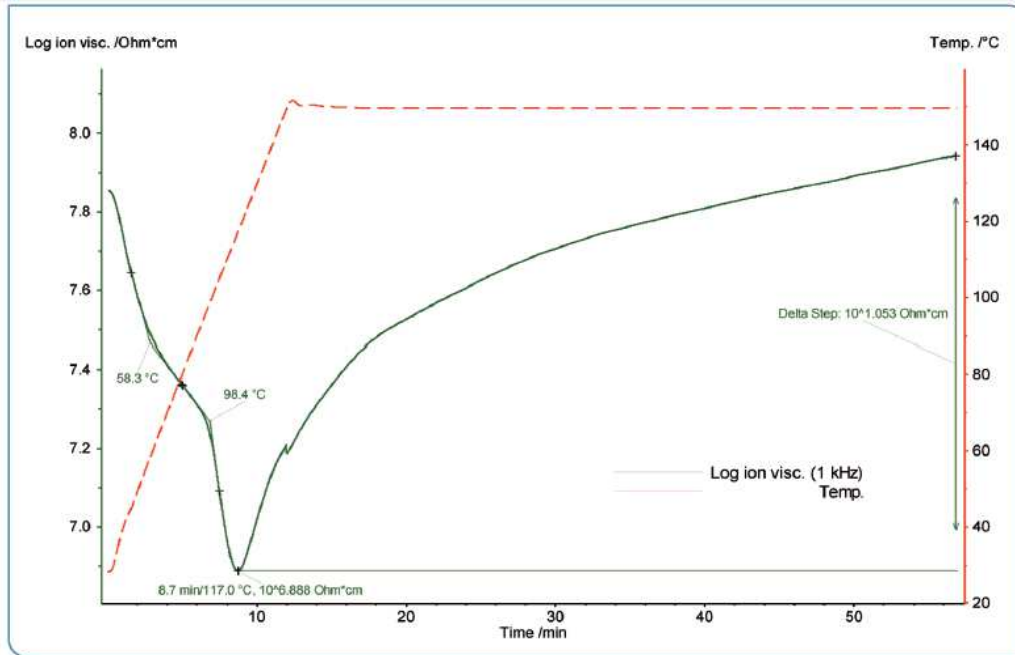
Figure 2. DEA measurement curve for an epoxy resin as a function of temperature and time.

In this work, *Netzsch* DEA 288 *Epsilon* instrument, with frequency range up to 1 MHz and data acquisition < 5 ms, has been used, employing two types of sensors:
  - Implantable: See Fig. 3(a). Disposable standard IDEX (interdigitated electrode) sensor consisting of comb electrodes on an inert film substrate which can be positioned at the desired location in the composite part
  - Reusable: See Fig. 3(b). Reusable tool mount sensors (TMS) which is placed into the mould to monitor the curing of composites inside the cavity. TMS contains an integrated thermocouple and offer a long service life due to their mechanical and thermal robustness.

Temperature has been controlled by means of thermocouples type K, and DEA results have been monitored in software Proteus 70.

Figure 3. Netzsch DEA 288 Epsilon sensors, (a) Implantable, (b) Resusable

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2.4. Setup

A standard cure cycle (acc. to material specification) of the material was monitored by means of DEA sensors and use as baseline.

Afterwards, different cure cycles, with shorter stabilization times were perform. The degree of cure (determinated by M(DSC)) and glass transition temperature (determinated by DMA) were measured so that these results were contrasted with the information obtained by the DEA and the predictions given by Neztch's kinetic model.

The kinetic model is based on measurement series of at least 3 different heating ramps or three different isothermal temperatures. From these measurements the activation energy and the pre-exponential factor (in literature also found as coefficient of impact) can be calculated. Afterwards the measurements data are fitted with mathematical algorithms like the ones for autocatalytic, diffusion controlled or inherent reactions that could also be found in literature and are implemented into Neztch kinetics software, simulating reaction behavior of the resin. Finally, results from DSC predictions can be correlated with ion viscosity values obtained in DEA measurements.

The kinetics modelling was carried out by *Netzsch* experts, with results recorded by DEA and DSC measurement of the resin, using software *Kinetics Neo.*

Complete study will be presented during the ECCM18 conference. In this paper, only trials performed with the standard cure cycle using disposable sensors are presented as example.

3. Results

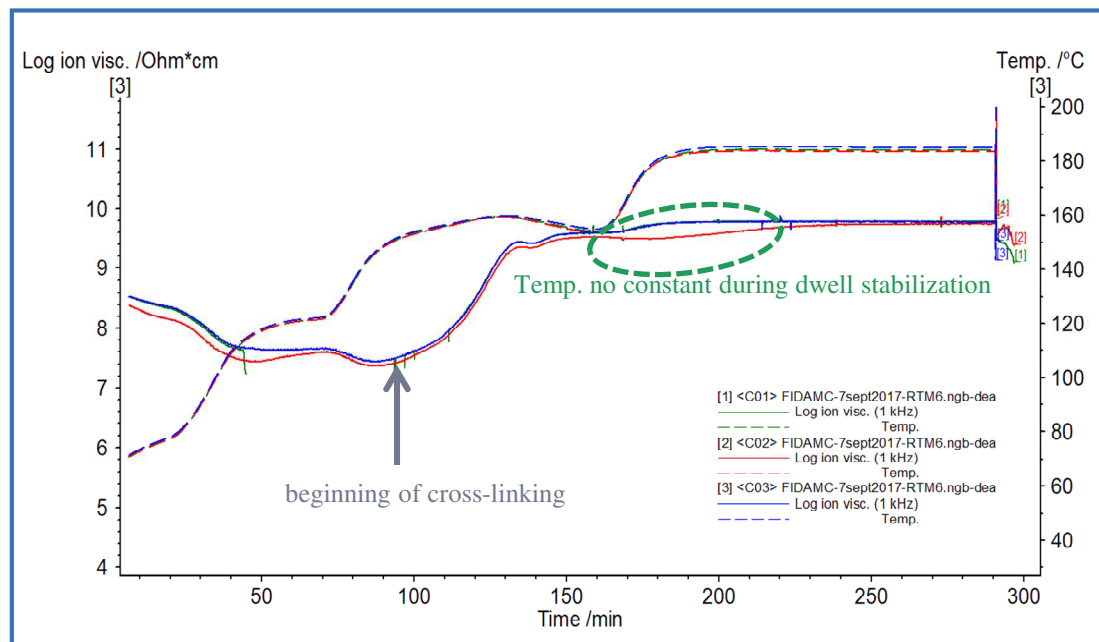Figure 4 shows the cure monitoring DEA measurement for the RTM resin.

Figure 4. DEA measurement curve for RTM resin.

Table 1 shows DSC and DMA results from meassurements of the samples cured in the standard cycle monitoried displayed above (Fig.4), as well as the kinectic model predicted values.

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Table 1. DSC and DMA results (of RTM resin w. standard cure cycle)

	$T_{g\text{-}onset}$ (°C)	$T_{g\text{-}loss}$ (°C)	T_{gpeak} (°C)	ΔH_A (J/g)	α (%)
DMAexp	205.4 ± 1.0	208.3 ± 0.8	216.1 ± 0.3	N/A	N/A
DSCexp	214.1 ± 0.7	N/A	219.8 ± 3.2	414.8 ± 0.3	93.2 ± 0.1
Predictive correlation*			216.73		98

*: Predictive correlation by knetic model.

As expected since this was the monitoring of the standard cure cycle of the RTM resin employed, Tg and α (%) fulfill the material requirements acc. to its specification.
DSC isothermal measurements of the material (not shown here) were performed at different temperatures, and each temperature at different heating rates, in order to use this data together with the DEA meassurements to make a prediction correlation of material behaviour and degree of cure expected at different curing temperatures or times.

Regarding the accuracy of the kinetic model prediction, even if the Tg value is close to the value measured experimentally, the temperature variations during dwell stabilizations (highlighted in green in Fig. 4) affects the ion viscosity making their values not consistent in the last stage of the cycle, and therefore, it is not possible to correlate ion viscosity values to a degree of cure over 90% and hence the discrepancy observed between the degree of curing measured by DSC and that predicted by the kinetic model.
Preliminary results of RTM epoxy resin curing monitored with reusable tool mount sensors (TMS) integrated in the curing tool showed a fine control of the temperature along the whole curing cycle, and thus, and accurate predition of the phase transitions as a function of ionic mobility, thus further work focused in cycles monitored with in-mold reusable TMS.

4. Conclusions

When using implantable disposable sensors for dielectric analysis, the comparison of simultaneous dielectric and differential scanning calorimetry measurements during the curing of a RTM epoxy resin shows that the determined values of glass transition temperature, gel-point and viscosity are in good agreement with the kinetic model prediction, however, the lack of temperature control at the last stage of the curing, results in discrepancies as far as the degree of curing is concerned. Nevertheless, when using in-mold reusable DEA sensors, results of the kinetic correlation model are accurate and more reproducible.
Therefore, based on these results, dielectric analysis as in-situ measurement technique promises contributing to the next big step toward a fully automated sensor-based composite manufacturing.

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