

## **IN SITU ON-LINE CURE MONITORING OF COMPOSITES BY EMBEDDED INTERDIGITAL SENSOR**

Y. Yang<sup>a\*</sup>, G. Chiesura<sup>b</sup>, G. Luyckx<sup>b</sup>, T. Vervust<sup>a</sup>, F. Bossuyt<sup>a</sup>, M. Kaufmann<sup>c</sup>, J. Vanfleteren<sup>a</sup>, J. Degrieck<sup>b</sup>

<sup>a</sup>Center for Microsystems Technology (CMST), Interuniversity Microelectronics Centre (IMEC) and Ghent University, Technologiepark 914, Gent-Zwijnaarde 9052, Belgium

<sup>b</sup>Department of Materials Science and Engineering, Ghent University, Technologiepark 903, Gent-Zwijnaarde 9052, Belgium

<sup>c</sup>Sirris Leuven-Gent Composites Application Lab, Celestijnenlaan 300C, 3001 Heverlee, Belgium

\*e-mail: yang.yang@elis.ugent.be

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### **Abstract**

*The continuous growth of the composites industry accompanied by the use of emerging new materials and more complex shapes and structures cause increasing difficulties in design, production and maintenance of composite products. One issue is the insufficient knowledge about the cure kinetics of the composites during production, which directly results in some badly cured composite parts. In this paper, the current progress of a dielectric sensor system for the in situ on-line cure monitoring of a composite material is presented. An interdigital sensor was fabricated by Flexible Circuit Board (FCB) technology. Dielectric properties of the resin, monitored by the interdigital sensor, changed over time during the curing. By analyzing the dielectric properties (relative permittivity, and loss factor), the degree of cure can be understood. The data obtained in the experiments clearly showed the different stages of the cure, which can be used with confidence for in situ and on-line monitoring of composites cure.*

### **1. Introduction**

In recent years, fiber reinforced composites have gained their popularity in many applications, such as aerospace, energy, automotive and advanced manufacturing industries [1-4]. The continuous growth of composites industry accompanied by the use of emerging new materials and even more complex shapes and structures caused increasing difficulties in design, production and maintenance.

An important stage during manufacturing of a composite component is the curing phase: a bad cure can lead to the scrap of the whole part (e.g. wind energy sector, aerospace). By controlling the curing phase one can obtain a superior quality component and, as a consequence, will increase the reliability and optimize the design of the part, leading to a decrease of the lifecycle cost (i.e. maintenance costs, material costs, design costs).

Several methods have been proposed to characterize the cure kinetics and monitor the cure process, for instance differential scanning calorimetry (DSC), dynamic mechanical analysis

(DMA), ultrasonic techniques, Raman spectroscopy, and dielectric analysis (DEA) [6-9]. However, most of these techniques are best suited in a laboratory environment under ideal conditions. For *in situ* and on-line monitoring of composites cure, DEA is of particular interest as the measurements can be made in processing environments such as ovens, presses and autoclaves [10-13]. DEA usually involves the measurements of the complex permittivity  $\epsilon^*$  of the material under test, which can be used to detect several phases occurring during cure such as phase separation, gelation and vitrification [14].

In this study, we investigated the feasibility of applying DEA for *in situ* and on-line monitoring of composites cure. The curing and post curing of a commercially available epoxy resin were monitored by an interdigital sensor, different phases occurring during cure were detected and studied.

## 2. Theory

Dielectric analysis (DEA) usually involves the measurement of a material's dielectric property  $\epsilon^*$ , which is represented in a complex form[15]:

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (1)$$

The real part  $\epsilon'$  is often referred to as 'relative permittivity' or 'dielectric constant'; it expresses the capacity of a material to store the electrical energy. The imaginary part  $\epsilon''$  is often referred to as the 'dielectric loss factor'. It expresses the energy loss entirely caused by the dielectric medium.

During the curing of the epoxy resin matrix composite, the dielectric properties of the resin change dramatically. The resin starts off as monomers or oligomers in a liquid state with low viscosity. The conductive ionic impurities, introduced during synthesis or preparation of the resin, are able to move freely within the resin. Ionic impurities accumulate at the surface of electrodes, causing interfacial polarization that leads to large increase in relative permittivity at low frequencies [16]. As the polymerization progresses, the crosslinking between monomers or oligomers continues and a 3D polymer network is formed and expanded. The formation of a polymer network/chain influences the change in permittivity. Furthermore, the resin becomes solid and highly viscous, thus the motion of the ion impurities is limited and a drop in loss factor is expected. By monitoring the dielectric properties of the resin, we can monitor different phases occurring during the curing.

The complex permittivity is analogous to the concept of complex impedance, and the two of them are related by [16]:

$$\epsilon^* = -j / \omega\epsilon_0 Z^* \quad (2)$$

Where  $\omega$  is the radian frequency of the applied AC voltage signal and  $\epsilon_0$  is the vacuum permittivity, with  $\epsilon_0 = 8.854 \cdot 10^{-14}$  F/m. Therefore, measurement of impedance values and evolution of them over time will provide information on material's dielectric properties.

The most widely used dielectric measurement system is based on the use of a parallel plate capacitor or an interdigital capacitor (IDC) [17]. A parallel plate capacitor is very useful to determine the bulk dielectric properties of the material. The advantages of a parallel plate capacitor are the easy interpretation of the measurement data and accurate estimation of

dielectric properties. However, this system can become problematic in practice, since it is difficult to control the distance between the electrodes precisely. IDC, on the other hand, doesn't suffer from this. It possesses many advantages, for instance high adjustability, one side access to the materials under test, easiness to operate [18]. Nevertheless, the calculation for an IDC is more complicated than for a parallel plate capacitor. Different mathematical models are available for the estimation of IDC [19-21]. Besides, finite element analysis (FEA) is also widely used to study the IDC based applications.

The basic geometry of an IDC is given in Fig. 1(a), where  $w$  stands for the width of each 'finger',  $g$  stands for the gap (spacing) between fingers, and  $L$  stands for the finger length. These parameters determine the sensitivity of the IDC, and the sensing depth (penetration depth) into the dielectric.

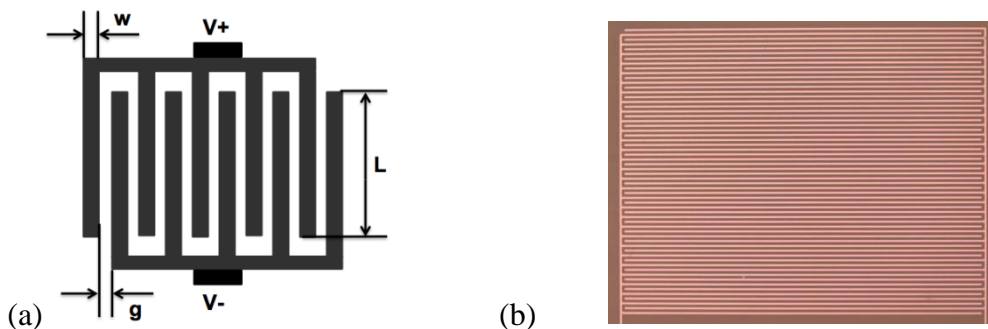


Fig. 1. (a) IDC geometry; (b) fabricated interdigital sensor with  $w = g = 100 \mu\text{m}$ ,  $L = 15\text{mm}$

### 3. Experimental

#### 3.1 DEA measurement

An HP 4284A LCR meter performed the impedance measurements in the frequency range from 100 Hz to 100 kHz with 10 measurement points per decade. The time required per measurement cycle was approximately 16 seconds. The measurement cell was a self-fabricated interdigital sensor (Fig. 1(b)) consisting of 2 layers:  $17\mu\text{m}$  thick copper track as the electrodes of the IDC, and  $50\mu\text{m}$  polyimide substrate as the flexible support. Frequency dependent impedances were then converted to dielectric properties  $\epsilon'$  and  $\epsilon''$ .

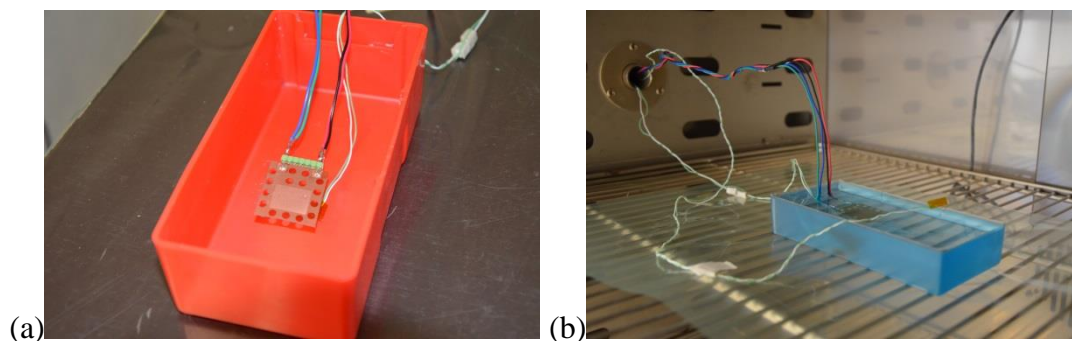


Fig. 2. (a) Curing; (b) post-curing setup

#### 3.2 Temperature measurement

2 thermocouples were installed: one next to the IDC for the monitoring of local temperature within the resin, one outside the resin for the monitoring of ambient temperature. A National

Instrument USB acquisition card was used for the temperature measurements, and data were logged through a Labview-based controlling software on PC.

### 3.3 Materials

The epoxy matrix system, supplied by Momentive, is a two part system consisting of the EPIKOTE™ MGS® RIMR 135 resin and the EPIKURE™ MGS® RIMH 137 hardner. The mixing ratio is 100:30±2 by weight. As stated in the datasheet a complete cure cycle usually takes 24h at room temperature, subsequently followed by a 15h post-curing at 80 °C.

### 3.4 Curing test and post curing test

Before start, the IDC was suspended in a beaker, into which the resin would be poured (Fig. 2(a)). The IDC was connected to the LCR meter and calibrated. One thermocouple was suspended next to the interdigital sensor for local temperature measurement, and another one was suspended outside the beaker for ambient temperature measurement. The experiments were performed in isothermal conditions at 20 °C. 300g of RIMR135 (epoxy) and 90g of RIMH137 (hardener) were thoroughly mixed by a mechanical blender and degased. Then the mixture was slowly poured into the beaker, until the IDC and the thermocouple were completely covered by the mixture. The mixture was cured for 24 hours. Afterwards, the resin was put in an oven (Fig. 2(b)). The dielectric measurement and thermal measurement were reconnected and re-calibrated. The oven was heated up to 80 °C in a rate of 80 °C/hour, kept at 80 °C for 15 hours, and then shut down to cool down the resin to 20 °C. A 2<sup>nd</sup> temperature cycle followed the post curing, the oven was again heated up to 80 °C in an hour, kept at 80 °C for 7 hours, and then shut down.

## 4. Results and discussions

### 4.1 Curing monitoring

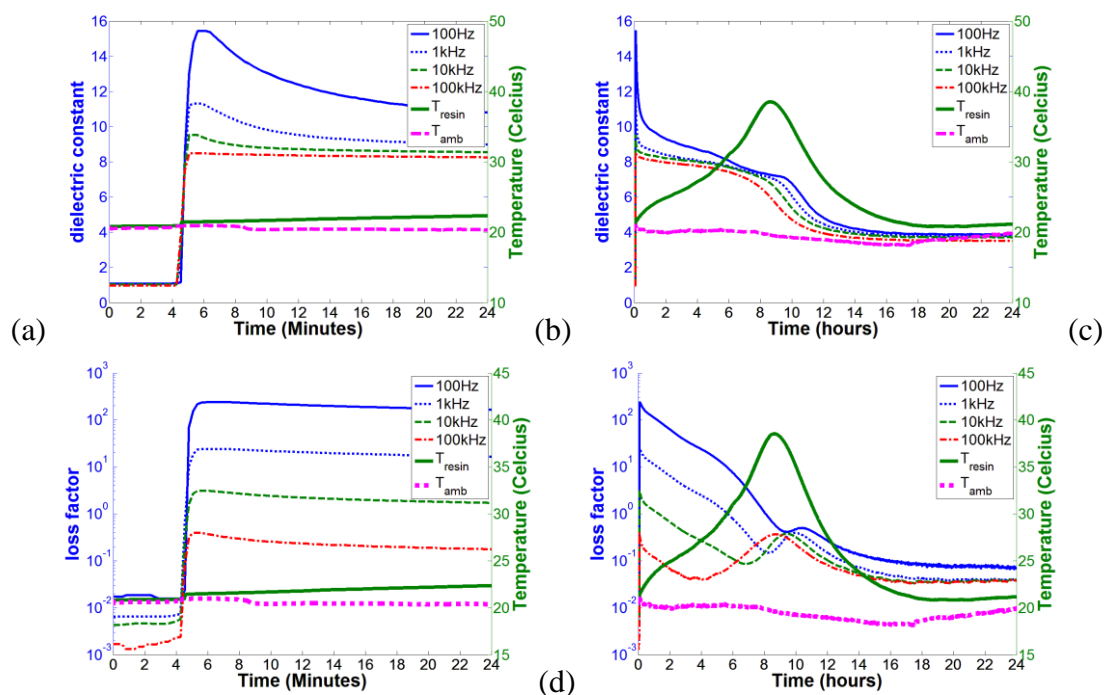


Fig. 3. (a)  $\epsilon'$  change during the first 24 minutes; (b)  $\epsilon'$  change during the first 24 hours; (c)  $\epsilon''$  change during the first 24 minutes; (d)  $\epsilon''$  change during the first 24 hours

Dielectric data and temperature data for the resin cured at 20 °C are shown in Fig 3. At the beginning of Fig. 3(a)(c), we observe huge increases in both relative permittivity and loss factor at around minute 4: indicating that the resin has flown over and completely covered the interdigital sensor. The relative permittivity  $\epsilon'$  increased from 1, stating air being the medium measured by the sensor, to 16, stating the resin being the medium measured by the sensor. Likewise, loss factor increased by an order of magnitude of at least 2, due to the fact that the measured medium by the sensor is changed from air to the resin. It's clear that the interdigital sensor is very sensitive to the change of the medium. At the meantime, however, little changes in temperature are observed.

The large increase in relative permittivity is caused by the ionic impurities in the resin. As the resin starts off as a liquid with low viscosity, the ionic impurities in the resin are able to move freely. Ion impurities accumulate at the electrode surfaces, causing interfacial polarization at the electrodes that leads to the large increase in relatively permittivity at low frequencies [18]. As the cure progresses, cross-linking between monomers or oligomers is continued and a network is expanded. The resin system becomes more viscous and the ionic diffusion gets restricted. The restricted ionic diffusion results in a decrease of conductivity. Electrode polarization disappears first at higher frequencies, and gradually shifts to lower frequencies (Fig. 3(b) (d)).

Ionic conductivity affects the loss factor in the form [22]

$$\epsilon'' = \sigma / 2\pi f \epsilon_0 \quad (3)$$

Where  $\sigma$  is the conductivity,  $f$  is the test frequency and  $\epsilon_0$  is the vacuum permittivity. During the early stage of the cure, the ionic impurities are free to move within the resin and the ionic conductivity is the main contribution to loss factor. Fig. 4 shows a log-log chart of frequency and loss factor at the early stage of cure. A linear relationship between  $\log \epsilon''$  and  $\log f$  with a slope of -1 is observed during the first 4 hours. At this stage, the loss factor is frequency dependent and we conclude that ionic conductivity dominates the loss factor. With the progress of the cure, the cross-linked polymer network restricts the ionic diffusion. The dominance of ionic conductivity is less significant and the dipolar relaxation appears first at higher frequencies. As shown in Fig. 4, after 5 hours, the linear relationship between  $\log \epsilon''$  and  $\log f$  is not valid anymore above 10 kHz, and this becomes more obvious after 6 hours.

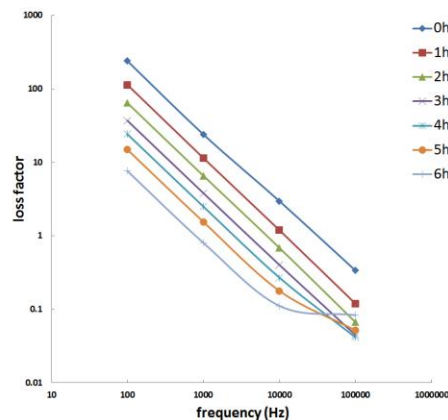


Fig. 4. Loss factor at different frequencies at different time of cure

As shown in Fig. 3(d), after around 9 hours into the cure, a major peak in loss factor is observed first at 100 kHz. This peak then moves to lower frequencies. During the cure, as the resin becomes more viscous, the dipolar movement is not able to follow the excitation signal at higher frequencies, and needs longer time for the re-orientation and relaxation, marked by the peak of loss factor at higher frequencies. Moreover, a relatively steep decrease in  $\epsilon'$  is observed at the peak of loss factor, indicating the transition of the resin from a gelly state into a glassy state, as suggested by previous researchers [22-23].

Fig. 3 also shows the local temperature change within the resin. During the first 9 hours, an increase in resin temperature was observed, caused by the exothermic heat generated during the polymerization. After the peak, a decrease of the resin temperature was detected as less exothermic heat is generated with the slowdown of cure. More heat is lost into the ambient compared to the heat accumulated by exothermic reaction marked by the decrease of local temperature. We found that the peak of temperature happens almost simultaneously as the peak in loss factor, or the relatively steep decrease in relative permittivity in this case. Thermocouple can be used as a rough estimation of vitrification in this case. However, thermal measurement is strongly influenced by the environment. At the surface of the resin, the accumulation of exothermic heat is less profound, since the heat is more easily lost to the ambient. In any case, the thermocouple only indicates the heat change during the cure instead of underlying change in physical or molecular properties of the resin.

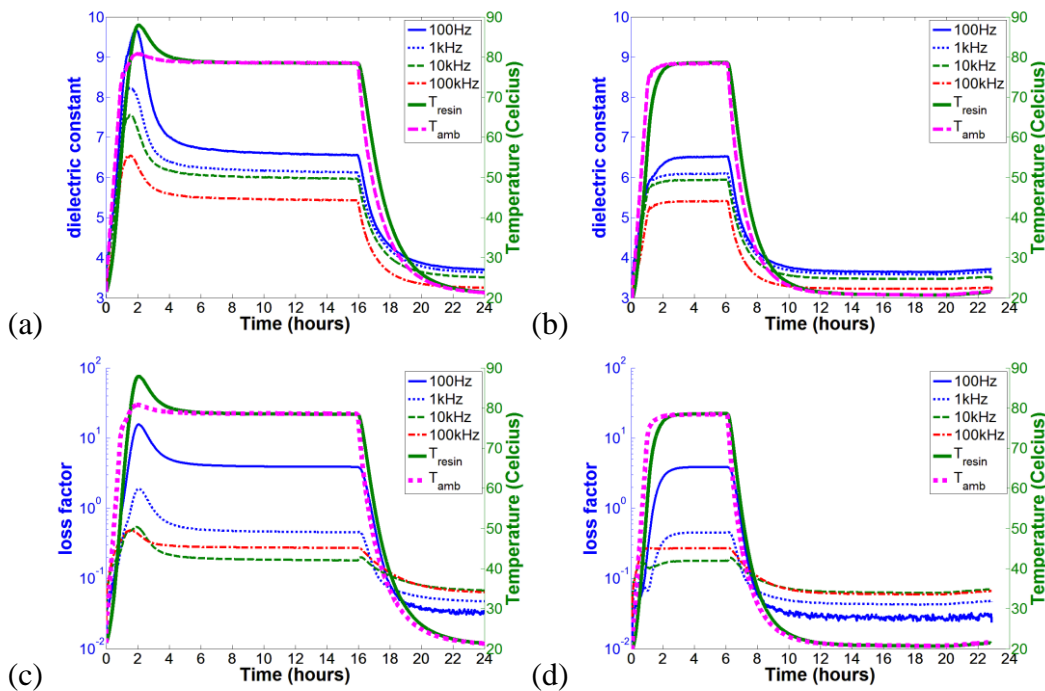


Fig. 5. (a)  $\epsilon'$  change during the 1<sup>st</sup> post curing (b)  $\epsilon'$  change during the 2<sup>nd</sup> post curing (c)  $\epsilon''$  change during the 1<sup>st</sup> post curing (d)  $\epsilon''$  change during the 2<sup>nd</sup> post curing

#### 4.2 Post-curing monitoring

The heating up of the oven leads to an increase in resin temperature. As the dielectric properties are temperature dependent, an increase in dielectric properties is observed in the first hour of post curing (Fig. 5 (a - d)). In Fig. 5(a) (c), a peak of  $\epsilon'$  and  $\epsilon''$ , which indicates the further polymerization, are observed. This further polymerization is confirmed by an overshoot of the resin temperature to almost 90 °C, caused by the exothermic reaction during

the polymerization. After the peak, dielectric values decrease and saturate to nearly stable values since the oven is kept at 80 °C. After 16 hours, the oven is shut down, and the decrease in temperature causes the drop in dielectric values.

Unlike the 1<sup>st</sup> post curing, the peak of dielectric properties and the overshoot of temperature are not observed at the 2<sup>nd</sup> temperature cycle (Fig. 5(b) (d)). What we observe, instead, is a pure temperature dependent effect: a smooth increase of dielectric properties along with the temperature raise. Since the cure is almost completed, no profound polymerization is happening anymore. The dielectric change is mainly dependent on the temperature. This can be proved by the fact that the observed dielectric values at 80 °C at the 2<sup>nd</sup> post curing is very close to the one at the 1<sup>st</sup> post curing.

## 5. Conclusion and outlook

An interdigital sensor was designed and fabricated for the on-line cure monitoring of an epoxy-based resin. Experimental data clearly show the different stages of the curing process. Ionic conduction dominates the early stage of the cure when the resin is still in a liquid state. As the cure progresses, the cross-linking between monomers or oligomers takes place, a 3-D polymer network is gradually formed and limits the ionic diffusion. The dipolar movement gets more significant, and a peak in dielectric loss appears first at higher frequencies, and gradually moves to lower frequencies. The peak in dielectric loss, as well as the relatively big decrease in relative permittivity, marks the reach of the vitrification point, indicating a transition of the resin from a gelly state to a glassy state. During the post-curing, a peak in dielectric loss and relative permittivity observed at the beginning of the post-curing cycle marks the completion of the cure. The different effects in dielectric behavior observed during the experiment can be used as a tool for *in situ* on-line monitoring of composites cure. In future work, we will apply DEA to optimize the cure cycle.

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