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RESIN FLOW FRONT AND CURE MONITORING IN RESIN TRANSFER MOLDING (RTM) PROCESS USING A DIELECTRIC SENSOR

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SUMMARY: On-line resin flow front and cure monitoring have been demonstrated to be important to the process development and quality control of composite structures manufactured by Resin Transfer Moulding (RTM). In this study, RTM process was used to fabricate a composite flat panel. To provide support to the process modification, a dielectric sensor has been used to monitor both resin flow front and cure. During resin injection, it was observed that when the resin reached the sensor, there was a jump in the ionic conductivity, indicating the flow front. To monitor the degree of cure and glass transition temperature of the composites panel, dynamic and isothermal measurements by Differential Scanning Calorimetry (DSC) were conducted at first to characterize the resin system used in the experiment. Correlations between ionic conductivity and degree of cure as well as glass transition temperature were created. Degree of cure and glass transition temperature of the composite panel were displayed in real time.

KEYWORDS: Differential Scanning Calorimetry (DSC), Resin Transfer Moulding (RTM), resin flow, cure

INTRODUCTION

Resin transfer moulding (RTM) has been used to manufacture large, complex composite structures with good surface quality. It offers the advantage of fabricating cost effective high performance composite structures. During the RTM process, a dry preform is first placed in a mould, then resin is injected into the closed mould cavity to impregnate the preform; the part is removed from the mould after a curing process. The mould filling and the curing process have significant effects on the quality of the composite parts produced. It is important for the mechanical properties of the composite structures that the preform is fully wetted by resin to reduce voids and dry spots. To reach this goal, the resin flow front in the preform has to be tracked to provide information about the impregnation of the preform as well as for further modification of the mould filling process (e.g. tool design, vent, injection port location, etc.). After mould filling, in order to obtain optimal properties of composite structures, the resin must be cured properly according to a cure cycle outlined by the manufacturer. However, these cycles often need to be adjusted because of the particular shape or non-uniform thickness of the part being fabricated. These problems are commonly solved using trial-and-error and/or process modeling. Unfortunately, these approaches are often time consuming and labor intensive. Also, an optimal cure cycle developed by these methods does not always produce the best results because of variations in materials and operating conditions. Due to these problems, a sensor system that can monitor the curing process on-line would be very useful for RTM process.

It has been reported that on-line dielectric monitoring has been used in resin transfer moulding process in the past years [1-5]. Dielectric sensor measures the change in the dielectric loss factor, which is mainly contributed by the ion conduction during resin curing process. The change in ion conductivity is an indication of the mobility of the ions present in the resins, which is then related to the arrival of the resin flow front, as well as the viscosity change induced by the resin cure reaction.

In this study, a dielectric sensor system was used to monitor the resin flow front and cure progress in a RTM process. The acquired dielectric data were correlated to the critical parameters such degree of cure and glass transition temperature. Furthermore, on-line dielectric cure monitoring was carried out in a RTM process. The goals of this work include: (a) Monitor resin flow front; (b) Monitor the curing process and display the development of *Tg* and degree of cure in real time.

THEORY

Thermosetting resins belong to dielectric materials. The capacitive and conductive properties displayed by these resins is caused by dipoles existing in function group of the molecules, as well as by the ions present in the resins due to the inherent impurity of thermosets, for example, sodium and chloride ions occur in epoxy and dominate the ionic conductivity. The dielectric responses of the resins are mainly caused by the dipole orientation and ion migration. Before an electric field is applied, the dipoles and ions in the resin have random orientation. When an electric field is applied, the dipoles start to orient and the ions begin to conduct an electric current by moving towards the electrode with opposite polarity. Based on the capacitive and conductive nature of the resins, the complex permittivity of the resins can be written as:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \qquad (1)$$

where ε' is the dielectric constant or relative permittivity and ε'' is the dielectric loss factor. The relative permittivity (ε') is mainly associated with dipole orientation, while the dielectric loss factor (ε'') is a measure of the total energy lost in a dielectric material, which is influenced by both dipole motion and ion migration. Since dielectric loss induced by both dipole relaxation and ion migration, the dielectric loss factor can be expressed as follow [6]:

$$\varepsilon'' = \frac{(\varepsilon_r + \varepsilon_u)\omega\tau}{1 + \omega^2\tau^2} + \frac{\sigma}{\omega\varepsilon_0} \qquad (2)$$

where ε_u is the unrelaxed permittivity; ε_r, is the relaxed permittivity; τ is the relaxation time; ω is the angular frequency, σ is the ionic conductivity and ε_0 is the permittivity of the free space. In fact, it was reported that at low frequency, the contribution of dipole orientation to the total dielectric loss is negligible, the ion conductivity dominated the dielectric loss [6]. In this case, the dielectric loss, which is mainly contributed by the ion migration, can be given as:

$$\varepsilon'' = \frac{\sigma}{\omega\varepsilon_0} = \frac{\sigma}{2\pi f \varepsilon_0} \tag{3}$$

where σ is the ionic conductivity, ε_0 is the permittivity of the free space, and f is the test frequency in Hz.

From Eqn. 3, the ion conductivity of the resin can be calculated. Because ion conductivity is related to the ion mobility, which is a function of the resin viscosity, therefore, the change in ion conductivity can be used as an indicator of the arrival of the resin flow front as well as the curing state of composites. To display on-line the development of *Tg* and degree of cure in a composites manufacturing process, the correlations between ion conductivity and *Tg* as well as degree of cure have to be established first. Following equation shows the correlation between ion conductivity and *Tg* [7, 8]:

$$\frac{\log\sigma}{\log\sigma_0} = \phi + \varphi\, T_g \tag{4}$$

where σ_0 is the initial ion conductivity, which is the ion conductivity before the start of the curing reaction; ϕ and φ are material parameters. Furthermore, following expression has been proposed to describe the correlation between ion conductivity and degree of cure [9]:

$$\frac{\log\sigma}{\log\sigma_0} = \lambda_1 + \frac{\lambda\alpha}{1-\lambda_3\alpha} \tag{5}$$

where α is degree of cure, and λ_1, λ_2, and λ_3 are material parameters.

EXPERIMENTAL

Materials

The resin system used in the experiment is the Cycom 890 RTM epoxy resin system from CYTEC Industries. It is available as a one-part resin system. The viscosity of this resin system is low enough at 80ºC (175ºF) for resin transfer molding (RTM) process. The manufacturer suggested cure cycle for the resin system is 2 hours at 180ºC for full cure. The glass transition temperature of the resin system is 190 ºC (E’ onset) for full cure and 213 ºC after postcure. The carbon fiber used in the experiment is a 5-harness satin woven fabric from Cytec Engineered Materials Inc.

Differential Scanning Calorimetry

DSC (Q1000, TA Instruments) was used to determine the total heat of reaction. First, DSC tests were conducted on uncured resin samples using the dynamic scanning mode at the heating rates of 2, 3, 4, 5, 8, 10, 12, 15, 20°C/min. The samples were about 10 mg and were heated from –50°C to 350°C under nitrogen atmosphere. In the measurement, 18 samples were tested. Second, a series of isothermal scanning of uncured samples was conducted at three different temperatures: 160°C, 180°C, and 200°C for different time periods (up to 5 hours). To reach the desired isothermal temperature fast, the samples were heated up at a rate of 100°C/min. Dynamic scanning was conducted following the isothermal measurements, in order to determine the glass transition temperature (T_g) and the residual heat of reaction. Degree of cure is also calculated using the residual heat of reaction. The heating rate in these dynamic measurements was 4°C/min.

Dielectric Measurements to Create Correlation between DSC and DEA Data

A 10-channels dielectric sensor system, DEA 230/10, from NETZSCH Instruments was used in the study. The sensor used in the experiment is a tool-mounted sensor, which has two planar interdigitated comb electrodes placed on a flat ceramic substrate. The resin sample (about 8g) was held by the sensor surface and sealed using sealant tape. Isothermal cure of the epoxy resin samples was conducted at three different temperatures: 160°C, 180°C, and 200 °C in an oven for about 5 hours. Dielectric measurements were conducted at various frequencies, from 0.1 Hz to 10 kHz. The test set-up is shown in Fig. 1. Release agent was applied to the sensor surface to allow resin samples to be removed easily.

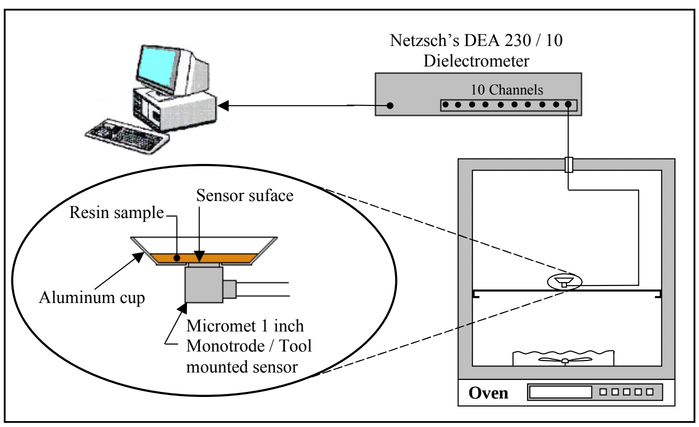

Fig. 1 Test set-up for dielectric measurements.

On-line Dielectric Resin Flow Front & Cure Monitoring in RTM Process

A 1-inch tool-mounted dielectric sensor was mounted on the RTM mold to monitor the resin flow and cure. A flat panel preform with nine plies woven carbon fiber was prepared and put in the mold cavity. To avoid direct contact of the electrodes of the sensor with the carbon fiber preform, a small piece of woven glass fiber was used to isolate the sensor surface. The location of the dielectric sensor is shown in Fig. 2. A custom-made computer program is used to transfer the dielectric data into degree of cure and the glass transition temperature and display them in real time.

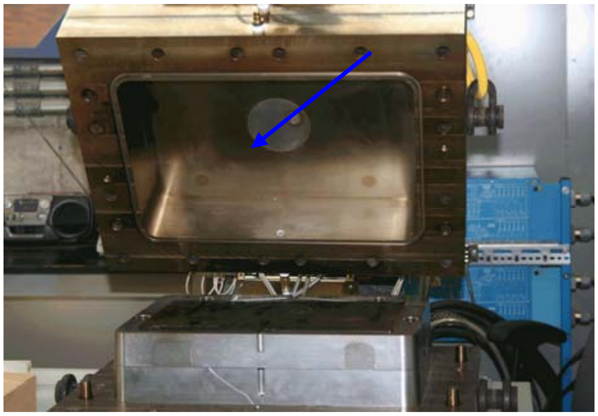

Fig. 2 Dielectric sensor location in the RTM mold.

RESULTS AND DISCUSSION

On-line Monitoring of Resin Flow Front

In the RTM process, the preform was first put inside the mold cavity, then the mold was closed and preheated to about 100 °C. After that vacuum was applied to the mold cavity and resin was injected. To monitor the resin flow front, the data acquisition of the dielectric sensor system was started to collect data before the beginning of the resin injection. The dielectric ion conductivity change during resin injection is shown in Fig. 3.

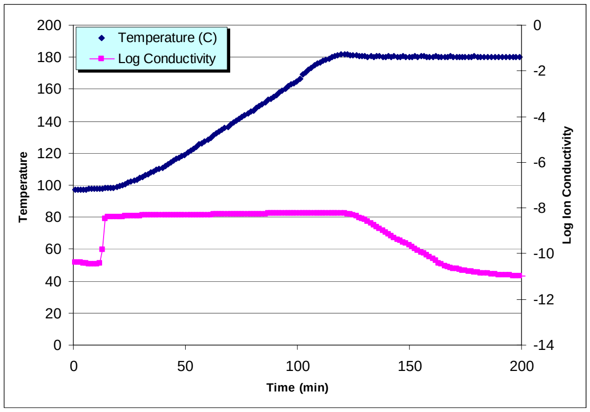

Fig. 3 Ion conductivity change during resin injection.

It can be seen in Fig. 3 that the Log Ion Conductivity was about -11 (unit: Log Siemens/cm) before the resin is injected. After resin reached the sensor, the Log Ion Conductivity increased to a value of -8.5 and then kept almost constant before curing reaction started. Fig. 3 confirmed the feasibility of using dielectric sensor to monitor resin flow front in real time.

Correlation between Dielectric Ion Conductivity and Degree of Cure, and *Tg*

To correlate dielectric ion conductivity and curing process of the epoxy resin, degree of cure and glass transition temperatures at three isothermal temperatures were determined using DSC. First, the total heat of reaction of the epoxy resin system was measured by using dynamical DSC. The average value of the total heat of reaction obtained in all the 18 dynamic DSC measurements with different heating rates is 374.7 J/g. Second, a series of isothermal scanning of uncured samples was conducted at three different temperatures: 160°C, 180°C, and 200°C. Degree of cure and *Tg* at these three temperatures were calculated for different time periods (up to 5 hours). Third, a dielectric sensor was used to monitor the ion conductivity change at the above mentioned three isothermal temperatures. To simplify the data interpretation, only the ion conductivity at 1 Hz was used to correlate to the *Tg*, degree of cure in this study. The measured Log Ion Conductivity vs. time plot under the three isothermal conditions is shown in Fig. 4.

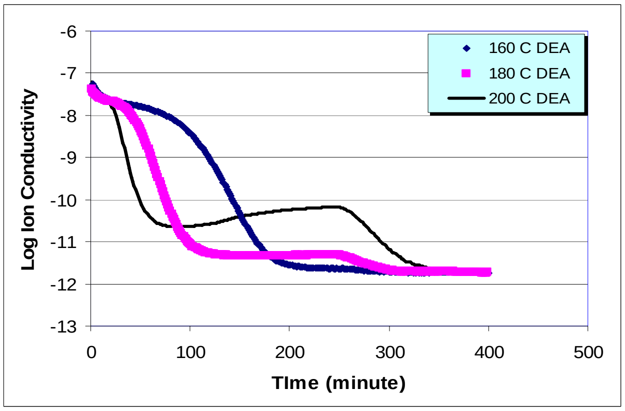

Fig. 4 Log Ion Conductivity under different isothermal temperatures.

Furthermore, to ensure the accuracy of the correlation between the Log Ion Conductivity and *Tg*, as well as degree of cure, temperature influence on the measured ion conductivity has been removed. The ion conductivity as a function of the glass transition temperature is shown in Fig. 5. It can be seen in Fig. 5 that the correlation between the ion conductivity and the Tg agrees with Eqn.5 very well. The parameters in Eqn.5 are therefore obtained by fitting the experimental data: $\varphi = 0.0156$ and $\phi = 1.8105$.

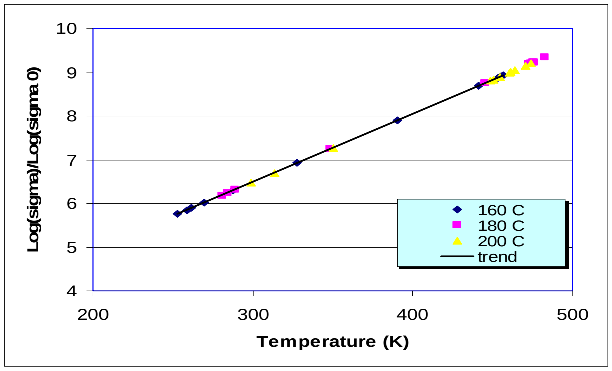

Fig. 5 $Log\sigma/Log\sigma_0$ as a function of *Tg* (Kelvin).

The correlation between ion conductivity and degree of cure is shown in Fig. 6. The parameters in Eqn. 6 are determined by fitting the measured data for the CYCOM 890 RTM resin system: $\lambda_1 = 5.4669$, $\lambda_2 = 2.729$, and $\lambda_3 = 0.3053$. These parameters will be used in on-line cure monitoring in the non-isothermal RTM curing process. The *Tg* vs. degree of cure plot obtained by Eqn.5 & Eqn.6 is Fig. 7.

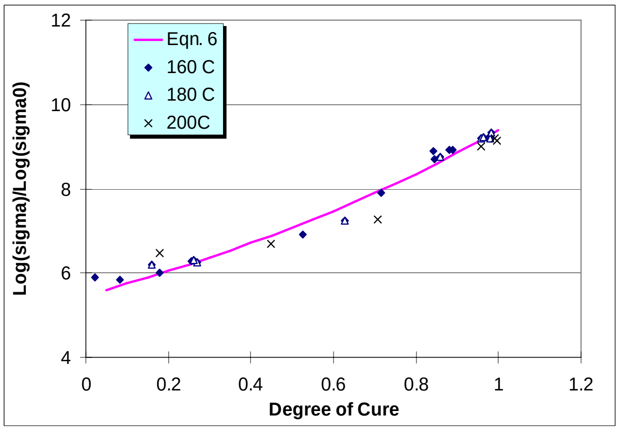

Fig. 6 The $Log\sigma/Log\sigma_0$ as a function of degree of cure.

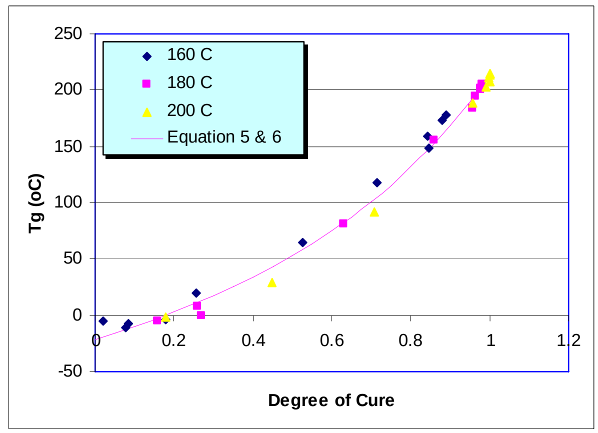

Fig. 7 *Tg* vs. degree of cure plot obtained by Eqn.5 & Eqn.6

On-line Cure Monitoring of the RTM Process

In the RTM process, the resin injection was stopped as resin went out of the vacuum port. It was assumed that the preform was fully saturated at that stage. Then injection port and the vacuum ports were blocked. After that a one-step cure cycle was used in the experiment to cure the part. The mould was ramped to 180°C at a rate of 0.8 °C/min and held for two hours, and then the mould was cooled down to room temperature. The actual temperature profile of the part is shown in the following Fig. 8 and Fig. 9.

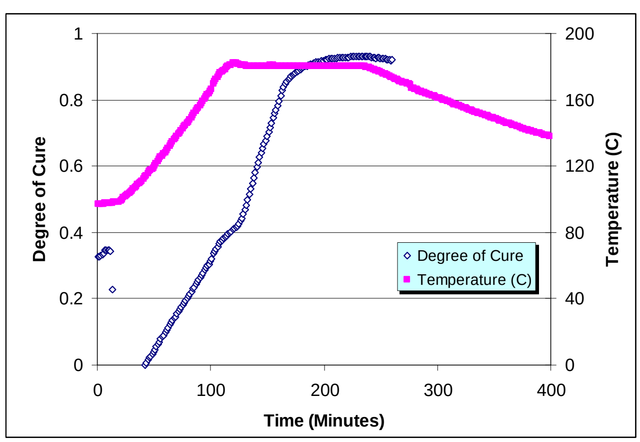

Fig. 8 Evolution of the degree of cure under the non-isothermal cure cycle.

Dielectric measurements were conducted throughout the cure cycle. The degree of cure and glass transition temperature of the part during the curing process were displayed in real time, which are also shown in Fig. 8 and Fig. 9 respectively. Fig. 8 shows that the RTM part was not fully cured after the cure cycle was completed. The final degree of cure displayed on-line was 0.93. Fig. 9 shows that the glass transition temperature displayed on-line is 189^{o}C. The results show that the resin system hasn't reached the maximum properties. Thus, a post cure for the resin system is suggested after the cure cycle. It is noted in Fig. 8 and Fig. 9 that both glass transition temperature and degree of cure have a slight tendency to decrease during the cooling stage. This could be induced by the mismatch of the coefficient of thermal expansion between the composite panel and the tool, and therefore causing the separation of the part and the sensor during the cooling process. The results of the dielectric cure monitoring indicate that it is feasible to monitor the development of degree of cure and glass transition temperature in RTM process in real time.

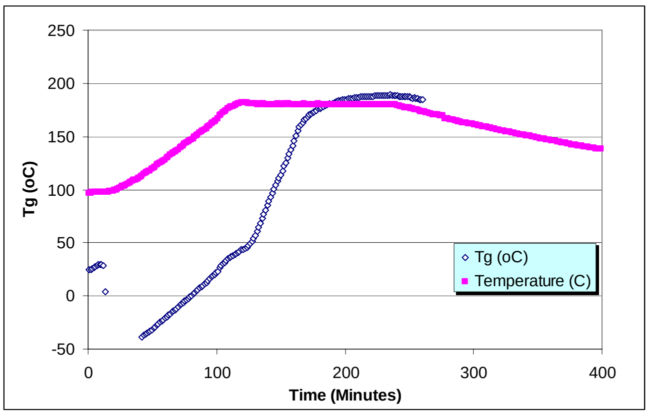

Fig. 9 *Tg* development under the non-isothermal cure cycle.

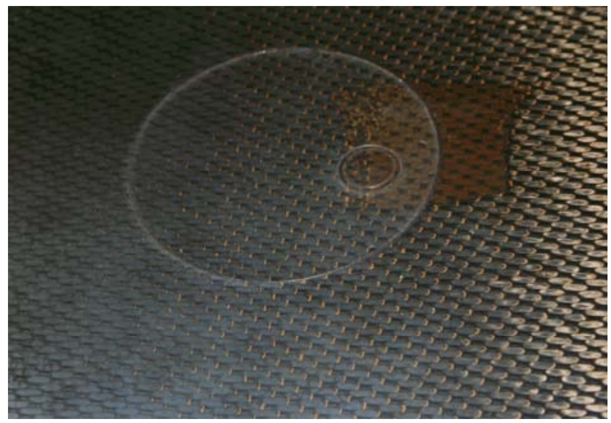

Fig. 10 Imprint of dielectric sensor in the coupon.

Fig. 10 shows the composite panel fabricated in the RTM process. It can be clearly seen from Fig. 10 that the tool-mounted sensor used in the experiment leaves a mark on the part surface. The influence of the mark on the mechanical property of the part will be investigated in the future.

CONCLUSIONS

In this study, a carbon fiber/epoxy flat panel was fabricated using RTM process. The resin flow front during resin injection and the development of the degree of cure and cure cycle were monitored using a dielectric sensor in real time. The main conclusions of this study stand as follows:

- In resin injection process, when resin reaches the dielectric sensor, there is a sharp increase in the measured ionic conductivity, indicating the resin flow front. This result shows that the on-line dielectric flow front monitoring is useful for verification of resin flow simulation results.
- Results in this study show that it is feasible to display the development of *Tg* and degree of cure in real time in RTM process after the correlations between dielectric ionic conductivity, degree of cure and *Tg* of the resin system have been established.

- The tool-mounted dielectric sensor leaves a mark on the composite part surface. The influence of the mark on the mechanical property of the part has to be studied.

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REFERENCES

1. Kranbuehl, D.E., Kingsley, P., Hart, S., Hasko, G., Dexter, B. and Loos, A., "In-situ Sensor Monitoring and Intelligent Control of the Resin Transfer Moulding Process", *Polymer Composites*, 15(4): 299-305, 1994.

2. Kranbuehl, D.E. and Loos A., Data Acquisition: Monitoring Resin Position, Reaction Advancement and Processing Properties, Resin Transfer Moulding for Aerospace Structures, Edited by T. Kruckenberg and R. Paton, Published by Chapman & Hall, London, ISBN 0412731509, 1998.

3. Engelbart, R. W., "Sensors for Resin Transfer Moulding", *Proceeding of 44th International SAMPE Symposium*, 44: 1227-1232, 1999.

4. McIlhagger, A., Brown, D. and Hill, B., "The Development of a Dielectric System for the On-line Cure Monitoring of the Resin Transfer Moulding Process", *Composites Part A*, 31, pages 1373-1381, 2000.

5. Maistros, G. M., Pantelelis, N. and Kanarachos, "A., Dielectric Cure Monitoring and Optimization in RTM", *Proceeding of ICCM 13*, Beijing, 2001.

6. J. Mijovic, J. M. Kenny, A. Maffezzoli, A. Trivisano, F. Bellucci, L. Nicolais, "The Principles of Dielectric Measurements for In-situ Monitoring of Composites Processing", *Composites Science and Technology*, 49 277, 1993.

7. J. P. Eloundou, O. Ayina, H.N.Nga, J. F. Gerard, J.P. Pascault, G.Boiteux, G.Seytre, "Simultaneous Kinetic and Microdielectric Studies of Some Epoxy-Amine Systems", *Journal of Polymer Science, Part B*, 36 2911, 1998.

8. J. P. Eloundou, Étude diélectrique de systèmes époxy-amine. 2. Cinétique chimique et conductivité, *European Polymer Journal*, 35, 1481, 1999.

9. J. Chen and M. Hojjati, "Micro-Dielectric Analysis and Curing Kinetics of an Epoxy Resin System", *Polymer Engineering & Science*, Volume 47, Issue 2, pages 150 – 158, 2007.