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Additional Information

MICROWAVE SENSOR SYSTEM FOR CONTINUOUS MONITORING OF ADHESIVES CURING PROCESSES

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Abstract

A microwave sensor system has been developed for monitoring adhesives curing processes. The system provides continuous, real-time information about the curing progress without interfering with the reaction.

An open-coaxial resonator is used as the sensor head, and measurements of its resonance frequency and quality factor are performed during cure to follow the reaction progress.

Additionally, the system provides other interesting parameters such as reaction rate or cure time. The adhesive dielectric properties can be also computed off-line, which gives additional information about the process.

The results given by the system correlate very well to conventional measurement techniques such as Differential Scanning Calorimetry, combining accuracy and rate with simplicity and an affordable cost.

Keywords: microwave sensor, open-ended coaxial resonator, cure process, monitoring, adhesives, polymers.

1. Introduction

Thermosets are polymeric composites with a good balance of mechanical/electrical properties and price, which are widely used as industrial products for materials manufacturing or assembling by adhesive consolidation.

The bond strength of thermosetting adhesives is obtained after a curing process which is carried out for a defined period of time, and this curing process determines the final properties of joint structures [1]-[3]. Both undercuring (no mechanical stability) and overcuring (too brittle joints) may be critical.

Adhesive cure cycles are usually provided by the material suppliers but unfortunately curing behavior is very sensitive to the composition and manufacturing conditions. Therefore manufacturers have problems to supervise the quality of joint structures [1],[3]. This is the reason behind years of research work to develop non-destructive methods for on-line monitoring of thermosets curing processes.

The existing monitoring techniques can be divided into methods which are directly sensitive to the chemical reaction (Differential Scanning Calorimetry (DSC), infrared spectroscopy, nuclear magnetic resonance spectroscopy, chromatography) and methods which detect changes in microscopic material parameters: mechanical (dynamic mechanical analysis, viscosimetry, ultrasound) or electrical (DC and AC conductivity, dielectric analysis) [4].

Among these methods, dielectric analysis (DEA) is frequently used for in-situ measurements [4],[5]. Dielectric measurements are sensitive to the mobility of molecule dipoles in the presence of an electric field. As cure progresses, this mobility becomes drastically decreased. Therefore, the use of dipoles as molecular probes is very attractive because it provides a direct measurement of the chemical and physical state of the matter in real time [5]-[7]. In addition, changes in dielectric parameters are related to critical points in the cure process, such as cure reaction onset, gelation, end-of-cure, build-up of glass-transition temperature, etc. [3],[8],[9]. In this sense, there is a vast range of applications of dielectric spectroscopy in processes including crystallization, vitrification, phase separation, etc., as pointed out in [10],[11].

The instruments most widely used for dielectric spectroscopy are capacitive sensors, with parallel plate or comb electrodes [12]. Measurements of conductivity of the material are performed using an impedance analyzer over many decades of frequency (typically from 10^2 Hz to 10^5 Hz) [5],[13], giving information about different molecular motions and relaxation processes [12]. However the dielectric method in this frequency range does not work with all thermosets [4]. Some adhesives result in high conductivity, masking the curing process in the low frequency range [4],[5],[14]. On the

other hand, there are some adhesives whose ionic conductivity is not significant and it is necessary to monitor the process controlling the dipole relaxation [15]. Furthermore, electrode polarization at low frequencies can induce large errors in conductivity measurements [15],[16]. Little electrode spacing is used to avoid this problem, but this involves a little sensing volume within the adhesive (from tens of micrometer to a few millimeters) [15].

To overcome these difficulties, high frequency dielectric measurements (from 10^8 Hz to 10^{10} Hz) are recommended. This technique will be henceforth referred to as µWDEA.

For frequencies in the GHz range, for instance, the mobility of the molecules plays the main role and is not masked by conductivity [4]. Despite the advantages shown by µWDEA, measurements above 1 MHz are much less common [12]. The high cost of network analyzers and the lack of a deeper understanding of the relations between the sensed parameters and the chemo-physical information, have prevented a wider use of microwave sensors for monitoring polymers and adhesives cure reactions [17],[18]. Some studies have been performed with transmission lines [19]-[21], or cavities [22], but most of measurements were performed on already cured samples.

Great efforts have been made in high frequency instrumentation and signal analysis techniques, and only recently has the technology developed to the stage to make in-process use possible [17],[23].
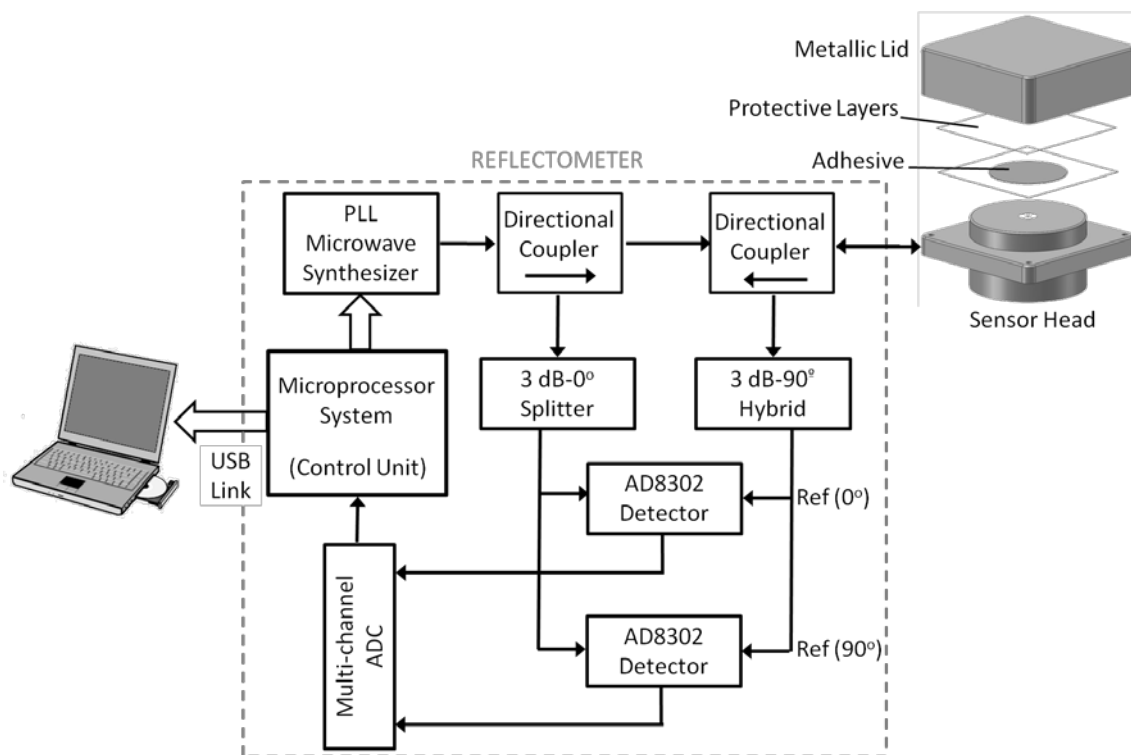
In this work, a µWDEA sensor system for monitoring adhesive cure reactions is described. The design consists of an open-ended coaxial resonator integrated in a self-contained system which includes the microwave circuitry and the control software.

The system as a whole represents a step forward in the development of curing monitoring techniques because it represents, for the first time, a complete solution for continuous and real-time monitoring of adhesives curing at microwave frequencies.

Results show that non-invasive measurements of the adhesives cure can be performed in a convenient way. Parameters of interest such as dielectric properties, degree of cure, reaction rate or cure time can be obtained with the proposed system.

Measurement results have been correlated with conventional DSC measurements, and a good agreement has been found between the two techniques.

2. Microwave sensor system

Fig. 1. Microwave sensor system for the adhesive cure monitoring.

Fig. 1 shows the microwave system designed for adhesive cure monitoring. The device comprises a microwave sensor head, a reflectometer to measure the reflected signal from the sensor and a control unit to direct the whole measurement system.

The sensor head is an open coaxial resonator emitting a low-intensity microwave signal which interacts with the adhesive. When the electromagnetic wave penetrates into the adhesive, its molecules tend to orient with the external field and the material gains certain polarization depending on its dielectric properties. As the cure progresses, the adhesive reflects part of the microwave signal back to the sensor and absorbs the remaining part. The reflected signal determines the resonant frequency and quality factor of the coaxial resonator. If measurements of these sensor parameters are continuous, it is possible to verify the chemo-physical evolution that occurs inside the adhesive.

In order to treat all the microwave signals involved (transmitted and received), impedance analyzers or automatic Vector Network Analyzers (VNAs) have been traditionally used, due to their possibility to measure many decades of frequencies,

which has been traditionally employed to identify different relaxation processes in materials.

The high cost of commercial VNAs is a disadvantage which prevents the industrial use of microwave sensors. Peak detectors may be used as an alternative to decrease the cost of the receiver system. However, measuring only the signal magnitude is not enough to determine resonant frequencies and quality factors, especially when the sensor is strongly coupled, as pointed out in [24]. In order to provide a complete system at an affordable cost, a microwave receiver is proposed, based on a commercial gain and phase detector (AD8302).

The microwave system is based on the block diagram shown in [23]. However, relevant modifications have been implemented to adapt the system to this application. The microwave source is designed as a PLL-based synthesizer (ADF4113) with voltage control oscillator (from 1.5 to 2.6 GHz). With this configuration, the number of frequency sweeps of the microwave source has been increased up to 10 measurements per second allowing fast resonant frequency and quality factor calculations for on-line cure monitoring. On the other hand, the separation network has been implemented in this case with two directional couplers, improving the system performance. The directional couplers used in the system are surface-mount bi-directional couplers from Mini-Circuits®, with a Directivity $\geq$ 21dB in the frequency range from 1.5GHz to 2.6 GHz. In the receiver, the ambiguity in phase of the AD8302 circuit has been solved by using two receivers with signals shifted 90º, as illustrated in Fig.1.

The reflectometer system is connected to a PC through an USB port, to perform the required calculations and to transform the outputs into the desired display (including dielectric properties, cure rate, end point detection, etc.).

3. Electromagnetic analysis of the microwave sensor

Fig. 2 shows a more detailed representation of the microwave sensor head. The design is based on an open-ended coaxial resonator radiating to a multilayered material.

The microwave signal is emitted from a PTFE-filled coaxial tip into a thin film of adhesive material through a protective layer (to prevent the adhesive from sticking to the sensor). At the other side, the adhesive is in contact with a second protective layer and shielded by a removable metallic lid (metal sheet in Fig. 2).
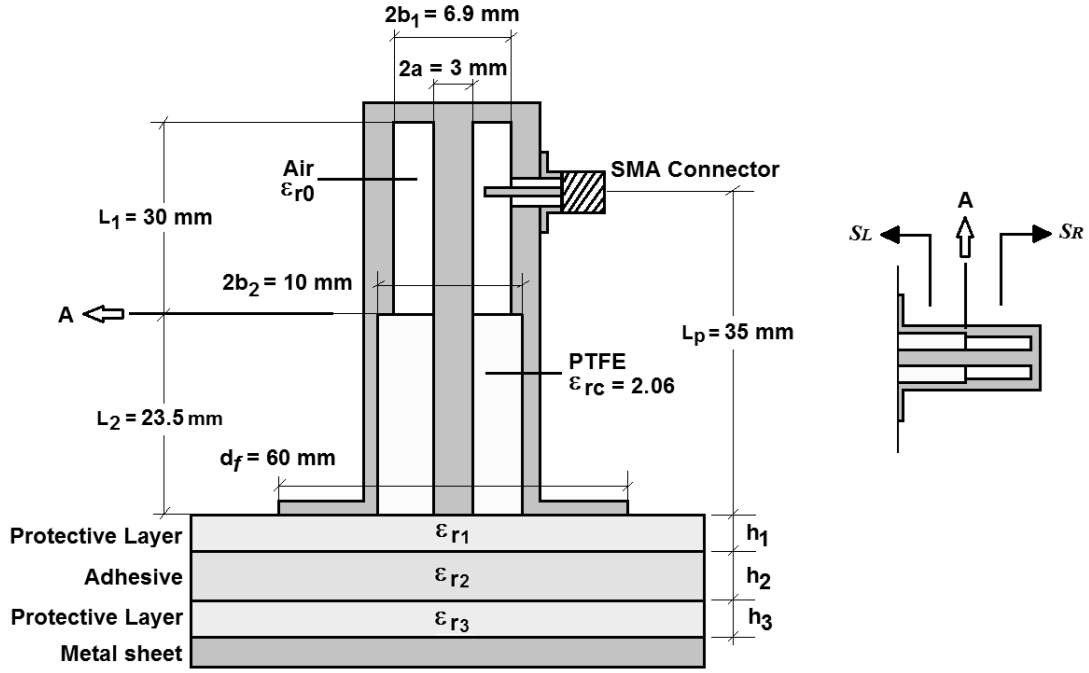
Fig. 2. Open-ended coaxial resonator used as a sensor head.
The adhesive is placed in a multilayered structure with protective layers
$(h_1 = h_3 = 0.1$ mm, $\varepsilon_{r1} = \varepsilon_{r3} = 4 - j*10^{-4})$ and a metallic sheet.

The coaxial line is terminated at the other end by a short-circuit, thus the microwave sensor is considered as an open-ended coaxial resonator. For the determination of the complex resonant frequency (Ω_U) of the sensor, the coaxial resonator is divided in two parts, at both sides of plane A (see Fig. 2). The first part (Right) is the short-circuited air coaxial line (the probe coupling is not considered for the moment). The second part (Left) is a dielectric-filled coaxial line opened to a layered dielectric media. By modelling each part with its multimodal scattering matrix ($S_R(\Omega_U)$ and $S_L(\Omega_U)$), the complex resonant frequency is determined with the application of the transverse resonance condition at plane A [25]-[28]:

$$S_R(\Omega_U) \cdot S_L(\Omega_U) = 1 \quad . \tag{1}$$

The unloaded resonance frequency f_U and quality factor Q_U are given in the complex resonance frequency as follows:

$$\Omega_U = f_U \left(1 + j\frac{1}{2Q_U}\right) \tag{2}$$

$$f_U = \text{Re}\{\Omega_U\}$$

$$Q_U = \frac{\text{Re}\{\Omega_U\}}{2\,\text{Im}\{\Omega_U\}}$$

(3)

Alternatively, the values of the complex resonance frequency can be applied in (1) to numerically determine (with an iterative procedure) the adhesive complex permittivity ($\varepsilon_{r2} = \varepsilon'_{r2} - j\varepsilon''_{r2}$), provided that the rest of parameters (permittivity and thickness of the rest of layers) are known [27]. The formulation details, which are similar to those shown in [27], are here omitted.

In order to evaluate the system accuracy in the determination of the adhesive dielectric properties, an uncertainty analysis was performed following the general procedures that can be found in [29],[30]. The accuracy was obtained to be about 1% in dielectric constant (ε'_{r2}) (in the range from 1 to 100) and from 2 to 5 % in the loss factor (ε''_{r2}) (in the range from 10^{-3} to 10 respectively).

3.1 Coupling network modelling

The microwave sensor is fed by an electrical probe which penetrates a certain distance into the resonator (see Fig. 2). The use of a feeding network to couple energy into the sensor modifies its theoretical unloaded response: the resonance frequency f_U is shifted to f_L (loaded resonance frequency) and the quality factor Q_U is lowered to Q_L (loaded quality factor) [24]. If the aim is to follow the adhesive cure process, it would be enough to monitor relative changes in loaded resonance frequency and quality factor. However, if the user is interested in the adhesive permittivity values (off-line or on-line if the adhesive dimensions are fixed), it is thus necessary to model and correct the effect of the coupling network. Many authors neglect this effect and use resonators in highly undercoupling condition (the energy is weakly coupled into the resonator) [24],[31]. However, the undercoupling condition involves an important limitation: materials exhibiting medium or high losses cannot be measured because they absorb and attenuate most of the microwave energy, and the sensor resonance disappears [31]. Most adhesives present moderate loss factors, especially at the initial stages of curing [22],[32],[5], and some others cause reaction by-products which also result in high conductivities and losses [14]. Then, to cope with any kind of adhesive cure reaction, the sensor is designed with the energy strongly coupled (overcoupling condition), and

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consequently the effect of the coupling network of the sensor is modelled to correct the disturbance effect [24],[28],[33].

The detuning of a resonator due to the coupling network - relation between loaded (f_L, Q_L) and unloaded resonator parameters (f_U, Q_U) - according to the model described in [24],[34], is given by the equations:

$$f_L = f_U \left(1 + \frac{A}{Q_e^\alpha} \right) \tag{4}$$

$$Q_L = \frac{Q_U}{1+k} \tag{5}$$

where Q_e represents the quality factor of the feeding network, k is the coupling factor, and A, α are the model parameters. Values of f_L, Q_e, Q_L and k can be obtained from the sensor reflection by Kajfez procedure [33].

The model parameters A and α depend on the electromagnetic fields into the cavity (i.e. cavity dimensions, resonant mode, type and location of coupling probe) and they are determined from calibration measurements of the resonator with different coupling factors (different probe dimensions) [24, 34]. Once the feeding probe is modelled, the unloaded parameters (f_U, Q_U) can be calculated from each measurement (f_L, Q_L) by using (4) and (5).

The accuracy in the determination of resonator parameters f_U and Q_U due to the random noise present in measurements has been studied following the procedure described in [33]. Standard deviations of values have been found to be around 5% for the Quality factors and around 0.0035% for the resonance frequency. Also, long-term measurements (120 hours) have been performed, obtaining that the resonance frequency is stable within a range of ±0.1MHz around the mean value, while the quality factor is stable within a range of ±0.5 around the mean value. The equipment response did not present any drift in the time periods evaluated in this study.

On the other hand, the effects of ambient temperature variations on the determination of resonator parameters f_U and Q_U was evaluated for operation temperatures in the range from 19ºC to 50ºC. The effect of temperature is evaluated to cause a linear change of 0.08MHz/1ºC in the resonance frequency. Temperature variations in the range studied had no effects on the quality factor determination.

3.2 Reaction Rate

From the sensor resonance frequency and quality factor measurements, the adhesive reaction rate can be readily calculated by numerically differentiating the resonance frequency with respect to time (alternatively, it can also be computed from the quality factor):

$$\left.\frac{\partial f_U}{\partial t}\right|_{t_i} \approx \frac{f_U(t_i) - f_U(t_{i-1})}{t_i - t_{i-1}} \tag{6}$$

where $f_U(t_i)$ and $f_U(t_{i-1})$ refer to the sensor resonant frequency in two consecutive time instants.

3.3 Fractional Conversion

Considering that the temperature is constant, the rate at which the resonance frequency changes can be assumed to be directly proportional to the reaction rate, since both are proportional to the rate at which permanent dipoles become unable to align with the applied field [37]. Therefore, the resonance frequency can be supposed to be proportional to the conversion extent (C), as follows [7],[32],[37]:

$$C = \frac{f_U(t_i) - f_U(t_0)}{f_U(t_{end}) - f_U(t_0)} \tag{7}$$

where t indicates the time elapsed from the beginning of the cure process, and $f_U(t_0)$ and $f_U(t_{end})$ are the values of resonance frequency at the beginning and at the end of the reaction, respectively. The onset of reaction is defined here as the time instant of minimum resonance frequency, as reported in [36],[17].

When the reaction is exothermic, the effects due to the temperature rise and the effects due to the chemical reaction compete and might overlap. If the adhesive cure process is isothermal, the effects of the temperature rise are commonly neglected [35], [38], and (7) can still be applied.

If the conversion curves are required on-line, measurements of similar samples of the adhesive have to be conducted prior to the cure monitoring in order to determine $f_U(t_{end})$ since this parameter is not available during the cure process. The procedure is in essence similar to other techniques, such as DSC, in which previous measurements are used to obtain the total heat of reaction [3], [36]. The value of resonance frequency

at the end of the cure reaction $f_U(t_{end})$ is used then to obtain the fractional conversion in real-time for subsequent measurements of the same adhesive. This method provides good results if repeatability of experimental data is ensured between similar samples [35].

4. Experimental

4.1 µwDEA Measurements

Figure 3 shows a picture with the steps followed for the adhesive cure monitoring:

Step 1. The adhesive is mixed, weighted and applied to one of the protective layers.

Step 2. The protective layer with the adhesive is placed on the sensor surface.

Step 3. A second protective layer is placed on the adhesive sample. With the aid of the metallic lid, a slight pressure is applied to get a uniform adhesive layer with the required thickness, and rid the bond of air bubbles.

Step 4. The cure monitoring starts, on-line computations are performed (unloaded resonance parameters, reaction rate, etc.). Once the curing process is ended, the sample can be removed (together with the protective layers).

Step 5. Off-line computations are performed (complex permittivity, frequency/cure curves, etc.).

4.2. DSC Measurements

Additionally, in order to provide a basis for comparison and validation, results from µwDEA measurements were compared to data on the same material obtained using differential scanning calorimetry (DSC). The basic assumption for the application of DSC is that the measured heat flow is proportional to the reaction rate [39, 40].

Data reported in this study were obtained with a Q100 differential scanning calorimeter (TA Instruments), calibrated with Indium according to [41]. Adhesive samples (~10mg) were sealed in aluminum DSC pans, and the calorimetric data were obtained under isothermal conditions. In order to obtain comparable results, the DSC was set to 23ºC which was the room temperature for the µwDEA experiments, and measurements were
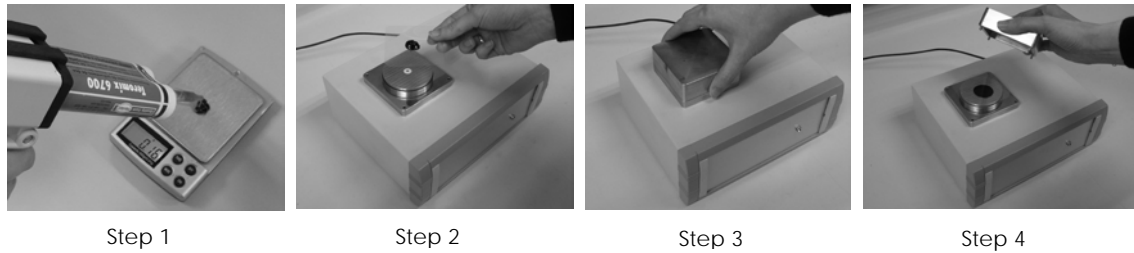
| Step 1 | Step 2 | Step 3 | Step 4 |

Fig. 3. Measurement process to monitor the cure of adhesive samples in the laboratory.
collected up to the moment at which a constant heat flow was observed. The study of
the progress of reaction was based on the measurements of the total heat flow which
allows calculating the degree of conversion (*C*) [40].

5. Results

An example of application of the microwave sensor system is the cure monitoring of the
TEROMIX 6700 (*Henkel*) adhesive. This polyurethane-based adhesive consists of two
components and it is typically applied to bond automotive parts.

The components were uniformly mixed with an applicator gun and placed in between
two flexible polyester sheets, according to the procedure described in Fig. 3. Thickness
of the adhesive film (h_2) was 0.3 mm. Room temperature was 19ºC.

Figs. 4a) and b) show the main parameters provided by the microwave sensor: the
unloaded resonance frequency (f_U) and quality factor (Q_U) for two samples of
Teromix 6700, after removing the effect of the coupling probe (model parameters
$A = -0.664142$ and $\alpha = 0.711780$). Fig. 5 shows the dielectric properties of the
adhesive ($\varepsilon_{r2} = \varepsilon'_{r2} - j\varepsilon''_{r2}$) during the cure, calculated from the sensor resonant
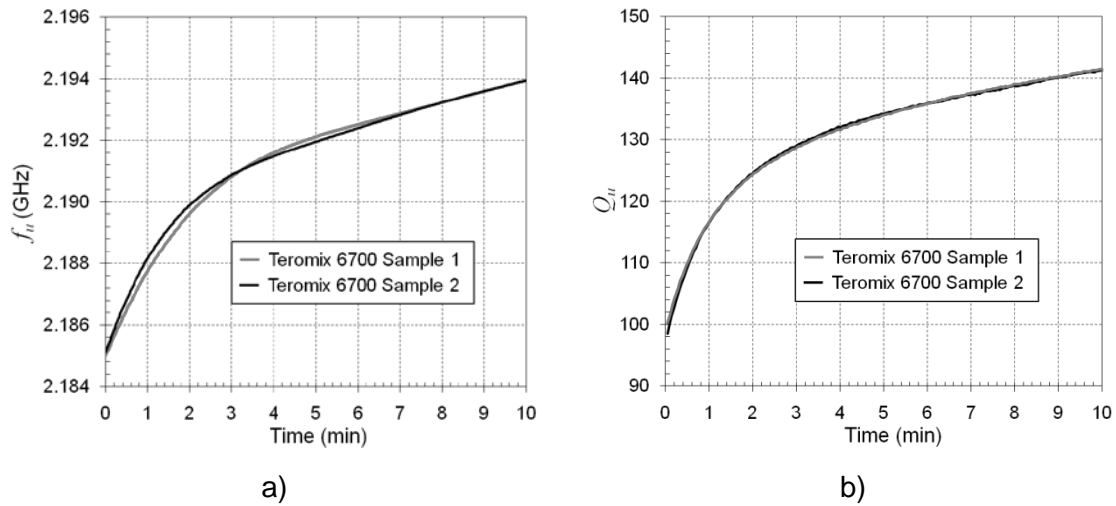frequency and quality factor of Fig.4.

Fig. 4. Time evolution of a) resonance frequency (f_U) and b) quality factor (Q_U) of Teromix 6700 samples during cure (at 19ºC).

The figures illustrate that both parameters change when the adhesive reaction progresses, showing a typical behaviour for these systems [40]. This means that the increase of the adhesive viscosity causes a drop of the molecular mobility, and thus, the dielectric properties of the adhesive are decreased. This fact involves an increase of the sensor resonance frequency and quality factor during cure.

The repeatability of the microwave response given by the system can also be appreciated in Fig.4 for two different experiments of the same adhesive. This repeatability is evaluated to be around 1-2% approximately.

Fig. 6 shows the adhesive fractional conversion curve (C) given by (7) as a function of the sensor resonance frequency (f_u). The µwDEA measurement taken as the reference is plotted with a solid line, allowing the determination of fractional conversion of subsequent measurements (squares). The good repeatability of measurements under the same conditions allows an accurate determination of fractional conversion in real-time.

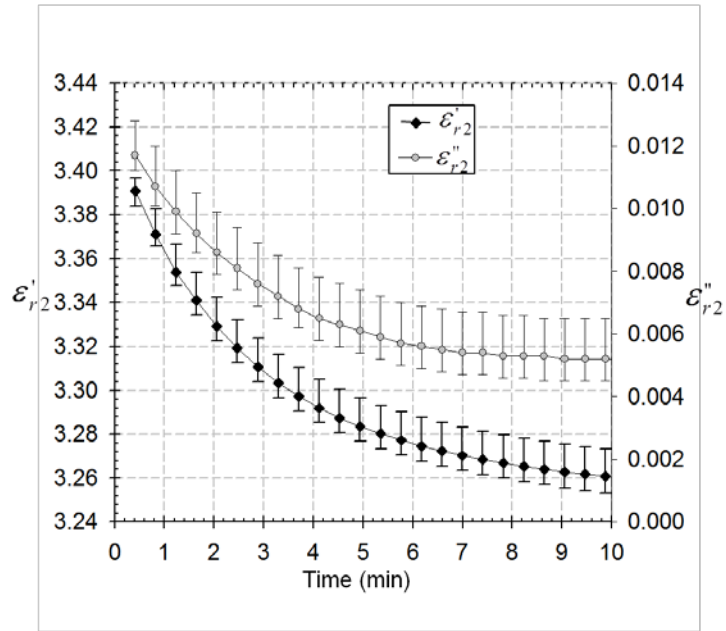Fig. 5. Time evolution of dielectric constant (ε'_{r2}) and loss factor (ε''_{r2}) of Teromix 6700 during cure (at 19ºC).
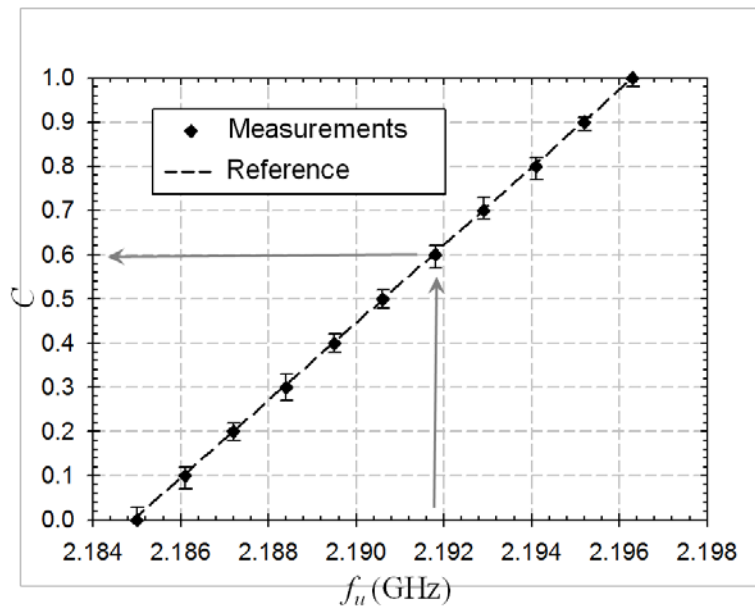
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Fig. 6. Fractional conversion (C) as a function of the sensor resonance frequency for the Teromix 6700 samples. The µwDEA measurement considered as the reference is represented as a solid line and a subsequent measurement with squares.
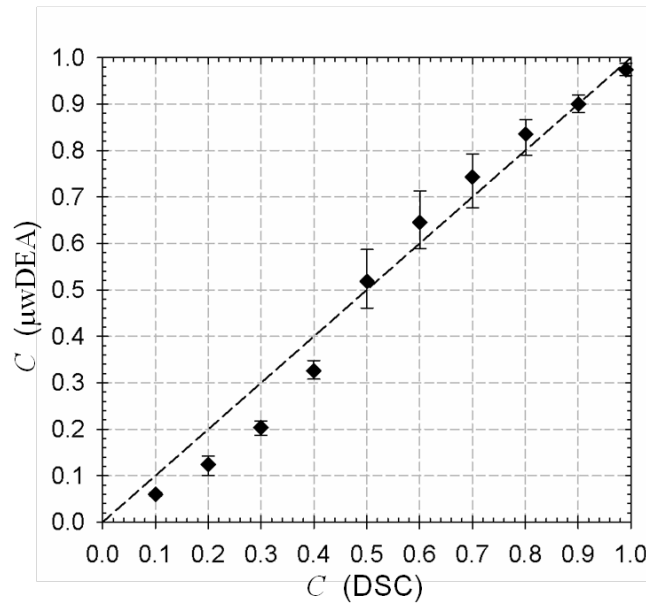
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Fig. 7. Fractional conversion of several adhesive samples determined with the microwave sensor (µwDEA) compared to the conversion values provided by DSC.

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Fig. 7 shows the fractional conversion of several adhesive samples determined with the microwave system (µwDEA) compared to the conversion values provided by DSC experiments for the same samples. In order to correlate the degree of cure obtained with DSC and µwDEA, two samples were prepared, and the degree of cure was simultaneously determined with both techniques.

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From Figure 7, it can be seen that there is a good correlation between both techniques, especially for fractional conversions higher than 0.5. DSC equipment needed about 3 minutes to stabilize to the desired temperature which was an inconvenient because around 50% of cure takes place during the first 3 minutes. Then, to obtain DSC data for low fractional conversion (DSC points between 0 and 0.5), measurements were collected almost immediately after inserting the pan inside the equipment, without stabilize the temperature in the equipment.

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The error was considered to be small because the room temperature (23°C) was similar to the isothermal temperature of DSC experiments. However, the authors are aware of the error introduced in DSC results for fractional conversion lower than 0.5 due to this fact. Despite of this, the results shown in Fig. 7 suggest that the data obtained with the sensor correlate very well with those obtained using DSC (the Pearson product-moment correlation coefficient $r = 0.9924$).

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Fig. 8 shows the µwDEA reaction rate computed with (6) for a Teromix 6700 sample normalized with respect to its value at the beginning of the cure. The reaction rate obtained from a DSC measurement is also presented in the figure for comparison.

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Again, both monitoring methods present good agreement for the studied material. It is observed in the figure that a great reaction rate is given at the beginning of cure, since the slope in the resonance frequency is higher at the early stage of the process. As the adhesive cure proceeds longer, the rate of reaction is gradually decreased. At the final cure stage the value of the resonance frequency becomes more constant, thus providing a lower reaction rate.
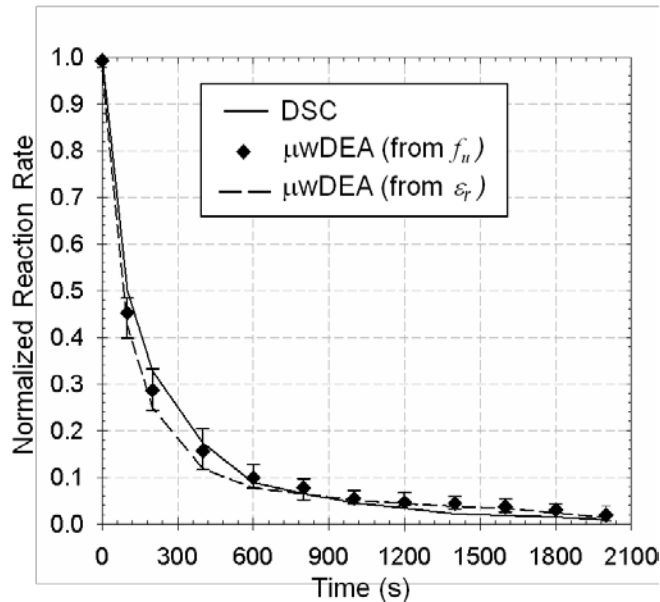

Fig. 8. Normalized reaction rate of Teromix 6700 samples (23ºC). DSC measurements (solid line) are compared to µwDEA results computed from the sensor resonance frequency (points) and from the adhesive dielectric constant (dashed line).

For illustrative purposes, Fig. 8 also includes the normalized reaction rate computed by differentiating the adhesive dielectric constant with time. The results are very similar to the reaction rate computed from the resonance frequency. This indicates that both set of parameters (resonant frequency/quality factor or dielectric constant/loss factor) can be used to verify the cure process. However, the determination of the adhesive dielectric properties needs some processing time, so if the monitoring process requires fast measurements, the use of resonance frequency and quality factor is preferable.

The cure time can be defined as the time at which the sample has reached a fractional conversion close to 100%. This is a parameter of high interest for manufacturers which need to optimize cure cycles to improve their process efficiency. Since the fractional conversion is provided by the microwave system in real-time, the cure time can be readily determined.

The cure time has been obtained for Teromix samples analyzed with the microwave system and with DSC, and the results are shown in Table I. The good correlation

observed between fractional conversion measurements performed with DSC and µwDEA leads to very similar curing times determined with both techniques.

Table I. Cure time determination for various Teromix 6700 samples at 23ºC, using the microwave system (µwDEA) and DSC equipment.

	Cure Time (min)	
	(C = 90%)	(C = 99%)
µwDEA Sample 1	9.45	39.36
µwDEA Sample 2	9.36	36.33
µwDEA Sample 3	9.70	32.60
µwDEA Sample 4	9.23	31.55
DSC	9.61	30.11

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6. Conclusions

10 A microwave sensor system for continuous monitoring of adhesives cure has been developed. Parameters such as reaction rate or cure time are provided in real-time by the system. Additional information such as the adhesive dielectric properties can be also obtained off-line.

The results given by the system correlate very well to conventional measurement
15 techniques such as DSC, combining accuracy and rate with simplicity and an affordable cost.

The system is presented as a complete solution for measurements of adhesives cure in-lab. However, it can be considered as representative of the application of this technology in an industrial environment, where it would provide the possibility to
20 monitor, optimize and adjust the cure cycle on-line.

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