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How broad band (from radio frequency to microwaves) dielectric parameters describe synthetic chemical reactions

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Large differences in the dielectric responses of isolated molecules and associated reactive mixtures are observed over a wide frequency spectrum ranging from low to microwave frequencies. We present the results obtained for the curing (cross-linking) of a resin mixed with a hardener. Electrical dipoles contribute to orientation polarization whose responses lie in the 1 kHz to over 1 GHz frequency range, which is predominantly higher than the 0.1 Hz–10 kHz range in which ionic conductivity is observed. It is the relaxation frequency of the reactive mixture that will be considered as the reaction marker. We also describe the results obtained with the saponification of an ester in the presence of a catalyst, with the reactive mixture containing – as in the previous case – electric dipoles and ions, but with responses superimposed in the 1 MHz–10 GHz frequency band. In this case, and for simplification reasons, the low frequency band ionic conductivity is the reaction marker. The aim of this paper is to translate synthetic chemical reactions into electronic terms, in order to allow electronics engineers to understand the interaction between electromagnetic waves and materials. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: broad band dielectric measurement; saponification; curing; ionic conduction; dipolar relaxation frequency

INTRODUCTION

This paper constitutes a summary of a series of analyses by broad band dielectric spectroscopy – which ranges from low frequencies to microwave frequencies – of isolated systems and reactive mixtures in synthetic chemistry. Dielectric characterization down to microwave frequencies enables molecular systems with electric dipoles or ions present in the reactive medium to be monitored as the temperature increases during the reaction progress. In the first part, we present the results obtained for the curing (cross-linking) of a resin mixed with a hardener. Electrical dipoles contribute to the orientation polarization whose responses lie in the 1 kHz to over 1 GHz frequency range, which is markedly larger than the 0.1 Hz–10 kHz range in which ionic conductivity is observed. It is the intrinsic relaxation frequency of the reactive mixture that will be considered as the reaction marker. In a second part, we describe the results obtained with the saponification of an ester in the presence of a phase transfer catalyst, with the reactive mixture containing – as in the previous case – electric dipoles and ions, but with intrinsic responses superimposed in the 1 MHz–10 GHz frequency band. In this case, the low frequency band ionic conductivity will allow the description of the reaction progress.

This method was applied in our laboratory first to conventional heat treatment and then to microwave treatment, and will form the subject of a third part in a future paper[1] to be published. Previous papers[2,3] report more details on the conventional heat treatment.

At present, we consider dielectric spectroscopy over very wide frequency ranges, including microwaves, to be a valuable aid for comparing behaviour and differentiating the reactive paths in the two methods of heat treatment: using the Arrhenius law, the activation energy of the relaxation phenomenon is calculated. This parameter has to be obtained for the comparative study described in the third part and needs microwave frequency for greater accuracy.

Besides, our aim is to translate synthetic chemical reactions into electronic terms: relaxation frequency instead of relaxation time or viscosity, ionic conductivity instead of degree of

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conversion. This will allow electronics engineers to understand the interaction between electromagnetic waves and materials and, in a very near future, the interaction between electronic devices and biological tissues in the case of ultra wide band sources, in relation with radars.

THE DIPOLAR RELAXATION FREQUENCY AS THE REACTION MARKER

State-of-the-art about the dielectric response of a pure resin and a resin mixed with a hardener

Work similar to ours described in the literature concerns the monitoring of curing reactions of diglycidyl-ether of bisphenol A (DGEBA) resin over wide frequency ranges, down to microwave frequencies. Firstly, the work of Mijovic *et al*.[4,5] concerns epoxy systems of variable molecular weights, observed at discrete frequencies from the MHz scale up to several tens of GHz. It is noteworthy that the epoxy chains they used, unlike our resins, contain OH groups that make the dielectric spectrum more complex. These authors wanted to show how the intermolecular arrangements were governed by the molecular and dielectric structures, which we have also attempted to demonstrate using just two resin/hardener mixtures, namely DGEBA + DDS and DGEBA + DDM. The hardeners DDS and DDM have very different overall dipolar moments and both are used in our industrial environment. In subsequent articles, the authors performed a modal analysis of the relaxation phenomena.[6–9] Similar systems were studied by Williams *et al*.,[10] who modelled the relaxations using Fuoss–Kirkwood[11] and Kohlrausch–Williams–Watts[12,13] models. Rolla *et al*. finely analysed different polymers and DGEBA relaxations at frequencies up to 3 GHz[10,14–17] and beyond,[18–21] aided in this by calorimetric measurements. Kim and Char[22] studied the curing of a DGEBA + DDM mixture jointly with low-frequency dielectric measurements (0.1 Hz–100 kHz) and calorimetric measurements, and associated the relaxation with the curing rate.

We would stress the fact that our aim was to study the curing of a hardenable mixture during a temperature increase followed by a step of constant temperature by conventional heat treatment and define the process dielectric parameters in order to subsequently compare this treatment method with microwave heat treatment, for which dielectric characterization is a suitable means of investigation. Consequently, we in no way considered an isothermal polycondensation[23,24] during the whole curing process, like in the studies of Mangion and Johari[25] and Kranbuehl *et al*.[26] who have also worked at fixed low temperatures and arbitrary low frequencies. When Parthun and Johari[27] look at the dielectric behaviour of thermosets during their curing under non-isothermal conditions, they use a fixed frequency (1 kHz) during the ramp heating. In our paper, dynamic high temperatures mean dynamic high relaxation frequencies for molecular dipoles up to microwaves during the curing time.

Material studied: DGEBA, DDS, DDM, DGEBA + DDS, DGEBA + DDM

The study focused on epoxy resin-based reactive systems and two types of hardener.

DGEBA resin

DGEBA epoxy resin is solid at room temperature and becomes liquid when heated to about 40°C. The resin has to be in liquid form to be introduced into the sample holder for dielectric analysis.

The DGEBA molecule (Table 1) was modelled on the assumption that it contained no OH group, which was subsequently confirmed by infrared spectroscopy. The main dipole is that of the epoxy function —CH_2CHO—. The Debye moment of the localized epoxy functions given in the literature was confirmed by the MOPAC[28] software used in this study, and is $\mu_{epoxy} = 1.9$ D ($1\ D = 1/3 \times 10^{-29}$ C m). As concerns the overall Debye moment of the DGEBA molecule in non-planar configuration, it varies according to the configuration – that is the relative orientation of the two epoxy groups – from $\mu_{DGEBA} = 2$ to 0.3 D, values that were obtained using the MOPAC software.

The DDS and DDM hardeners

The DDS (4,4′-diaminodiphenyl sulphone) and DDM (4,4′-diaminodiphenyl methane) hardeners are powders at room temperature.

The dipolar moments. Delocalization of electrons

The modelling of the DDS hardener (Table 1) shows that its configuration is not planar. DDS carries two dipoles, namely —NH_2, a reactant, and —SO_2, which we call the 'actor' given the size of its dipolar moment which confers to the molecule a high global Debye moment of $\mu_{DDS} = 7$ D.

The DDM hardener also carries two dipoles: one is the reactant amine dipole —NH_2, the same as that in DDS, while the other, the actor, is —CH_2. The modelling of DDM (Table 1) shows a virtually planar molecule. Given that the methyl group —CH_2 is very weakly polarized, the DDM molecule has a low global Debye moment of $\mu_{DDM} = 0.2$ D.

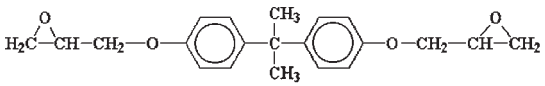
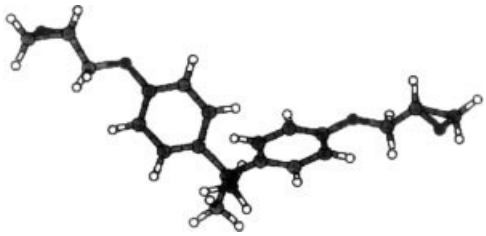
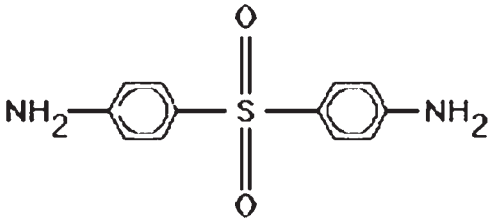
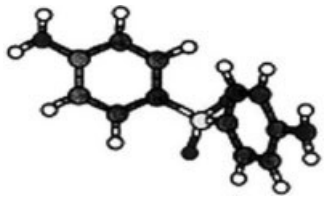
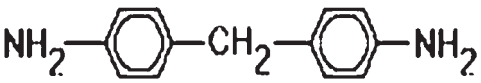
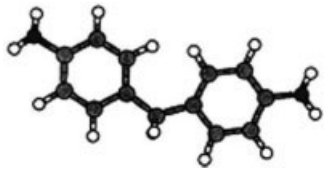
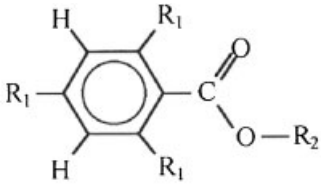
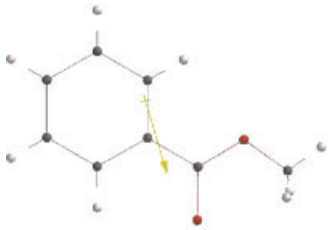
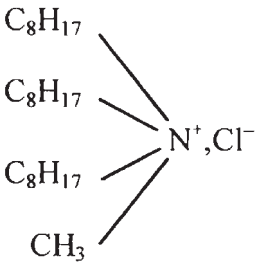
As for the reactivity of the two hardeners, if we consider DDS, SO_2 is a very strong electron puller and delocalizes the electrons of the benzene cycles and the free electrons of the amino groups. Consequently, these groups are far less nucleophilic in DDS than in DDM. Given that the curing reaction is based on a nucleophilic attack by the —NH_2 groups on the epoxy functions, one can deduce that, all else being equal, the reaction with DDM will be faster than that with DDS. DDS introduces a high polarity, which means that the —NH_2 is more highly charged and remains free to react with the epoxy groups.

Moreover, the low polarity of the —CH_2 group in DDM creates two sections in the molecule that behave independently of each other: the NH_2 groups are freer than in DDS, and therefore are more reactive. Consequently, one can predict that the reaction will be faster with DDM than with DDS, and will take place at a lower temperature.

Polycondensation of epoxy-amine systems

Reminder: polycondensation, curing or cross-linking, consists in the formation of a three-dimensional lattice from monomers (linear molecules) through the reaction of the epoxy functions of the resin with the amine functions of the hardener.[29] In a conventional and simple manner, three phases can be defined in the raising of the hardenable mixture to temperature, namely fluidification, gelification and vitrification (sol–gel–glass trans-

Table 1. Molecules studied and their MOPAC[28] or SPARTAN models

Molecule	Formula	MOPAC representation
DGEBA		
DDS		
DDM		
Methyl benzoate ($R_1 = H$, $R_2 = CH_3$)		 (SPARTAN)
Aliquat 336 (expressed as R_4N)		
Sodium hydroxide	NaOH	

formations). Before the reaction, the base resin and the hardener display low viscosity and high solubility. As the temperature rises beyond room temperature, the viscosity starts to diminish. This first phase is the fluidification phase. In the second phase, i.e. gelification, the mixture (resin + hardener) begins to polymerize: the viscosity increases very rapidly, the molecular weight of the mixture increases constantly, and the molecule chains get longer. Finally, in the third and last phase, named vitrification, where the molecule chains are bonded, the viscosity stabilizes and the system becomes solidified and insoluble. This is the cross-linking reaction.

We will see in section 'The DGEBA + DDS mixture' how our observations led to express these different phases in terms of the variation in an electrical quantity characteristic of the interacting molecular systems.

Description of the broad band (100 Hz–10 GHz) dielectric spectroscopy instrumentation. Definition of the measured parameters

Description of the instrumentation

Dielectric characterization is carried out over a wide frequency range owing to the frequency sweeping of several impedance and network analysers, type HP 4192 (5 Hz–13 MHz), HP4291 (1 MHz–1.8 GHz), HP 8510 (45 MHz–18 GHz) connected to the measuring cell containing the material by a circular coaxial cable in order to sweep the 100 Hz to 10 GHz band explored in this study. A conventional coaxial cell was used for the very low frequencies (100 Hz–1 MHz). In the remainder of the frequency range, a cell developed specifically in the laboratory was used.[24] This cell is made up of a hollow waveguide terminating in a short

circuit. The interface between the cell and the coaxial cable is abrupt. This system was subject to electromagnetic analysis by modal connection. In the most favourable cases (analyser precision, permittivity value of the material being characterized), it allows operation of the cell from DC to 18 GHz for a cable/cell assembly with an external diameter of 7 mm (standard APC7).[30]

The complex permittivity is deduced from this using the measurement of admittance or of the reflection coefficient of the cell containing the material, by numerical solving of the inverse problem through successive approximations[30,31] with a precision better than 10% throughout the frequency range.

The cell is placed in a ring oven controlled by a Eurotherm system. Temperature is measured using a Brion Leroux Pt100 probe.

The shrinkage of the polycondensed mixture in the final 'vitrification' phase, which is considerably less than with other resins such as polyester resins, was not observed in our dielectric measurements. It has been evaluated at less than 1% per unit length. The original instrumentation used in this study was built by Meyer *et al.*[31,32]

Dielectric parameters

In these studies, the behaviour of the reactive mixture is characterized by its complex permittivity which depends on the pulsing of the applied electrical field $\varepsilon(\omega) = \varepsilon_0(\varepsilon'(\omega) - j\varepsilon''(\omega)) = 1 + \chi(\omega)$ (where χ is the electric susceptibility and $\omega = 2\pi f$ (Hz), ε' and ε'' are the real and imaginary relative permittivity).

Monitoring the characteristics of the reactive medium during the heat treatment provides information on the polarization state of the medium and the nature of the absorption phenomena (dipolar relaxations or ionic conductivity). Only the dipoles, however, are considered in this paper. The dipoles present in the medium are oriented by the applied alternating current electric field. When the electrical stress is zero (changing of the electric field value from a non-zero value to zero), the polarization changes from a given value (tendency for the dipoles to adopt an overall direction) to zero (random distribution characterizing the disorder of the equilibrium state) non-instantaneously that is with a time constant τ.

This 'depolarization' time constant τ is defined as a first approximation by Debye for spherical entities of radius a in a medium defined by a viscosity term η and at temperature T.

$$\tau = \frac{4\pi a^3 \eta}{kT} \tag{1}$$

where k is Boltzmann's constant.

On the time scale of the relaxation phenomena, the fast processes are represented by a permittivity at infinite frequency ε_∞ which intervenes in the instantaneous polarization response. The permittivity at zero frequency is εs.

Debye's law elates $\varepsilon(\omega)$ to ε_∞, εs, τ and ω as follows:

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + j\omega\tau} \tag{2}$$

The evolution of this relaxation spectrum displays a peak in absorption (or in dielectric losses) at an angular frequency

$$\omega_r = 2\pi \cdot F_r = 1/\tau \quad \text{with} \quad F_r = kT/8\pi^2 a^3 \eta \tag{3}$$

The corresponding frequency F_r is called the relaxation frequency. Debye's model represents the change in the complex permittivity as a function of the angular frequency of the excitation field.

When possible, the variation in the relaxation frequency F_r is related to the temperature by an Arrhenius law in $F_r = A \exp(-W/kT)$ where W is the relaxation activation energy, k Boltzmann's constant and T the temperature of the medium.

Results. Polymerization of reactive systems

The DGEBA + DDS mixture

The DGEBA + DDS mixture in stoichiometric quantities ($R = 1$) was heated conventionally using a protocol that consisted in a fast temperature rise at a rate of about 8°C per minute for 20 minutes to reach a holding temperature of 190°C that is maintained for 20–30 minutes. Heating is stopped after 45 minutes, and the sample is left to cool naturally. The dielectric measurements are made during frequency sweeping from 1 MHz to 10 GHz every 2 minutes. Thus, with the rise in temperature from room temperature, the relaxation frequency of the mixture increases from 3 kHz to 700 MHz, the maximum observed frequency value: The degree of freedom of the molecules has increased: this is the fluidification illustrated by Debye's law.

We hypothesize that at the maximum of the relaxation frequency, the chemical bonds of the epoxy functions open and the cross-linking begins. The relaxation frequency then falls from 700 to 2 MHz thus materializing the reduction in the degree of freedom of the molecules present: this is the gelification phase followed by the vitrification phase.

A lattice of macromolecules begins to be established as from near the maximum frequency of 700 MHz. An exothermal reaction takes place, identifiable by the exceeding of the setpoint temperature. The minimum frequency value of 2 MHz – which will remain virtually constant during the natural cooling – expresses the glassy state. Figure 1 shows the variations in the complex permittivity of DGEBA + DDS over time during the rise in temperature from room temperature. Figure 2 shows these same quantities during the temperature holding period and cooling to room temperature.

The behaviour of the dipolar relaxation frequency is summarized in Fig. 3.

We have defined the transition points sol–gel and gel–glass in the following way:

The probability of a jump by a charge of dipole in a double potential well is derived from statistical thermodynamics. The number of dipoles jumping per time unit is the relaxation frequency F_r. So a hindrance, like chemical bond formation, changes this frequency: the relaxation frequency is related to the viscosity. So we think that the evolution of the relaxation frequency during the curing process resembles the behaviour of a viscoelastic marker.[33] On one hand, we have shown the slope dF_r/dt *versus* time in Fig. 3. This curve exhibits a first inflexion point just before the maximum of the relaxation frequency. We assume that this point is the sol–gel point. On the other hand, we observed a second inflexion point after the maximum of the relaxation frequency: this point is the gel–glass point.

We would have used the evolution of the electrical function tg $\delta = \varepsilon''/\varepsilon'$ *versus* time, like Boiteux *et al.*,[33] but even at the relaxation frequency, the ratio of these electric parameters is less accurate than the frequency velocity.

At last, the activation energy of the dipolar relaxation measured during the fluidification phase where the system

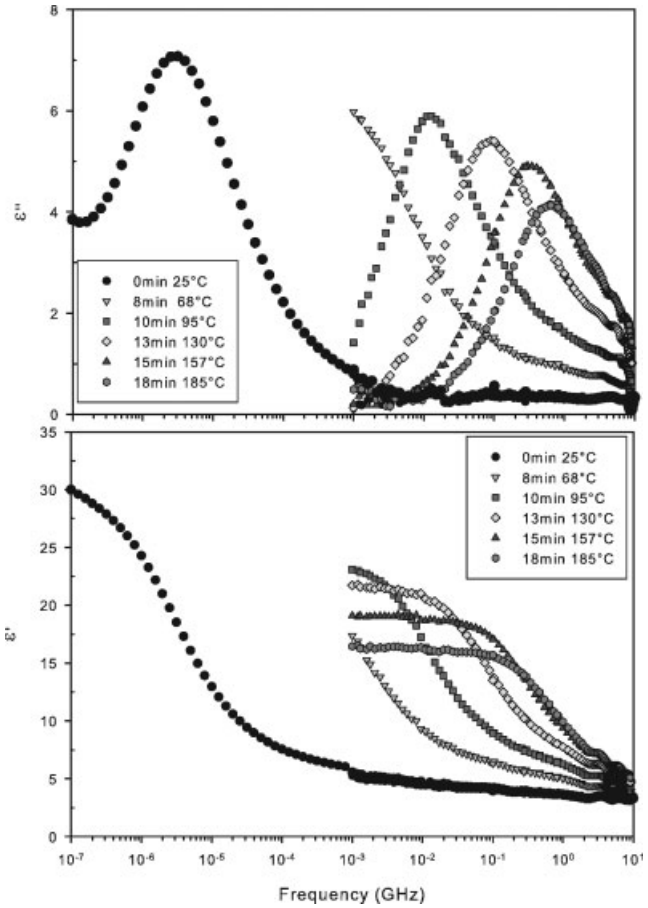


Figure 1. Variations in the complex permittivity of DGEBA + DDS ($R = 1$) as a function of frequency and temperature during the fluidification phase (first phase)

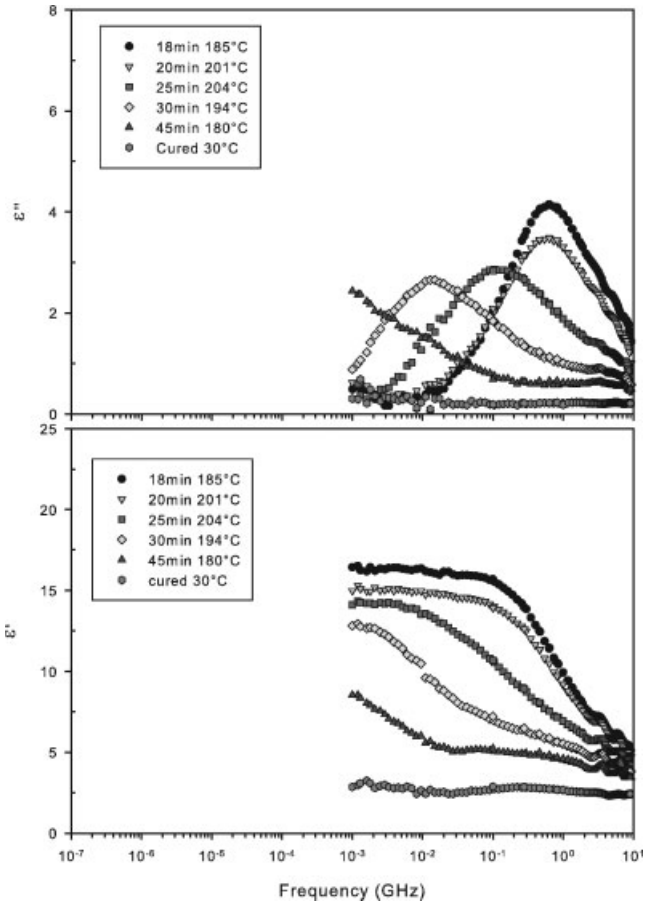


Figure 2. Variations in the complex permittivity of DGEBA + DDS ($R = 1$) as a function of frequency and temperature during the gelification phase (second phase) and the vitrification phase (third and final phase)

follows the Arrhenius law (Fig. 4) is evaluated at 96 kJ mol^{-1} at the beginning of the treatment.

The DGEBA + DDM mixture

The rise in temperature to a holding temperature of 120°C is achieved in 35 minutes ($dT/dt = 2.5$°C minute^{-1}). The reaction temperature of DGEBA + DDM (120°C) is lower than that of DGEBA + DDS (190°C). The DGEBA + DDM mixture displays the same phases as the DGEBA + DDS mixture, with a strong resemblance during the fluidification period with the development of the spectrum obtained for DGEBA, which confirms the lower dipolar interaction between DGEBA and DDM. Unlike the case with DGEBA + DDS, in which one observes an absorption

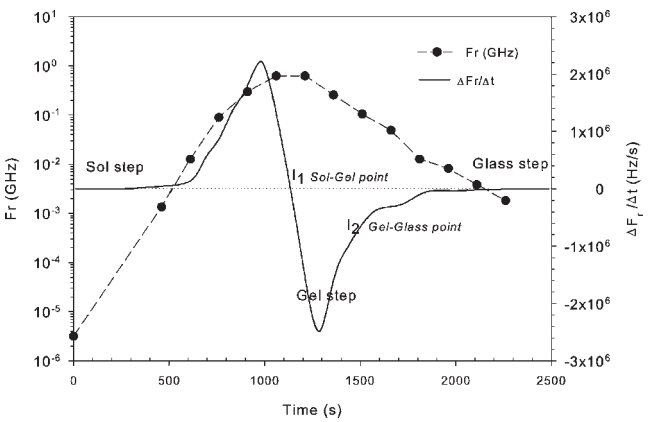


Figure 3. Variation in the frequency F_r and dF_r/dt of DGEBA + DDS ($R = 1$) as a function of heating time

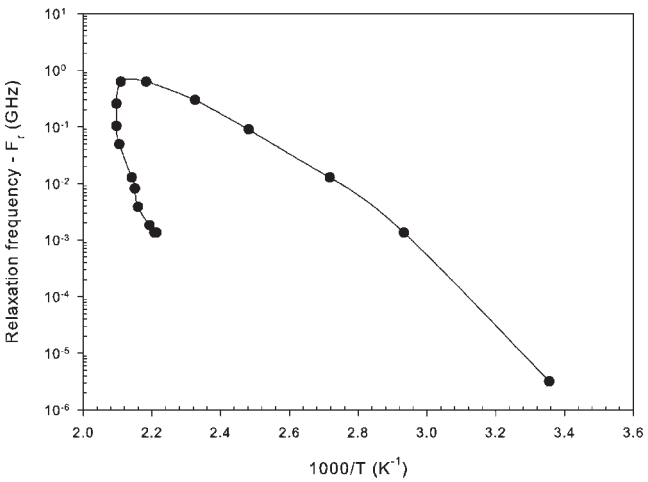


Figure 4. Variation in the relaxation frequency F_r of DGEBA + DDS ($R = 1$) as a function of temperature

spectrum that corresponds to the very strong coupling of DGEBA with the global dipole of DDS, it can be seen that the spectrum observed with DDM is very similar to that of DGEBA.[1] Furthermore, it is very probably this low level of interaction between DGEBA and DDM that favours the reaction of the amine functions with the epoxy functions, enabling them to position themselves more easily during the temperature rise. In other words, a low level of dipolar interaction in an initial mixture induces a lower relaxation activation energy during the heating of a reactive system, which leads to a lower reaction temperature. Therefore, the chemical reaction takes place more easily. This result confirms the conclusion of section 'Description of the broad band (100 Hz–10 GHz) dielectric spectroscopy instrumentation. Definition of the measured parameters' that the amine groups are less nucleophilic in DDS than in DDM. The DGEBA + DDM mixture displays a resulting relaxation at 4.5 MHz and we have justified the difference in reaction temperature of the two mixtures by showing that the respective activation energies went in the same direction, namely 96 kJ mol^{-1} for the DGEBA + DDS mixture and 40 kJ mol^{-1} for the DGEBA + DDM mixture, this value being identical to that estimated by Kim and Char.[22]

Discussion of the first part

In this first part, we have shown the usefulness of spectroscopy at radio and microwave frequencies combined with molecular modelling for the real-time monitoring of a chemical cross-linking reaction in a mixture (resin + hardener), and predicting how it progresses. Observation of the orientation polarization absorption is relatively easy, and the relaxation frequency of the molecular system formed by the reactants becomes a reaction marker. Further to these studies, we have redefined the polycondensation phases as follows. When the relaxation frequency increases to a maximum value as the temperature is raised from room temperature, this is the fluidification phase: the DGEBA molecule gains the energy necessary to open the epoxy bonds. Then, when the temperature is held constant, the relaxation frequency decreases, bringing the gelification phase in which there is a reaction between the amine and epoxy groups: the degree of freedom of the molecules decreases and their mass increases. In the final phase, the reduced relaxation frequency remains constant at a low value: this is the vitrification phase. A more precise definition of the transition phase points is given in terms of the relaxation frequency evolution. They allow the monitoring of cross-linking reactions by an electromagnetic method. We are currently transforming our instrumentation into a non-destructive testing technique.[34] It will allow the real-time monitoring of a chemical reaction by radio and microwave frequency spectroscopy to be extended to large quantities of products placed in tanks.

THE LOW FREQUENCY IONIC CONDUCTIBILITY AS THE REACTION MARKER

Introduction

In this second part, we describe the dielectric responses obtained for the saponification of an ester under phase transfer catalytic conditions. The reactive mixture contains, as in the previous case, orientation polarization electric dipoles and ions, but with responses superimposed in the 1 MHz–10 GHz frequency band. In this case, it is the ionic conductivity at the low end of the band that can be used to describe the progress of the reaction. The instrumentation used in this study was specially designed and built in our laboratory by Chevalier.[35]

Material studied: methyl benzoate, Aliquat 336, [Aliquat + sodium hydroxide (soda)], [methyl benzoate + Aliquat + soda]

The study focuses on saponification of an ester, methyl benzoate, by sodium hydroxide, NaOH, in the presence of a catalyst Aliquat 336.

Methyl benzoate

Methyl benzoate $C_8O_2H_8$ is a planar molecule for which the developed formula and the modelling representing the most probable stable conformation obtained using the SPARTAN software[36] are given in Table 1.

The dipole in the C═O bond (carbonyl function of the ester) confers to the molecule a large part of its dipolar moment, whose value is estimated in this study at 2.1 Debyes. The groups R_1 and R_2 near the reactive site of the ester are H and CH_3, respectively, therefore not very bulky. It is a liquid with a molar mass of 136 g mol^{-1}, and a density of 1094 kg m^{-3}; which means that a given volume of methyl benzoate contains a larger number of dipoles than the same volume of an ester with larger R_1 and R_2 groups, therefore is more voluminous and in our case heavier. Consequently, the studied sample, that is methyl benzoate, is more highly polar than its counterparts with similar Debye moments.

Aliquat 336, the Aliquat 336 + NaOH mixture

Tricaprylmethylammonium chloride, or Aliquat 336, $CH_3N^+[(C_8H_{17}]_3$, Cl^-, whose chemical formula is given in Table 1, is made up of loose ion pairs where the electrostatic interaction between the ammonium ion and the chloride ion is weak. It plays the following catalysing role: further to an equilibrium exchange of ions with Na^+, OH^-, a new entity is formed $CH_3N^+[(C_8H_{17}]_3$, OH^- in which the electrostatic interactions between positive ions and negative ions are much weaker than is the case with NaOH. Thus, the OH^- ions are more likely available and reactive to attack the ester. Consequently, Aliquat lowers the activation energy of the chemical reaction.

The reactive mixture [methyl benzoate + Aliquat 336 + NaOH]

It has been shown[37,38] that the presence of the R_1 and R_2 groups near the reactive site of the ester can, depending on the nature of the groups, slow down or even inhibit the chemical reaction. The resulting hindrance can efficiently obstruct the approach of the hydroxide ion OH^- to the reactive carbon of the ester. With the relatively unhindered methyl benzoate, the chemical reaction that occurs when the reactive medium is heated at 210°C for 2 minutes, resulting in sodium carboxylate and methanol, gives an efficiency of 90%.

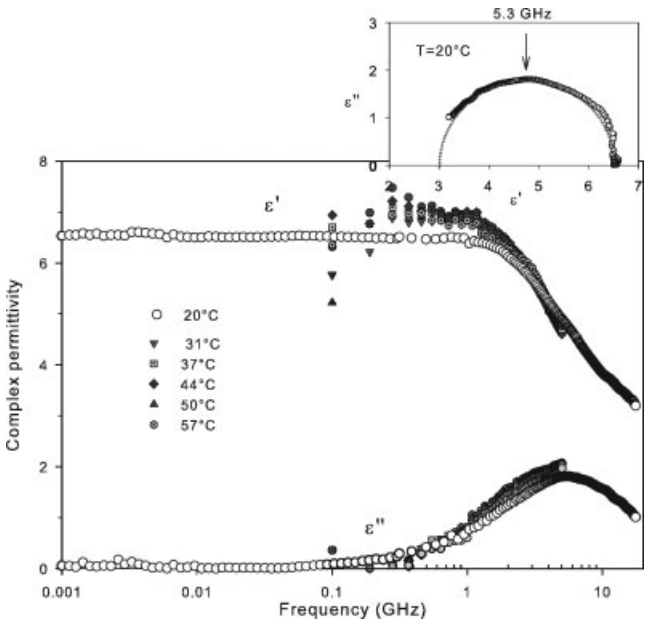


Figure 5. Methyl benzoate complex permittivity as a function of temperature and ambient Argand diagram of methyl benzoate

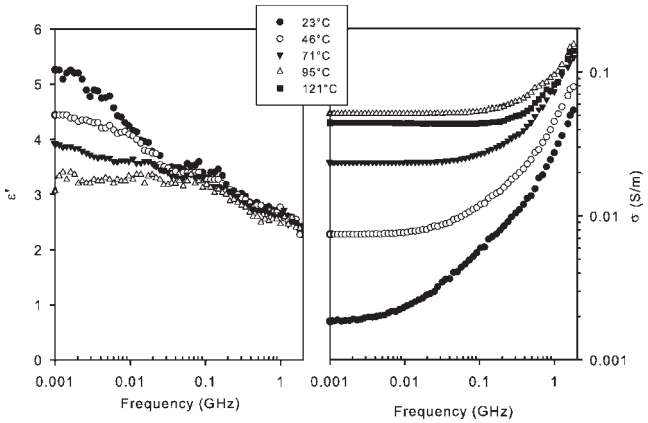


Figure 6. Real permittivity and conductivity of the Aliquot *versus* frequency and temperature

Dielectric characterization during heat treatment from room temperature

Methyl benzoate

We have seen that the carbonyl function (C═O bond) of the methyl benzoate carries the dipole resulting from the molecule. One observes that it induces a phenomenon of dielectric relaxation at microwave frequencies, that is 5.3 GHz in the present case (Fig. 5).

This high frequency is due to the low molar mass of the ester. The Cole–Cole diagram[39] reveals high static permittivity ($\varepsilon_s = 6.5$) and strong polarization ($\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty = 3.5$).

Figure 5 shows the time dependence of permittivity. As expected, the relaxation frequency F_r increases with temperature in accordance with the Arrhenius law,

$$F_r = F_0 \exp\left(\frac{-W_1}{kT}\right) \tag{4}$$

where W_1 is the activation energy of the relaxation phenomenon. This is the height of the potential barrier that the dipoles cross when the medium changes from a polarized state to a depolarized state, which in the present cases equals 3.7 kJ mol^{-1} (0.04 eV).[3] This very low value means that the molecule is highly mobile, particularly due to the absence of H bonds. It increases as a function of the molar mass and the steric effect in the vicinity of the carbonyl dipole of the ester.[3]

Aliquat 336

Unlike the ester, whose dielectric losses are exclusively of dipolar origin, low frequency conductivity phenomena appear (Fig. 6) in the case of the Aliquat, which is the reaction catalyst.

These can be viewed as a phenomenon of free charge conductivity, with the chloride ions (the free charges) moving between quaternary ammonium ions, which are considered as potential wells for the chloride ions. This conductivity phenomenon is intrinsic to Aliquat.

Figure 6 shows that the polarization ε' of the Aliquat diminishes with temperature, while ionic conductivity increases, particularly at low frequencies.

An activation energy obeying Arrhenius law can be associated with this function, which describes the jumps of the chloride ions between the sites of quaternary ammonium ions.

$$\sigma T = A \exp\left(\frac{-W_2}{kT}\right) \tag{5}$$

This energy represents the height of the potential barrier that a chloride ion must cross to break a chloride–ammonium bond, and form a new chloride–ammonium complex. The measured height is 47 kJ mol^{-1}[3]. It is noteworthy that the conductivity decreases as the temperature increases from about 100°C, most probably further to decomposition of Aliquat (elimination of HCl and octane, forming a tertiary amine in a Hoffmann's degradation reaction[40]).

The Aliquat 336 + NaOH mixture

As concerns the mixture [Aliquat + NaOH], another phenomenon appears at the same time, associated with the process of ion exchange between Aliquat and sodium hydroxide, and constitutes step '0' of the ester saponification reaction. It can be noted, as expected, that the static permittivity of the mixture [Aliquat + soda] is higher than that of Aliquat alone.[3] The conductivity of the mixture however is much lower than that of Aliquat alone, which can be explained by the combination of two phenomena. Whatever the molecular system studied, the permittivity and conductivity are measured at constant volume (650 mm^3). From the moment one tests the mixture [Aliquat + NaOH], the concentration of Cl^- ions decreases when the relative quantity of NaOH is increased (r = [NaOH]/[Aliquat]) whereas that of the OH^- ions increases. The first step, which is the activation of the OH^- ions, depends on the number of Cl^- ions. Therefore, when r increases, the conductivity phenomenon decreases. Moreover, there are intermolecular interaction forces between Aliquat and NaOH that make the ion exchanges in the

mixture more difficult. We confirmed that when the proportion of NaOH in the mixture increases for values of *r* varying from 0 to 20, the viscosity increases, which limits the conductivity phenomenon, with conductivity diminishing constantly.[3]

The behaviour of the mixture is identical to that of the Aliquat alone for ratios '*r*' less than 1. For *r* values higher than 1, the polarization ε' increases as does the conductivity. A maximum level of conductivity is reached at around 100°C, whatever the proportion of soda in the mixture. This phenomenon could correspond to the degradation of the Aliquat, already envisaged in the case where it is alone.

In the same way as for Aliquat alone, the conductivity of the mixture follows an Arrhenius law.[3] The activation energy W_3 associated with the phenomena of low-frequency conductivity in the mixture increases with the NaOH proportion. This result tends to show that when the conductivity phenomenon associated with the dissociation of NaOH in the mixture becomes predominant, it leads to an increase in the overall activation energy of the system. We would point out that owing to its corrosive nature, we were unable to carry out an experiment at the ratio $r = 20$, corresponding to the proportions of NaOH and Aliquat used in the reactive mixture.

The reactive mixture [methyl benzoate + Aliquat + NaOH]

Lastly, the characteristic of the overall reactive mixture [methyl benzoate + Aliquat + NaOH] at ambient temperature observed in the same volume of 650 mm^3, is very different of that of the isolated systems we have just described (Fig. 7). The dipolar relaxation of the isolated ester can no longer be observed directly; the actual permittivity and the conductivity are greatly increased at low frequencies compared with those of the mixture [Aliquat + NaOH], whereas the initial concentration in ionic entities in the global mixture is lower in the mixture [Aliquat + NaOH] observed alone in the same volume. We conclude from this that the presence of the ester favours the ionic dissociation even at room temperature, which explains the strong polarization observed.

The proportions of reagents were defined as follows: *n*(sodium hydroxide)/*n*(ester) = 2 and *n*(Aliquat)/*n*(ester) = 1/10, i.e. $r = 20$. The overall volume of the mixture is 650 mm^3.

The following kinetics were adopted to observe the saponification reaction: the duration of the reaction is 110 minutes, with temperature increasing from room temperature to

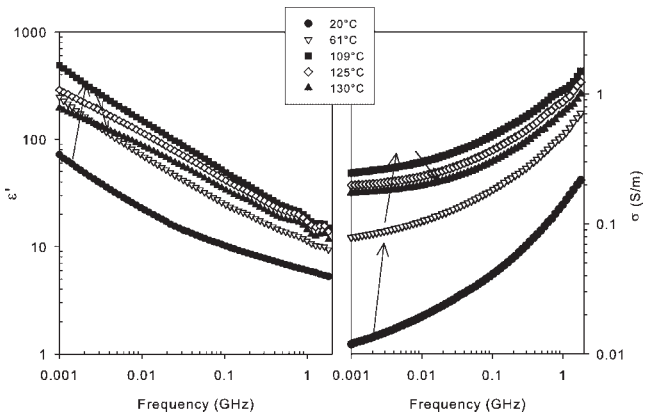


Figure 7. Real permittivity and conductivity of the reactive mixture [methyl benzoate + Aliquot + soda] as a function of temperature

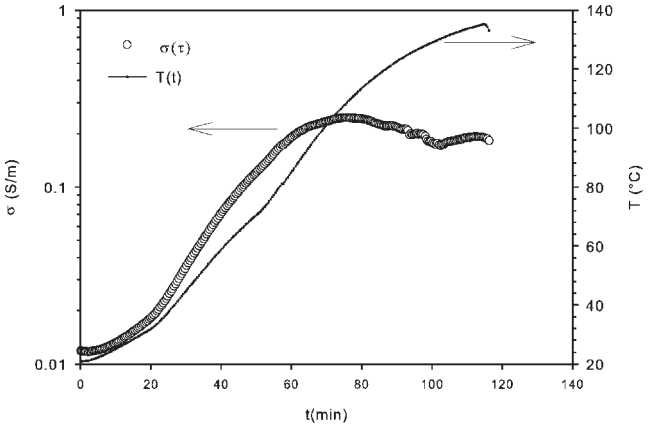


Figure 8. Variation in the conductivity of the reactive mixture [methyl benzoate + Aliquot + soda] and temperature as a function of heating time

130°C at a rate of 1°C $minute^{-1}$. The real and imaginary parts of the total permittivities and the total ionic conductivity increase up to about 110°C, then decrease (Fig. 7). By analogy with Fig. 3 which represents the time dependence of the dipole relaxation frequency during a curing reaction, we have represented the time dependence of the ion conductivity in an experiment of saponification of methyl benzoate (Fig. 8). In a first step, the conductivity increases with the temperature: this is the ion diffusion step. It reaches a maximum then decreases: this is the chemical reaction step, therefore the step of the consumption of sodium ions (NaOH). When it becomes constant, the reaction is finished.

The measured efficiency is 80%, a value similar to that obtained in a conventional system.[4] One considers the saponification of the octyl mesitoate for which the R_1 and R_2 groups are CH_3 and C_8H_{17}, respectively, making the reactive centre a strongly hindered site and giving this ester a higher molar mass than that of methyl benzoate, that is 276 g mol^{-1}. Consequently, it has a lower density (930 kg m^{-3}) and a lower relaxation frequency (923 MHz.). Its Debye moment $\mu = 1.95$ D, its static permittivity $\varepsilon_s = 3.9$, and its polarization $\Delta\varepsilon = \varepsilon_s - \varepsilon_{inf} = 1.2$ are therefore also lower. Its density shows that the concentration in dipoles and ions is lower, therefore the permittivity of the isolated ester is also lower. The activation energy of the reactive mixture of this hindered ester, however, is 28 kJ mol^{-1}, which is lower than that of the methyl benzoate. This tends to prove that the conduction phenomenon associated with the ion exchange between Aliquat and NaOH occurs more easily in the mixture containing the octyl mesitoate than with methyl benzoate. But far fewer ions are concerned and the reaction site is poorly accessible. The chemical efficiencies obtained confirm this hypothesis: under the same experimental conditions, the efficiency obtained for octyl mesitoate is 0%.

Polarization of the reactive site plays a major role. To obtain another evidence of this, we decomposed the dielectric response of the mixture [methyl benzoate + Aliquat + NaOH], that is we discriminated in the reactive mixture the response of the ions at low frequencies (free ions), that of the ion jumps at medium frequencies, and that of the orientation polarization dipole of the ester, i.e. that of the reactive site. We concluded that the overall dipolar moment of the reactive site increases with temperature in the case of low hindrance, indicating high reactivity.[3]

Discussion of the second part

In this second part, we have again demonstrated that spectroscopy at radio and microwave frequencies, coupled with molecular modelling, is a valuable tool for the real-time monitoring of a chemical reaction, and secondly we have tried to predict how the reaction proceeds. Here, we study the saponification of an ester in the presence of a catalyst in the same frequency band; the observation of the absorption due to ionic conductivity phenomena is superimposed on that of orientation polarization. Only a decomposition technique allowing the two phenomena to be discriminated enables the behaviour of the dipole carried by the reactive site to be understood.

CONCLUSION

To conclude, two electric parameters, the dipolar relaxation frequency and the ionic conductivity, are reaction markers of chemical reactions.

Furthermore, it will be possible to compare this process with a microwave heat treatment, as is planned. Dielectric characterization over a wide frequency range is a suitable technique for investigating microwave heat treatment, compatible with heating to frequencies within or beyond the spectrum used.

These combined studies have led to a further study of microwave treatment of the same molecular systems, in which the variation in the dielectric properties were monitored and compared with the results set forth in this paper.[1]

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