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On the use of WLF equation to study resin curing by dielectric spectroscopy

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Abstract

The aim of this study is a new investigation into thermosetting resin cure by dielectric analysis. In a first part, a semi empirical model of cure conversion determination, firstly tested on epoxy systems, is applied to cyanate ester resins. Parameters of the previous equation are adjusted. Secondly, the same equation is improved in a case of non-isothermal conditions. In this aim, a thermal agitation contribution on dielectric signal is studied and modelled by means of a WLF approach. Then, in the last part, we show the possibility and the reliability of a direct WLF use to determine cure conversion. C_1 and C_2 parameters of WLF approach are calculated and compared to literature data. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Dielectric spectroscopy; WLF equation; Cyanate ester resin

1. Introduction

Dielectric spectroscopy has been widely used to study resin curing [1]. Till now, it has been correlated to many others. For instance, in a case of PMR 15 resin, Stephan et al. [2] have shown that their studies indicated that the logarithm of Young modulus measured by dynamic mechanical analysis was proportional to the logarithm of dielectric permittivity all over the reaction time, with a slope of -2. In the same way, Wetton et al. [3] have studied an epoxy system and overlaid a linear relation between dielectric loss factor and torsion loss modulus G''. Carrozzino et al. [4] have correlated dielectric data with differential scanning calorimetry experiments and shown that ratio $\varepsilon''(t)/\varepsilon''(t=0) = 1 - \alpha$, where ε'' is dielectric loss factor and α is the resin conversion. Mathieu [5] has observed a linear relationship between the logarithm of ionic conductivity (σ) of the system and the logarithm of viscosity. The slope of the curve is ranging from -1 to $-0{,}5$ and it depends on the couple epoxy–amine used but not on curing temperature.

These works are some examples concerning extraction of resin curing conversion from dielectric data. They show that these data are strongly linked to usual techniques.

A different way is also investigated by the study of resin relaxation process during cure treatments [6–8]. This approach is a little more difficult to apply than previous ones because of heavy theoretical considerations. Moreover, relaxation processes are sometimes hidden by a strong conductive signal. That is why industrial use is less common. So, in this study, such an approach will not be used.

The purpose of this paper is to extract resin conversion from dielectric data by means of ionic conductivity signal. This has been done first by correlating σ to viscosity. But this correlation is based on a lot of empirical constants [9]. Moreover, on the one hand some viscosity equations have been demonstrated in the literature [10,11]. But on the other hand, those models have a singular point near gel point of resin (where viscosity is divergent); that is why they are but available for a conversion range lower than gel point. About the relation between σ and molecular motion, Deng et al. [12,13] have explored dielectric data to calculate diffusion limitation during cure process. They intend to study gelation of cyanate ester resin. The authors have taken into account that ionic conductivity was linked to molecular mobility and then to diffusional coefficient. They showed that ionic conductivity data could have been used to control limitation process during isothermal cure process and to calculate maximal conversion reached in this case.

In a first part, we have focussed on a semi-empirical approach proposed by Maffezzoli et al. [14]. This equation is based on previous work [15], which links conversion and σ by a simple relation for an epoxy system and under isothermal curing conditions, which is postulated by

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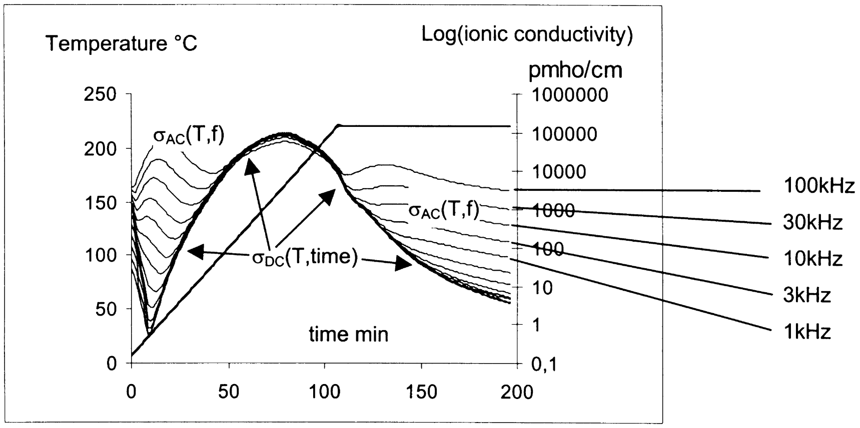

Fig. 1. $\sigma = \sigma_{AC}(T,f) + \sigma_{DC}(T,\text{time}) = \varepsilon_0\varepsilon''\omega$ versus time, temperature and frequency (1/2-decade step, from 100 kHz to 1 Hz).

Maffezzoli as:

$$\alpha = \alpha_{\max}\frac{\log\sigma_0 - \log\sigma}{\log\sigma_0 - \log\sigma_\infty}\left(\frac{\log\sigma_\infty}{\log\sigma}\right)^p \qquad (1)$$

where $\alpha_{\max}$ is conversion at the end of isothermal cure, σ_0 the ionic conductivity (S cm^{-1}) at the beginning of isothermal reaction, σ_∞ the ionic conductivity at the end of isothermal reaction, σ the ionic conductivity measured at time t and p an empirical parameter optimised to 1.75 for epoxy system considered.

We have studied this equation in a case of cyanate ester resin curing, first under isothermal conditions and then under a complete cure cycle. In this process, we have shown the application of Williams Landel Ferry [16] (WLF) equation to describe ionic conductivity evolution versus temperature. In a second part, we have applied the WLF equation directly to ionic conductivity to extract conversion from glass transition temperature calculation.

WLF equation applied to ionic conductivity is given as:

$$\sigma(T) = \sigma(T_0)\exp\frac{C_1(T-T_0)}{C_2+(T-T_0)} \qquad (2)$$

where $\sigma(T)$ is the ionic conductivity at temperature T, T_0 a reference temperature and C_1 and C_2 are two parameters.

2. Experimental

In this study, thermosetting cyanate ester resins (from CIBA: AROCY M: Bis(4-cyanato-3,5-dimethylphenyl)-methane) and AROCY B: 2,2′(4-cyanatophenyl)isopropylidene) are considered. Resins are formulated by using 2 phr of nonylphenol and a catalyst metal, acetylacetonate of chromium(III), corresponding to a metal concentration of 150 ppm.

Dielectric measurements were performed with a DEA 2970 dielectrometer from TA Instruments. A ceramic single surface sensor based on a coplanar interdigitated-comb-like configuration of electrodes was used. This apparatus enabled us to scan the frequency in the range from 1 Hz to 100 kHz in 1/2-decade steps. The principle of this technique consists in placing the sample under an alternative voltage and measuring the resulting current and the phase angle shift induced. The measured current is separated into capacitive and conductive components. An equivalent capacitance and conductance are then calculated and used to determine the dielectric permittivity ε' and dielectric loss factor ε''. ε' is proportional to capacitance and measures the alignment of dipoles. ε'' is proportional to conductance and represents the energy required to align dipoles and move ions.

3. Results and discussion

3.1. Ionic conductivity signal in detail

Ionic conductivity is strongly linked to loss components of dielectric material and deduced from loss factor by a simple relation:

$$\sigma = \varepsilon_0\varepsilon''\omega \qquad (3)$$

where ε_0 is absolute permittivity of free space (8.85×10^{-12} F/m) and ω the pulsation of applied voltage $= 2\pi f.\varepsilon''$ is divided into two components, a dipolar one (relaxation process) and a conductive one. As a consequence of Eq. (3), ionic conductivity σ can be expressed as a sum of two contributions:

$$\sigma(T) = \sigma_{AC}(f,T) + \sigma_{DC}(T) \qquad (4)$$

where σ_{AC} is the alternative component and σ_{DC} the direct current component.σ_{AC} is relative to relaxation process and σ_{DC} is attributed to pure conductive process and is closely linked to viscosity process. As a result, this direct current component σ_{DC} is commonly used to follow resin curing. An example of ionic conductivity signal versus temperature and frequency is illustrated on Fig. 1. Day et al. [17,18] have

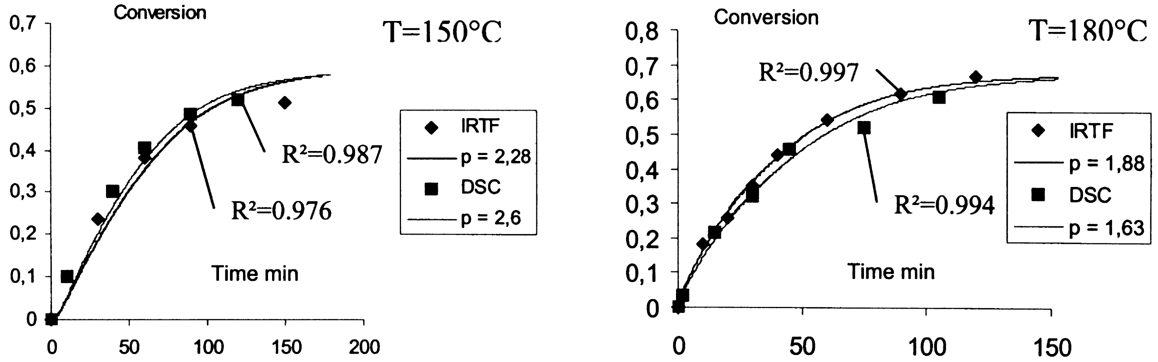

Fig. 2. Evolution of resin (AroCy M30) conversion versus time at two different isothermal curing (150 and 180°C); Effect of analytical technique (FT-IR and DSC) on the value of p coefficient.

developed a simple methodology to extract σ_{DC} form the total σ signal.

All over this study, σ must be considered the DC component of ionic conductivity signal.

To improve this analysis, we must keep in mind that σ_{DC} is linked to sample viscosity. It can be then divided into two different contributions:

- a thermal component, which increases as temperature increases (sample fluidification). This term σ_{th} can be analysed as a thermal agitation contribution on σ;
- a curing component, which increases resin molecular weight and then viscosity. By this way, molecular mobility decreases. This term σ_{cure} leads to a decrease in σ.

In case of isothermal curing, the first term is constant and the second one can be directly deduced form ionic conductivity signal. This will be the aim of the first part of this paper.

In case of non-isothermal treatments, curing reaction can start during the sample heating. In this way, σ evolution is influenced by both σ_{th}, which increases σ, and σ_{cure} and is responsible for σ decrease. As a consequence, it is necessary that one should deconvolute σ_{cure} and σ_{th} form σ signal to extract resin conversion. This will be the aim of the second part.

To go further, we will then show the application of WLF equation to determine resin conversion whatever the cure process applied may be.

4. Application of Maffezzoli equation to cyanate ester system

4.1. Isothermal studies

In the case of previous study [19], we have investigated cyanate ester resin cure kinetics by means of Fourier Transform Infra Red (FT-IR) spectroscopy and DSC. In this part, Maffezzoli equation (1), first developed for epoxy resins, is applied to our cyanate system. In the case of isothermal treatments, results are reported in Figs. 2 and 3. The value of α_{max} used in Eq. (2) is deduced form the evolution of T_g versus α. In the case of cyanate ester resin, Georjon and al [20] have shown that the dependence of T_g versus α was given by a Pascault–Williams equation (5) [21].

$$T_g = T_{g_0} + (T_{g_\infty} - T_{g_0})\frac{\lambda\alpha}{1 + (1 - \lambda)\alpha} \tag{5}$$

where λ is a parameter deduced from calorimetric data (heat capacity jump) $\lambda = 0.29$; T_{g_0} is glass transition temperature for $\alpha = 0$; $T_{g_0} = 26.5°\text{C}$; T_{g_∞} is glass transition temperature for $\alpha = 1$; $T_{g_\infty} = 293°\text{C}$.

Parameters of this relation have been calculated in a previous work [19] and compared to literature data. We consider [12] that reaction is nearly stopped when:

$$T_{g_{sample}} = T_{isothermal\ curing} - 50°\text{C} \tag{6}$$

α_{max} is deduced from Eq. (5) when $T_g(\alpha_{max}) = T_{g_{sample}}$. Then, parameter p is optimised to fit dielectric data and experimental data. Results obtained from FT-IR and DSC data and their influence on parameter p are reported in Table 1. We can observe that the value of p is nearly constant for our cyanate systems. It can be evaluated to be about 2.1 ± 0.3. This value is close to the parameter p obtained in case of epoxy system, 1.75 ± 0.1. As a conclusion, one can mention

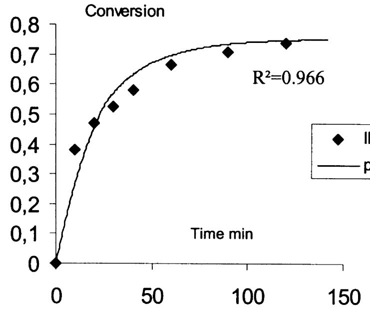

Fig. 3. Isothermal curing of AroCy B30 resin at 180°C. Data are obtained by FT-IR measurements.

Table 1
Value of p parameter versus resin nature, temperature of isothermal cure and analytical technique. R^2 is the correlation coefficient between experimental and fitted data

Curing	AroCy M30			AroCy B30	
	α_{max}	p (IRTF)/R^2	p (DSC)/R^2	α_{max}	p (IRTF)/R^2
150°C	0.58	2.28/0.976	2.59/0.987		
180°C	0.68	1.88/0.997	1.63/0.994	0.74	2.1/0.966

that Maffezzoli equation can be used to study cyanate system curing.

4.2. Non-isothermal treatments

4.2.1. Problem positioning

In case of isothermal treatment, a plot of σ versus time is reported in Fig. 4. The value of σ_0, which represents the value of σ at the beginning of isotherm, can be considered a baseline of σ from which resin conversion is calculated. As regards previous considerations, σ_0 can be considered the contribution of thermal agitation on σ since no cure phenomenon has occurred at the beginning: up to initial time, σ is only governed by temperature and then thermal agitation. With these assumptions, we can substitute σ_0 in Eq. (1) by σ_{th} introduced before. Then, during a whole temperature cycle, σ will be integrated not from a constant value σ_0 but from a temperature-dependent baseline represented by σ_{th}.

σ profile is plotted in Fig. 5, in a case of a non-isothermal cure process. One may observe that σ starts decreasing while temperature is still increasing. This means that cure process takes place during heating process. Then, by the same time, sample is heated (viscosity increases) and the cure process has begun (viscosity decreases). The competition between these two phenomena make it necessary to "substract" σ_{th} contribution from total signal to be able to determine the resin conversion and the temperature of the beginning of cure.

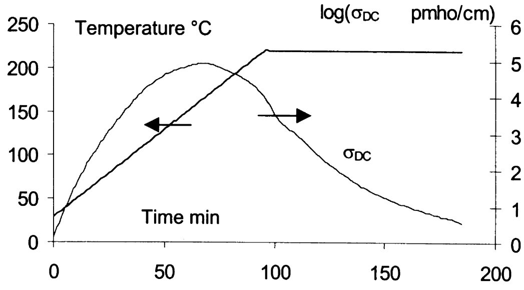

Fig. 5. Evolution of σ_{DC} versus time and temperature.

4.2.2. Thermal component of σ

As mentioned before, thermal contribution on ionic conductivity results from thermal agitation and is only temperature dependent. Then, by considering that σ_{th} is driven by viscosity of the medium, the WLF equation (2) has been used to describe σ_{th} evolution versus temperature. WLF equation is based on the semi-empirical Doolittle [22] equation, initially developed to describe liquid viscosity temperature behaviour. That is, by considering a possible relation between σ_{th} and viscosity, Sheppard et al. [23] have verified that σ_{th} evolution versus temperature was driven by a WLF equation. With this in mind, they have tested several epoxy systems and shown that $\sigma_{th}(T)$ could be expressed by a WLF equation on a range of a large scale of molecular weight.

To determine the C_1 and C_2 coefficients of the WLF equation, we plot $(T - T_0)/\log(\sigma/\sigma(T_0))$ versus $T - T_0$, as reported in Fig. 6. Since thermal agitation is the only phenomenon required, it is necessary that one should consider a σ region where the signal is not strongly influenced by curing. So the plot must be considered during the temperature ramp when curing has not yet begun. This σ area can be easily determined since the beginning of curing is observed when experimental data diverge from linear interpolation as showed in Fig. 6. Moreover, this plot presents the advantage to show the temperature of the beginning of cure (same value as measured by DSC at 2 K/min). Fig. 6 is an experimental representation of all of those considerations.

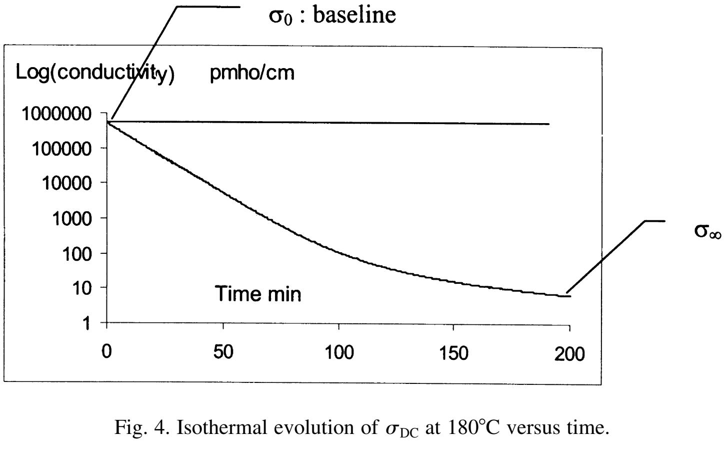

Fig. 4. Isothermal evolution of σ_{DC} at 180°C versus time.

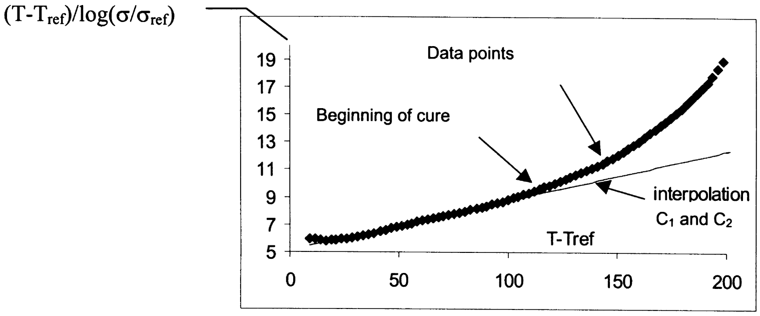

Fig. 6. Determination of C_1 and C_2 coefficient and temperature of beginning of cure.

In case of an AroCy M30 resin, reference temperature T_0 is taken as $T_g(\alpha = 0) = T_{g_0} = 26.5°C$. $\sigma(T_{g_0})$ is measured to be 0.558 pmho/cm. It is calculated experimentally: $C_1 = 10$ and $C_2 = 103.6$ K. We may postulate that C_1 and C_2 are constant all over reaction because they are representative of the thermal contribution, which is the same during curing. In Fig. 7, σ_{DC} and σ_{th} are then plotted versus time and temperature. σ_{th} increases as temperature increases and σ_{th} remains constant under isothermal conditions. Then, it is possible to measure the temperature when cure reaction begins, when σ_{th} does not recover σ_{DC} any more.

4.2.3. Experimental results

In the case of non-isothermal curing, Maffezzoli equation can be written as Eq. (7) by substituting σ_0 by σ_{th}, as demonstrated before. In other words, Eq. (7) represents the deconvolution between σ_{th} and σ_{DC}, and then between σ_{cure} and conversion:

$$\alpha = \alpha_{max} \frac{\log \sigma_{th}(T) - \log \sigma}{\log \sigma_{th}(T) - \log \sigma_\infty} \left(\frac{\log \sigma_\infty}{\log \sigma} \right)^p \qquad (7)$$

These results have been compared to experimental DSC data. Sample is heated at 2 K/min from room temperature to 350°C. Conversion is deduced from integration of the exothermic peak up to 220°C. Data are then compared to the model. Parameter p of Maffezzoli equation is taken equal to 2.1 as obtained before. The α_{max} value is taken to be 0.89 because it corresponds to value of conversion at infinite time at 220°C (calculations given by relation (6)). Fig. 8 shows good agreement between DSC data and dielectric considerations. Eq. (7) gives rise to the same temperature cure start and conversion value.

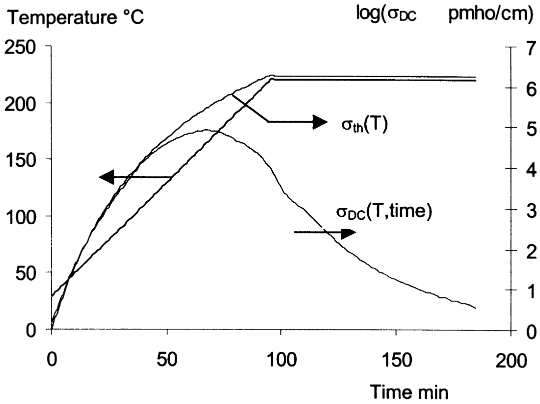

Fig. 7. Evolution of σ_{DC} versus time and temperature superimposed on $\sigma_{th}(T)$ evolution.

Dielectric data have been compared in a last step to kinetic model obtained in previous work [19]. Kinetics data were fitted by a model developed by Stutz et al. [24,25] in a case of cyanate thermosetting system. An excellent correlation is observed in Fig. 9.

As a conclusion, we have shown in this part that:

- Maffezzoli equation (1) first developed to study epoxy resin curing is still applicable in the case of cyanate ester resin;
- value of parameter p has been calculated for cyanate ester system;
- Maffezzoli equation (7) with thermal agitation correction is a good mean to study resin curing all over cure cycle. The temperature of the beginning of the reaction can be obtained in the same time;
- the use of WLF equation (2) to determine resin thermal agitation contribution on ionic conductivity signal is demonstrated.

The last part of this study will consist in exploring the WLF equation to determine directly the conversion without any empirical equation.

5. On the use of WLF equation

5.1. Problem position

In this last part, the WLF equation (Eq. (2)) is used to calculate cyanate ester system conversion versus cure process. This approach was introduced by Senturia et al. [1]. It consists in substituting T_0 in Eq. (2) by $T_g(\alpha)$. In other words, conversion could be extracted from ionic conductivity data by means of a T_g calculation. As mentioned before, T_g of a thermosetting system is representative of the degree of cure. In the case of cyanate ester

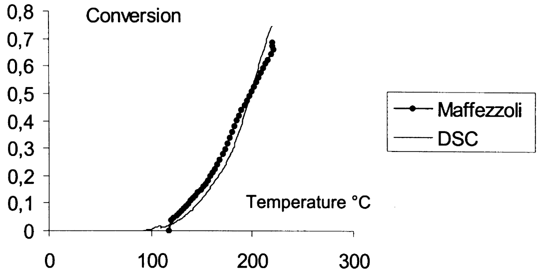

Fig. 8. Comparison between DSC data and conversion extracted from Eq. (7).

resin, Eq. (5) has been demonstrated to be a good relation to describe T_g evolution versus conversion.

The aim of this part is to show that WLF equation is applicable in a case of cyanate ester resin cure description as it has been shown for epoxy system. The form of WLF equation used in this study is written as:

$$\log\left(\frac{\sigma}{\sigma_0}\right) = \frac{C_1(T - T_g(\alpha))}{C_2 + (T - T_g(\alpha))} \tag{8}$$

where α_0 is ionic conductivity reference taken at $T_g = T_{g_0}$.

With such considerations and previous remarks, conversion is deduced from Eq. (8) by use of two simple mathematical calculations: first $T_g(\alpha)$ is extracted (Eq. (9)) and then α is calculated by reversing Eq. (5) (Eq. 10):

$$T_g = T - \frac{C_2}{\dfrac{C_1}{\log\left(\dfrac{\sigma}{\sigma_0}\right)} - 1} = \frac{C_1 T - \log\left(\dfrac{\sigma}{\sigma_0}\right)(C_2 + T)}{C_1 - \log\left(\dfrac{\sigma}{\sigma_0}\right)} \tag{9}$$

$$\alpha = \frac{1}{1 + \lambda\dfrac{(T_{g\infty} - T_g)}{(T_g - T_{g_0})}} \tag{10}$$

The difficulty consists here in the determination of C_1 and C_2 as well as their behaviour during cure process.

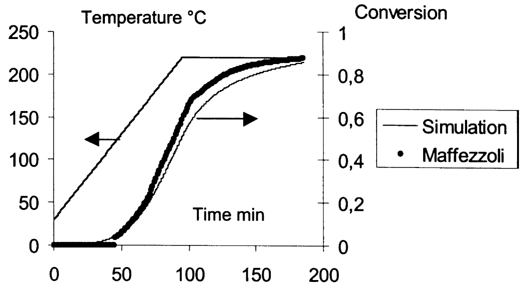

Fig. 9. Comparison of dielectric data (Eq. (7)) and Stutz model for cyanate ester curing.

Table 2
Calculations of C_1 and C_2 WLF parameters, directly from σ_{DC} measurements: calculation method 1. R^2 is the correlation coefficient obtained between linear fit and experimental data by plotting $(T - T_{ref})/\log(\sigma/\sigma(T_{ref}))$ versus $T - T_{ref}$

$T_{ref} = T_g$ in °C	C_1	C_2 (K)	R^2
26	10	103	0.995
71	9.8	125	0.973
151	10.5	240	0.952
160	10	210	0.852
195	10.8	298	0.861

5.2. C_1 and C_2 determination

Experimental determination of C_1 and C_2 have been investigated by two different ways.

5.2.1. Method 1

In a first approach, samples have been cured at different states, by isothermal full time treatments. Conversion value depends on cure cycle. It has been determined using Eq. (6). After cooling those partially cured samples, a second temperature scan is used to record σ versus temperature. Then, as described before, σ_{DC} is extracted from the whole σ measurement and its WLF evolution is extrapolated. In each case, C_1 and C_2 are determined by taking T_g at its corresponding conversion in comparison with the reference temperature. Experimental data are reported in Table 2. Results show that parameter C_1 remains constant whatever the conversion may be whereas parameter C_2 is an increasing function of the temperature. Parameter C_1 is measured to about 10.2 ± 0.4. It is on the order of magnitude of value reported for epoxy system. That is, this constant C_1 value has been already observed by Sheppard [23]. This observation is explained as follows. The simple free volume model of Cohen and Turnbull [26] suggests that C_1 is directly proportional to a critical volume for transport indicating that the critical free volume for ion transport is independent of the resin cure conversion. Based on this idea, C_1 is constant because of the small size of ionic charge carriers in the resin in comparison with the resin molecules size. In other words, mobility of ionic charge carriers is not affected by crosslink density and then by curing.

5.2.2. Method 2

According to these results and to go further into C_2 determination, a second way of investigation has been engaged. In this approach, we have crosslinked directly ionic conductivity data and previous kinetics determination. The stress have been put on FT-IR data, since it has been shown that DSC data leads to same kinetics results. In order to compare data, only isothermal conditions are considered. FT-IR conversion data are transformed into $T_g(\alpha)$ data (by use of Eq. (5)). T_g is recorded versus time of treatment under given isothermal conditions. The experiment is carried out in the same conditions and during the same time but the parameter

Table 3
Extrapolation of C_2 value obtained from isothermal treatments. Calculation method 2: C^2 is directly calculated from FTIR and dielectric data

Isotherm 150°C		Isotherm 180°C	
T_g (°C)	C_2 (K)	T_g (°C)	C_2 (K)
26	112	26	102
47.7	117	42	111
66.3	125	50.7	122
78.5	144	62.	130
88.5	201	75.9	134
		93.8	154
		111.8	198
		124.9	239

Table 4
Parameters of linear interpolation of C_2 versus $T_{cure} - T_g$, in each evolution area. R^2 is the correlation coefficient between experimental and fitted data

	Area 1	Area 2
M	318	152
N	−2.13	−0.28
R^2	0.88	0.7

C_2 of WLF equation is now calculated from ionic conductivity data so that T_g extrapolated from Eq. (9) should be equal to T_g obtained by FT-IR. By this way, C_2 values are collected and recorded versus T_g. The parameter C_1 is kept as 10.2 with regard to method 1 results.

Then, Table 3 reports values of C_2 calculations versus T_g for two different isothermal treatments. As a first remark, values of C_2 measured by this method are nearly the same as those obtained using the first approach. This remark is illustrated in Fig. 10 where C_2 is plotted versus difference $T_{cure} - T_g$. The legend "deduced from σ" refers to data calculated using method 1. On the other side, experimental data "iso X°C" refers to method 2. C_2 is deduced from isothermal curing at X°C.

For the end of paper, T_{cure} is noted T_c. We can go further and divide this evolution into two different areas. The first one is delimited by $T_c - T_g < 90°C$, and the second one is used for higher temperatures. In the first part $T_c - T_g$ is low which means that T_g is near T_c and then conversion is high. In this case, C_2 evolution is fast. On the contrary, for $T_c - T_g$ high, i.e. at low conversion, C_2 evolution is slow.

C_2 evolution have been then modelled by two linear areas as mentioned by Eq. (11):

$$C_2 = M_i + N_i(T_C - T_g) \tag{11}$$

where M and N are, respectively, the intercept and the slope of the linear interpolation, and i refers to areas 1 and 2. Table 4 reports the values calculated. For isothermal curing below 180 and 150°C, kinetic results are plotted by considering C_2 evolution mentioned before and the results are compared with FT-IR data. As expected, an excellent agreement is observed. But more important, we can remark that C_2 evolution leads to two different kinetic stages. For low conversion, or $T_c - T_g > 90°C$, the system is under kinetic limitations. On the contrary, for higher degree of cure, kinetic speed is lowered and C_2 evolution takes into account the diffusional limitations. Moreover, concerning cyanate ester system, Deng [12] reported that the change from kinetic limitation to diffusional influence occurs at about 40% conversion. This is well represented on Fig. 11; a signal break is observed when C_2 evolution is modified at nearly 40% conversion. This means that C_2 evolution extracted form WLF equation is an important parameter and closely linked to kinetics of curing. That is $T_c - T_g = 90°C$, overlaid clearly by C_2 plot, can be interpreted as the temperature when diffusional limitation becomes more important. This value of 90°C is more important than the difference temperature of the end of reaction mentioned before in Eq. (6). Those results are not contradictory since $T - T_g = 50°C$ refers to the end of reaction whereas $T - T_g = 90°C$ is attributed to the beginning of diffusional limitation during curing. In the case of Fig. 10, two linear fits are preferred to a smooth curve in order to highlight kinetic phenomena. The asymptotic scheme used in Fig. 10 shows and demonstrates the different mechanisms that influence and govern curing molecular process.

As a conclusion, this consideration could validate this WLF approach since C_2 parameter could be correlated to previous results and to some physical curing phenomena.

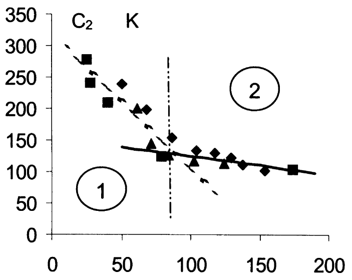

Fig. 10. Evolution of C_2 versus $T_{cure} - T_g$, obtained under different conditions. Legend "deduced from σ" refers to calculation method 1. Legend "iso X°C" refers to calculation method 2.

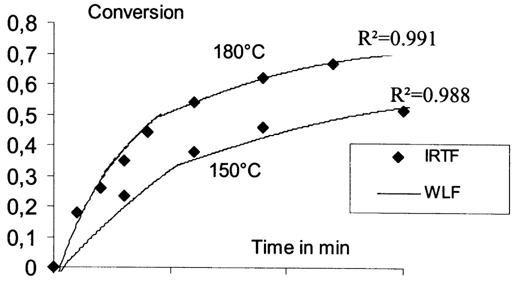

Fig. 11. Comparison between experimental IRTF data and dielectric data by using the C_2 two-step evolution.

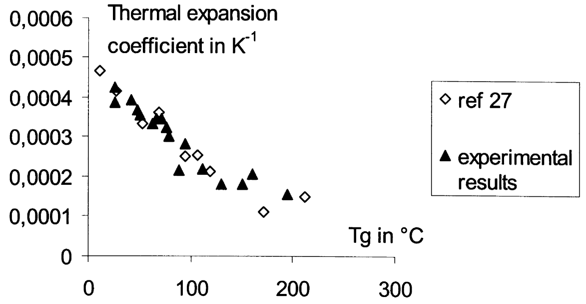

Fig. 12. Evolution of thermal expansion coefficient versus T_g obtained by Ref. [27] and by dielectric analysis (Eq. (13)).

5.2.3. Crosslink between C_2 and mechanical properties

To go further and to conclude this study, we have plotted the inverse of C_2 parameter versus T_g. According to WLF theory, C_1 and C_2 parameters are explained as follows:

$$C_1 = B/2.303f_0 \qquad C_2 = f_0/\delta \tag{12}$$

where B is a coefficient $= 1$, f_0 a fraction of free volume taken in the reference state at $T = T_{\mathrm{ref}}$, and δ is thermal expansion coefficient of the matrix. Then, from Eq. (12), it can be deduced that

$$\delta = B/(2.303C_1C_2) \tag{13}$$

Eq. (13) has been plotted versus T_g in Fig. 12. We can observe that δ decreases when T_g increases. Moreover, values reported by δ plot agree with values reported in literature data [27]. This evolution is linked to a decrease in free volume measured at low temperature near to the room temperature. This observation is characteristic of cyanate ester system and it has been mentioned recently by Hayashi [28].

By this way, it is shown that parameter C_2, obtained from a WLF exploration of ionic conductivity data, can be linked to mechanical properties and thermal expansion of matrix.

6. Conclusions

In this study, we have shown how to use the WLF approach to determine conversion during resin curing. This equation can be used either included in a semi-empirical equation as a thermal contribution on ionic conductivity signal or directly by means of T_g calculation. Those two approaches have been validated first by crosslinking data with more conventional techniques such as FT-IR and DSC. The direct WLF extraction of conversion has been realised thanks to a good correlation with literature data. For instance, C_1 parameter has been demonstrated to be constant and equal to about 10.2.

In the same way, C_2 evolution has been correlated to kinetics of cure and to mechanical properties of the matrix.

To go further in this study, $\sigma(T)$ described by WLF equation should be linked to the viscosity evolution of the sample during cure process. That is, $\sigma(T)$ could give a relative evolution of resin viscosity. Then, this kind of dielectric approach could lead to a dual information, both on conversion and viscosity, using a single measurement. It may represent an important information in order to choose cure process and, moreover, to optimise some cure cycle and resin moulding (choice of temperature of injection, time for moulding at T).

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