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Evolution of the coefficient of thermal expansion of a thermosetting polymer during cure reaction

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Abstract

The evolution of the coefficient of thermal expansion (CTE) of a thermosetting polymer during cure reaction is an important parameter for industrial applications such as composite processing since it influences the development of internal stresses in the material. The CTE being almost impossible to measure on a reacting thermoset, we propose to use an indirect method based on the modelling of ionic conductivity by a modified WLF equation, allowing to calculate the evolution of CTE from dielectric spectroscopy measurements. This method is applied to a dicyanate ester thermosetting polymer, leading to encouraging results both qualitatively and quantitatively.

Keywords: Dielectric spectroscopy; Thermoset; Thermal expansion

1. Introduction

The conditions of thermosetting polymers network formation have huge influence on final material properties. Therefore, the cure reactions of such systems have been studied extensively as well as the evolution of rheological properties [1,2].

Nevertheless, the evolution of other important properties such as the specific volume (m^3/kg) or the coefficient of thermal expansion (CTE) during the cure reaction, have been less studied [3–6]. During its three-dimensional polymerization, a thermosetting polymer undergoes an important volumetric shrinkage due to the formation of covalent bond between initially small molecules, leading to a solid network. This shrinkage is responsible for various problems in industrial applications, particularly in composites: As the fillers generally show no shrinkage, and due to the different thermal expansions of the matrix and the fillers, this leads to internal stresses in the material.

Both specific volume and CTE are difficult properties to measure on a reacting sample, especially for cure reactions which are in general highly exothermic. Two recent works [4–6] have been dedicated to the experimental study and the modelling of these properties during cure reaction. Nevertheless, while the specific volume could be measured during cure reaction in both cases, the CTE evolution during cure could only be estimated either by a linear interpolation between uncured and fully cured samples measured values [6], or by physical modelling, also based on the CTE values of uncured and fully cured samples [4,5].

In the present work, we propose to explore the possibility of estimating the CTE evolution during cure reaction experimentally. The method used involves dielectric spectroscopy measurements and is inspired by a recent paper by Bartolomeo et al. [7]. The estimation of the CTE from these measurements relies on the modelling of the ionic conductivity of the thermoset by a modified William Landel Ferry equation (WLF):

$$\log \sigma(\alpha, T) = \log \sigma_0 + \frac{C_1(T - T_g(\alpha))}{C_2 + (T - T_g(\alpha))} \tag{1}$$

where

- σ is ionic conductivity and depends on the two state variables defining thermosetting system during cure:

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Temperature (T) and degree of cure (α);
- σ_0 is the ionic conductivity of initial monomer ($\alpha = \alpha_0$) at initial glass transition temperature ($T_g = T_{g0}$);
- $T_g(\alpha)$ is the glass transition temperature.

The idea of using such an equation actually comes from the relation between ionic conductivity and viscosity, through the Stoke's law ($\sigma \propto \eta^{-1}$), in which ionic species are considered as rigid spheres moving through the liquid monomer(s). Part of the present work was dedicated to the study of the correlation between ionic conductivity and viscosity before cure reaction.

The two coefficients C_1 and C_2 are 'physical properties', given by the free volume theory:

$$C_1 = \frac{B}{f_g} \approx \frac{1}{f_g} \tag{2}$$

where f_g is the free volume fraction at T_g and B is a parameter close to 1, C_1 being proportional to the critical volume for transport (here it is the transport of ionic species responsible for ionic conductivity).

$$C_2 = \frac{f_g}{\delta} \tag{3}$$

where δ is the coefficient of thermal expansion (CTE) above T_g.

Consequently, knowing C_1 and C_2, it becomes possible to calculate the CTE:

$$\delta = \frac{1}{C_1 C_2} \tag{4}$$

In their paper, Bartolomeo et al. [7] fitted Eq. (1) to ionic conductivity before and during cure reaction, for a dicyanate ester thermoset. They observed that adjusted coefficient C_1 was always constant, whereas coefficient C_2 strongly varied with cure reaction. They deduced from this result that the mobility of ionic charges responsible for ionic conductivity is not affected by the cure reaction in this kind of polymer, because these ionic species (supposed to be residues of catalysts used for the elaboration of cyanate ester monomers) are much smaller than the monomers, dimers,… So that finally, the evolution of C_2 reflects only the evolution of the CTE δ.

All the experiments performed by Bartolomeo et al. were in isothermal cure conditions below the $T_{g\infty}$ of the network (more exactly a temperature scanning from 25 °C to a defined cure temperature, followed by an isotherm at this cure temperature, this procedure allowing them to correctly follow the thermal history of the sample, which they use to calculate the evolution of the cure degree α thanks to a kinetic model previously determined). As a consequence, the curing reaction was always incomplete due to the vitrification of the samples.

In the present work, we propose to use the same approach, but in temperature scanning experiment from 25 °C to temperatures above the glass transition temperature $T_{g\infty}$ of the fully cured network. Such experiments will thus allow us to investigate the evolution of the thermosetting system CTE δ during all the cure reaction. In parallel, the CTE of both initial monomers and fully cured network will be measured experimentally in order to compare them with calculated values.

2. Experimental section

2.1. Reagents

Cyanate ester thermoset (1,1-bis(4-cyanatophenol) ethane) (Fig. 1) was supplied by Ciba–Geigy under the trade name LECY. It contains about 1% impurity (monophenol–monocyanate and *ortho–para* substituted isomers). The main interest of using this monomer is that it is a low viscosity liquid at room temperature, allowing very good wetting contact when placed in DSC crucibles or on dielectric sensors (see below). Several studies have been devoted to the analysis of reaction mechanisms of cyanate esters. It appears that the major reaction pathway is a thermally activated step-growth polycyclotrimerization that gives birth to a highly crosslinked polycyanurate network (Fig. 1). An analysis by SEC shows that the phenol impurities initially present in LECY induced in our lot a conversion of 5%. No catalytic agent was used in our experiments.

Another interest of cyanate esters lies in the fact that the polymerization reaction theoretically does not involve proton transfers, which implies that the concentration of ionic species (impurities) will remain constant during the cure reaction. The evolution of ionic conductivity should therefore be only related to the mobility of these ionic species.

2.2. Rheological measurements

In order to study the correlation relation between ionic conductivity and viscosity of the unreacted monomer, rheological measurements were performed on a rotational rheometer (Rheometrics RSA II) with a cone plate geometry, in steady state conditions (10–100 s^{-1}) and for temperatures ranging from 25 to 120 °C. In order to avoid any influence of the cure reaction, the rheometer was pre-heated at the desired temperature, before the introduction of

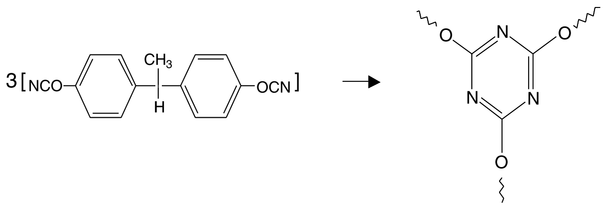

Fig. 1. Monomer used and cyclotrimerization of cyanate esters.

the sample, after which the viscosity measurement was done in less than 3 min.

2.3. Dielectric spectroscopy experiments

A dielectric spectrometer (DEA 2970—TA-Instruments) allowing to work in well controlled temperature scanning conditions was used. Interdigitated sensors on ceramic substrate were used, the liquid thermosetting systems being easily deposed on it as a wetting film ($e < 0.5$ mm). The dielectric response was measured over a large frequency range (0.1 Hz–100 kHz), during temperature scanning experiments from 25 to 350 °C at three different heating rates 1, 2 and 4 K/min.

When an alternative tension is applied to a thermosetting polymer placed between the electrodes of a condenser (here between the digits of the sensor), the corresponding current has two parts: One which is in phase with applied tension and another loss part. This phenomenon is due to a complex permittivity of the polymer:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \tag{5}$$

where ε' and ε'' are called the capacitive component (or permittivity) and the conductive (loss factor) component, respectively.

This effect is attributed to, on the one hand dipolar orientation phenomena inside the material, and on the other hand to a leak current due to the movement of ionic impurities present in the polymer material (which is theoretically an insulator). As a consequence, these dielectric spectroscopy measurements can be directly related to ionic mobility though the calculation of ionic conductivity σ:

$$\sigma = \omega\varepsilon_0\varepsilon'' \tag{6}$$

where ω is the applied pulsation frequency and ε_0 the permittivity of vacuum.

2.4. Differential scanning calorimetry experiments

A Perkin–Elmer DSC 7, with temperature modulation option was used under nitrogen atmosphere, for all experiments. Perkin–Elmer interface and Pyris software enable online PC control of measurements. The latter is also used for the processing of TM-DSC curve deconvolution. Apparatus calibration is done with indium and zinc standards for temperature and indium for heat flow. Sampling rate is 1 point/s. Typical sample mass is about 10 mg. Experiments are performed with aluminium pans. For each temperature program, two measurements were made: One with the sample and one with an empty pan. The signal obtained for the empty pan is then subtracted from that of the pan containing the sample, so that the resulting signal reflects only the thermal behaviour of the thermoset sample.

As explained in details in an earlier paper [8], using TM-DSC for studying the cure reaction of a thermosetting polymer has two main interests:

- First, it allows to directly access the rate of heat release by cure reaction, and thus the reaction rate by normalisation as well as the cure degree by integrating reaction rate.
- Second, it permits the measurement of heat capacity evolution during cure reaction which allows to detect possible vitrification (glass transition) of the material.

Two series of experiments were performed:

- Temperature scanning experiments were done in the same conditions as dielectric spectroscopy measurements (temperature scanning from 25 to 350 °C at three different heating rates 1, 2 and 4 K/min). The temperature modulation used was a saw tooth with an amplitude of 0.75 °C and a period of 60 s. As shown in an earlier paper [8], such optimized modulation does not affect cure reaction and allows correct calculation of both heat capacity and heat release rate by the apparatus. The purpose of this first series of experiments was to determine, with the highest precision, the evolution of the degree of cure during Dielectric Spectroscopy experiments described above.
- In parallel the evolution of the glass transition temperature of the thermosetting system was determined as a function of cure degree. The method used has been described elsewhere [9]: First a sample of thermosetting polymer is studied in DSC in order to determine the initial glass transition temperature and the total heat of reaction by integration of the exothermal peak. Secondly, a series of samples are partially cured in an oven or an oil bath in order to reach different degrees of cure. Each sample is then studied in DSC in order to measure its glass transition temperature and the residual heat of reaction. The degree of cure of the sample is then given by:

$$\alpha = 1 - \frac{\Delta H_{\text{residual}}}{\Delta H_{\text{total}}} \tag{7}$$

The results of these two series of experiments will allow us to predict, at each moment (time, temperature) of dielectric spectroscopy temperature scanning experiments, both the degree of cure α and the glass transition temperature $T_g(\alpha)$ of the thermoset, which will be used for the modelling of ionic conductivity by Eq. (1).

2.5. CTE measurements

The volumetric CTE of liquid monomer was measured using a 50 cm^3 volumetric flask. This was filled with 50 cm^3 of monomer at 20 °C and then placed in a temperature

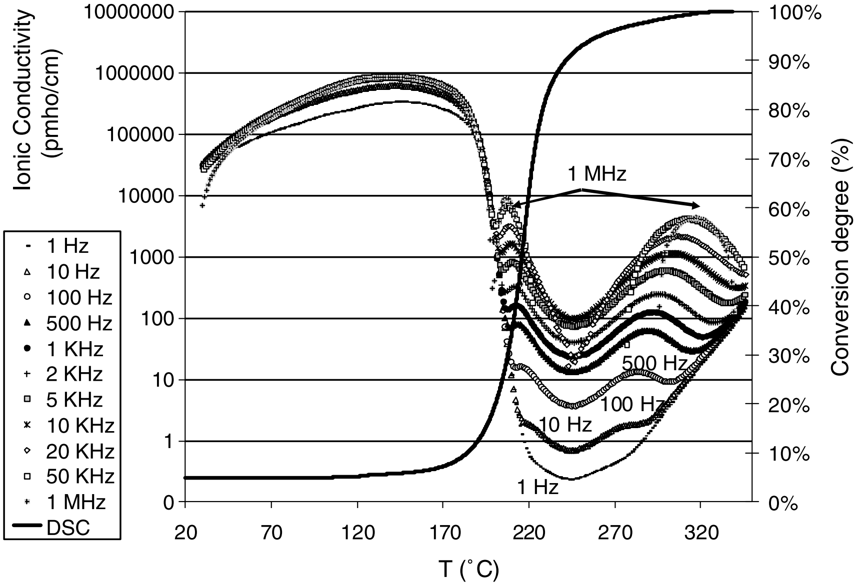

Fig. 2. Evolution of ionic conductivity and conversion degree for a temperature scanning experiment at 1 K/min.

regulated oven at temperature at higher temperatures (from 25 to 80 °C). The evolution of the liquid level in the cylindrical neck of the flask allowed to evaluate the expansion of the liquid. In this measurement, the thermal expansion of the boron silicate glass flask can be neglected as its extremely low (typically 6 ppm) when compared to that of a liquid (typically 100–1000 ppm).

The linear CTE of fully cured thermoset was measured using a SETARAM TMA92 apparatus with a 12 mm high, 10 mm diameter cylindrical sample, from 50 to 350 °C. The average linear CTE was calculated for both vitreous and rubbery states. These coefficients were multiplied by a factor 3 in order to estimate the volumetric CTEs. The fully cured sample used was obtained from the following cure cycle (1 h at 75 °C; 1 h at 125 °C; 1 h at 175 °C; 1 h at 225 °C; 1 h at 275 °C and 1 h at 325 °C).

3. Results and discussion

3.1. Dielectric spectroscopy and TM-DSC

Figs. 2 and 3 show the evolution of ionic conductivity σ (calculated using Eq. (6)) obtained for a temperature scanning rate of 1 K/min. As a comparison, the evolution of conversion degree α and heat capacity C_p obtained from TM-DSC are plotted on the two figures, respectively.

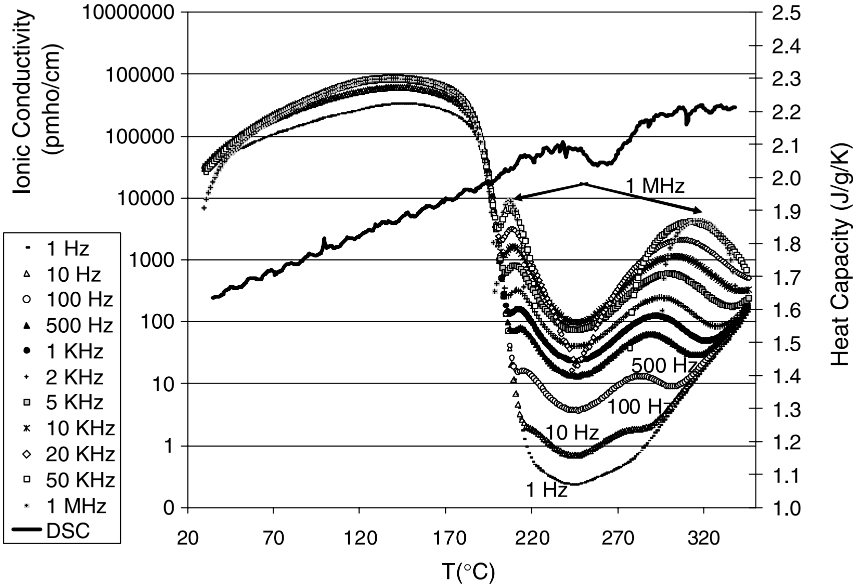

Fig. 3. Evolution of ionic conductivity and heat capacity for a temperature scanning experiment at 1 K/min.

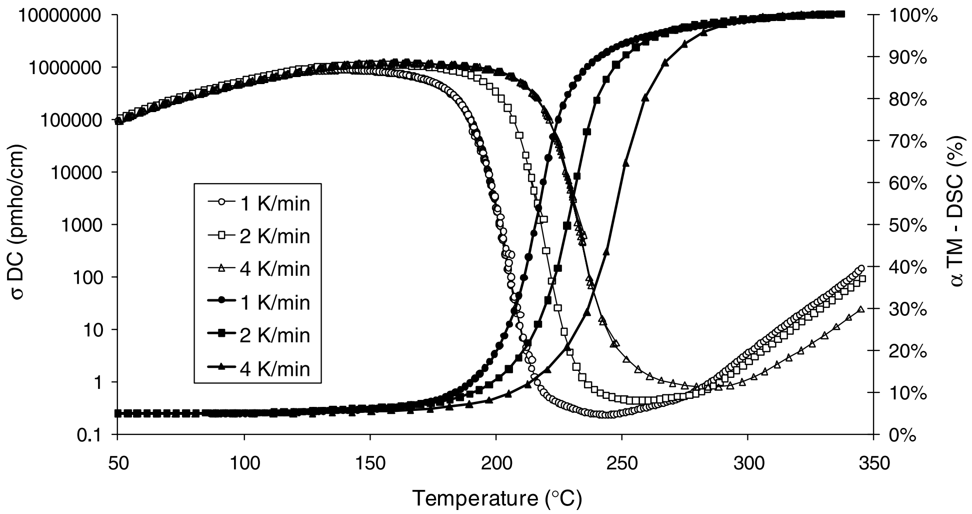

Fig. 4. Purely conductive part of ionic conductivity (unfilled symbols) for the three different heating rates and corresponding evolutions of cure degree (filled symbols).

In the case of a thermosetting polymer, ionic conductivity is a function of frequency pulsation ω, temperature T and cure degree α:

$$\sigma(\omega, T, \alpha) = \sigma_{\mathrm{Dc}}(T, \alpha) + \sigma_{\mathrm{Ac}}(\omega, T, \alpha) \tag{8}$$

where σ_{Dc} is the contribution of purely conductive phenomena (frequency independent) and σ_{Ac} is the dipolar contribution, related to relaxation phenomena such as the glass transition. In reality, σ_{Dc} is not completely independent form frequency due to electrode's polarisation. Nevertheless, at sufficiently high frequency, this phenomenon can be neglected, and it always exist a domain of frequencies for which the measured ionic conductivity is only representative of the mobility of ionic species [10].

Before the beginning of cure reaction, that is to say roughly below 140 °C, one can notice that ionic conductivity is frequency independent (for sufficiently high frequencies) and grows with temperature. When cure reaction begins, the ionic conductivity starts to strongly decrease due to the restriction of mobility caused by the formation of the three-dimensional molecules. Simultaneously, a relaxation process appears for higher frequencies (and then lower frequencies) which is directly correlated with the observation of a vitrification of the sample on the heat capacity curve (Fig. 3). This vitrification is followed by a devitrification at higher temperatures, also correlated with a second relaxation phenomena on the ionic conductivity curves (Fig. 3). After this second relaxation, the ionic conductivity becomes frequency independent again.

For the two other temperature scanning experiments (performed at 2 and 4 K/min, respectively), a similar behaviour was observed, except that the vitrification and devitrification phenomena where not as clear on the heat capacity curves as for 1 K/min. This is not surprising as these phenomena are the result of a competition between the imposed temperature ramp and the increase of thermosetting polymer T_g as cure reaction goes on.

For each temperature scanning rate, we have extracted σ_{Dc} (the contribution of purely conductive phenomena) from ionic conductivity (Fig. 4). Before reaction starts (cure degree equal to 5%), the three curves obtained for the different temperature scanning rates are superposed, demonstrating that σ_{Dc} is only temperature dependent. In this temperature domain, in agreement with the results of Bartolomeo et al. [7] on another cyanate ester system, the ionic conductivity of unreacted monomer is clearly described by Eq. (1), with the following adjusted parameters: $\ln \sigma(T_{g0}) = \ln \sigma_0 = -5.1$; $C_1 = 25.17$ and $C_2 = 58.07$.

For higher temperatures, as cure reaction begins, all ionic conductivity curves start to decrease, down to a sort of plateau for cure conversion degrees ranging from about 65 to about 95% (Table 1 and below). In this region, which corresponds to the lowest frequency response (1 Hz), the signal is of course perturbed by the relaxation phenomena observed on Fig. 3, the material becoming glassy with regards to the frequency used. Therefore, the ionic conductivity extracted in this range is not purely conductive and has to be considered has over estimated.

At higher temperatures, and when the cure degree reaches 100%, the σ_{Dc} ionic conductivity curves start to increase again. It is important to observe that, contrary to the case of initial monomer, the three curves are no longer superposed, especially for the 4 K/min experiment. If we assume that the concentration of ionic species does not change, a possible explanation for this phenomenon is that the crosslink density of the final network is higher for higher heating rates, which would explain the lower conductivity observed. The lower crosslink density for the samples heated at 1 and

Table 1
Extrapolated temperatures of vitrification and devitrification at 1 Hz and corresponding conversions

Heating rate (K/min)	T vitrification (°C)	T devitrification (°C)	α vitrification (%)	α devitrification (%)
1	221	278	66	97
2	238	278	69	97
4	259	286	80	97

2 K/min. could be explained by a slight thermal degradation cause by a higher exposition to high temperatures (above 250 °C). This hypothesis is supported by the observation of the samples after dielectric spectroscopy experiments, which were much brownish for lower heating rates, this change of colour being generally attributed to the beginning of thermal degradation in cyanate ester networks [11]. Another support for this hypothesis comes from the observation of the relaxations temperatures (vitrification and devitrification) on Figs. 2 and 3 (and similar plots for other temperature scanning rates). The temperatures of the maximums of the peaks observed on ionic conductivity curves for the different frequencies are shown on Fig. 5. It appears clearly that the devitrification temperature of the sample cured at 4 K/min is slightly higher (which means a higher crosslink density) than for the samples cured at lower heating rates.

Fig. 5 also points out the temperature domain (between vitrification and devitrification temperatures) were the purely conductive part of ionic conductivity is overestimated on Fig. 4. Table 1 shows the values extrapolated from Fig. 5 for vitrification and devitrification temperatures at the lowest frequency used (1 Hz), together with the corresponding values of cure conversion degree obtained from TM-DSC at these temperatures.

3.2. Evolution of the glass transition of the thermosetting polymer with conversion degree

In agreement with literature results [9] and as can be seen on Fig. 6, experimental data are well described by the relation of DiBenedetto modified by Pascault and Williams [12]:

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda\alpha}{1-(1-\lambda)\alpha} \tag{9}$$

where $T_{g0} = -60$ °C; $T_{g\infty} = 280$ °C and $\lambda = 0.255 \approx \Delta C_{p0}/\Delta C_{p\infty}$.

3.3. Rheological measurements and correlation with ionic conductivity

The temperature behaviour of initial monomer's viscosity, plotted on Fig. 7, can be described by the Doolittle equation:

$$\ln \eta(T) = \ln \eta(T_g) - C_1 \frac{(T-T_g)}{C_2 + (T-T_g)} \tag{10}$$

With adjusted parameters $\ln \eta(T_g) = 7.9$; $C_1 = 20.34$ and $C_2 = 79.5$.

It is noteworthy that the previous studies on the same system [9,13] had lead to the conclusion that initial viscosity followed an Arrhenian temperature behaviour. This is due to the fact that the authors used capillary rheometers and therefore had to limit their measurements to a smaller temperature range (below 75 °C) in order to avoid any chemical reaction. Indeed, if one takes into account only the measurements done in the present study between (25 and 75 °C), an apparent Arrhenian behaviour is observed, with

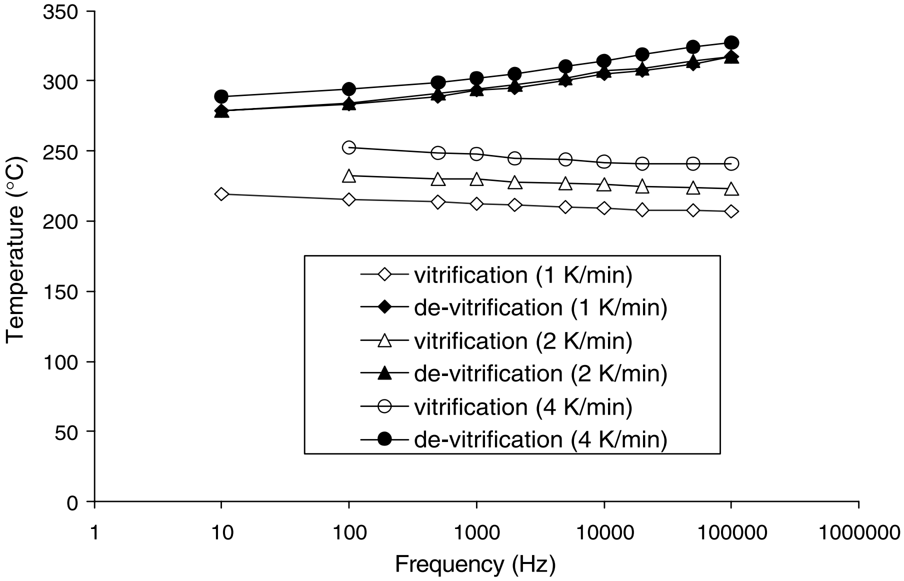

Fig. 5. Vitrification and devitricication temperatures during temperature scanning dielectric spectroscopy experiments.

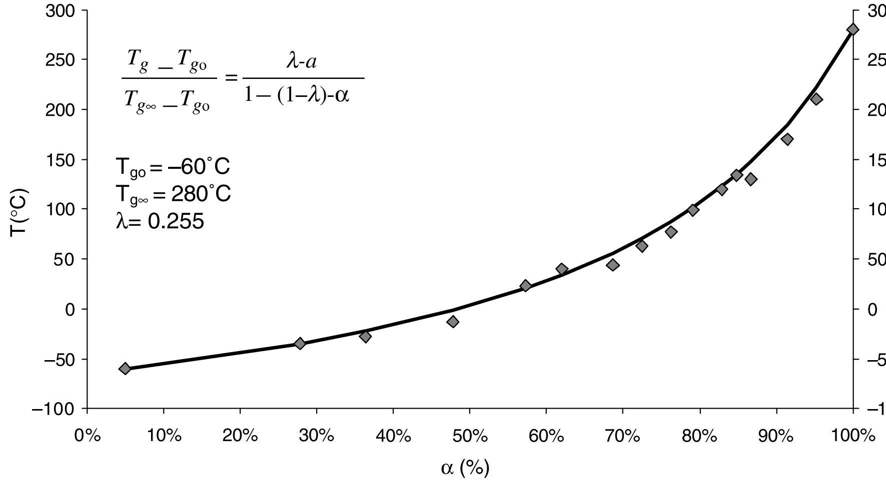

Fig. 6. Evolution of glass transition temperature with cure degree: Experimental values (symbols) and fit by Eq. (9) (line).

an activation energy of 44,600 J/mol, which is very close to the values found in these previous studies [9,13].

Assuming the ionic species involved in the ionic conductivity phenomenon are rigid spheres, the measured conductivity should be related to the viscosity of the thermosetting polymer by the Stoke's law:

$$\sigma = \frac{Zq^2N}{6\pi R\eta} \tag{11}$$

where Z, q, N and R are the average number of electric charges of ionic species, the electric charge of one electron, the concentration in ionic species and the average radius of the ionic species.

Fig. 8 shows the plot of ln σ vs ln η for initial monomer (experimental values have been used for viscosity, while corresponding values of ionic conductivity have been interpolated from dielectric measurements). A straight line of slope −1.02 is obtained, which seems to confirm the validity of Stoke's law for this system.

3.4. Estimation of CTE from ionic conductivity

Using Eqs. (1) and (9), we can now adjust the values of parameters C_1 and C_2 for each temperature scanning rate in order to be able to calculate the evolution of the coefficient of thermal expansion δ using Eq. (4). As described above, the initial values (before beginning of cure reaction) are ln $\sigma(T_{g0}) = -5.1$; $C_1 = 25.17$ and $C_2 = 58.07$. Following the approach of Bartolomeo et al. [7], the same values of log σ_0 and C_1 were used as fixed parameters and the value of C_2 was adjusted for each conversion degree in order to have a minimum least squares difference between experimental σ_{Dc} and the predictions of Eq. (1). All the obtained values for C2 were then used to calculate the evolution of the coefficient of thermal expansion δ using Eq. (4). The results obtained are shown on Figs. 9 and 10, as a function of temperature and cure conversion degree, respectively.

It is striking to observe that the three curves on Fig. 10 are superposed: The calculated values of δ are consequently only dependent on cure degree. The fact that they are almost

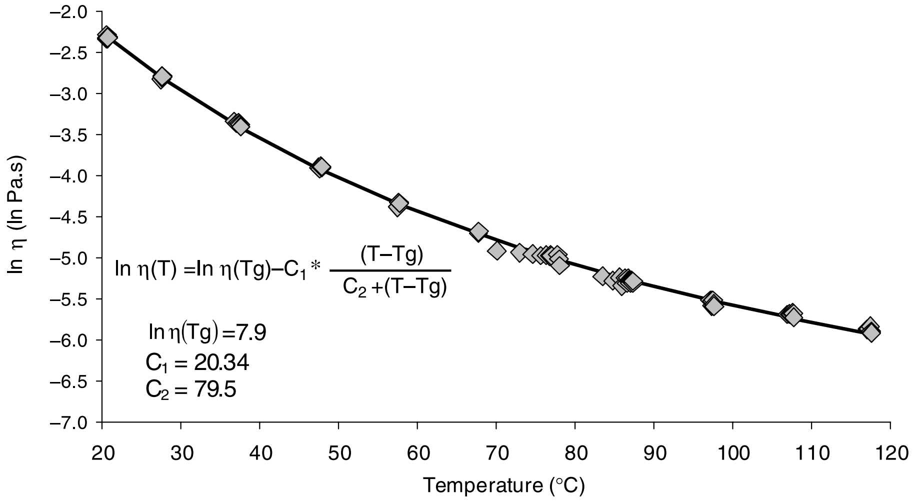

Fig. 7. Initial viscosity of cyanate ester monomer: Experimental values (symbols) and fit by Eq. (10) (line).

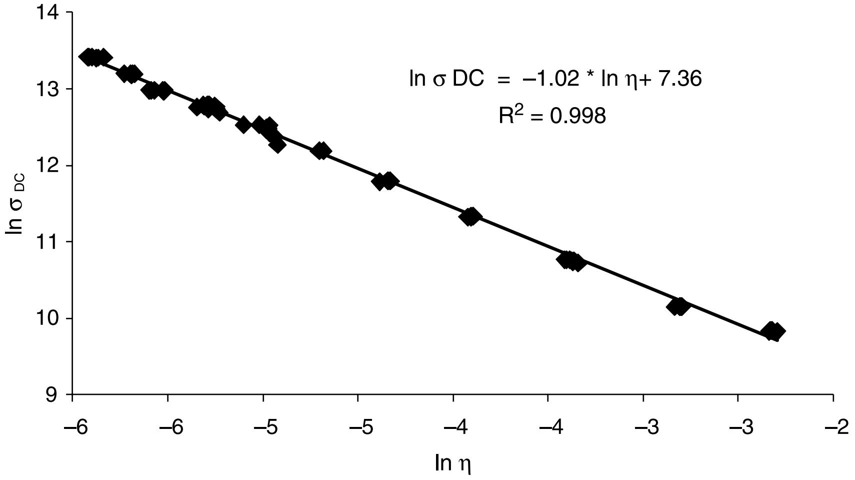

Fig. 8. Correlation between initial viscosity and purely conductive part of ionic conductivity: Verification of Stoke's law.

independent on the temperature heating rate (and so, on temperature) supports the validity of our calculations based on the approach suggested by Bartolomeo et al. [7].

Results in Table 2 are also supporting the validity of this approach, since the calculated values of CTE for uncured monomer and fully cured network are in the same range as our CTE measurements. Concerning the CTE of fully cured network, it is noteworthy that the calculated values are higher for temperature scanning dielectric spectroscopy experiments at lower heating rates, that is to say for samples having undergone a slight thermal degradation cause by a longer exposition to high temperatures (above 250 °C). Consequently, it is possible that the higher value measured by TMA for the rubbery state (beside being consistent with literature results on another cyanate ester [14]) is only due to a more important thermal degradation of the fully cured sample used, keeping in mind that in order to reach complete cure conversion, we had cure the sample isothermally up to 325 °C (see CTE measurements in Section 2).

The evolution of δ with conversion (Fig. 10) is consistent with the knowledge in physico-chemistry of thermosetting polymers. At low conversion, δ decreases strongly, due to the volumetric shrinkage caused by the growing size of the molecules. Nevertheless, when approaching the gel point which is located between 50 and 60% cure for cyanate ester systems [11], the (absolute value of the) slope on Fig. 10 decreases to nearly zero in the gel point region. This result is consistent with the structural transformation from a viscous liquid to a solid.

For a range of cure conversion degree above the gel point the vitrification and devitrification phenomena (Table 1) are superposed to the effect of cure reaction. This explains why δ remains constant, as the material state evaluates from partially to completely vitreous. This effect disappear at higher cure degree ($\alpha > 97\%$), showing that, contrary to the

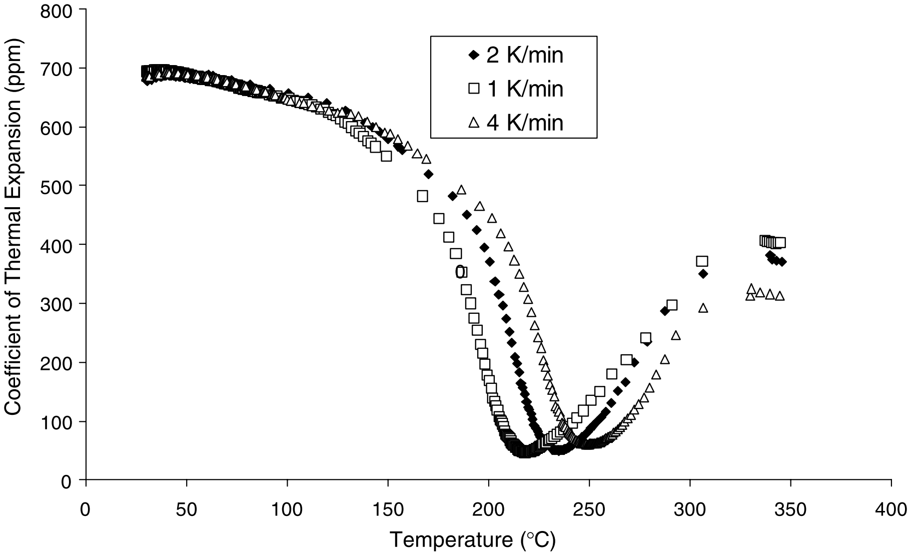

Fig. 9. Calculated evolution of CTE as a function of temperature.

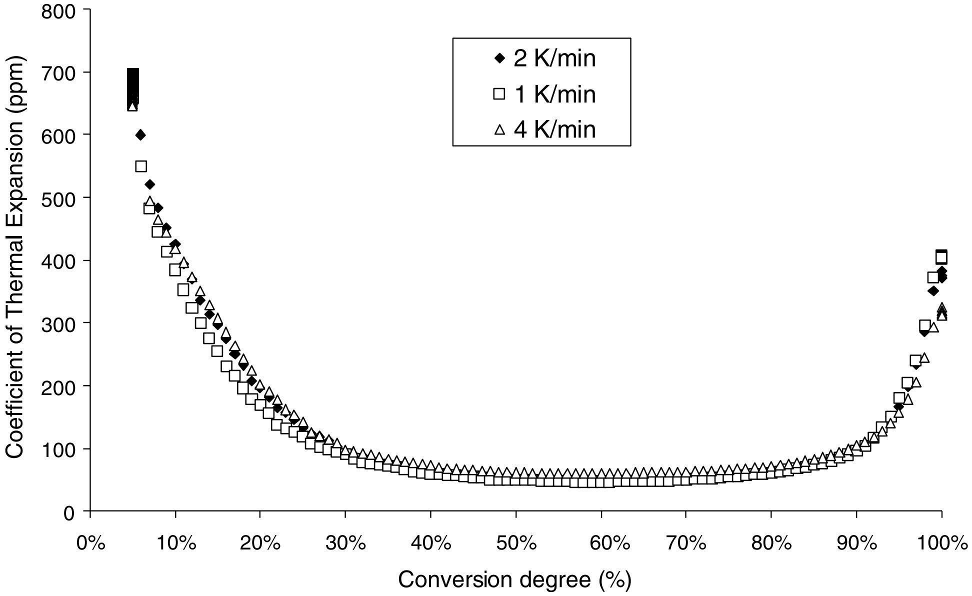

Fig. 10. Calculated evolution of CTE as a function of conversion degree.

liquid, the coefficient of thermal expansion δ of the rubbery solid strongly increases with cure conversion degree. This observation is in agreement with literature results showing that the specific volume of cyanate esters grows with cure degree at conversions higher than the gel point [15].

4. Conclusion

Using an indirect approach based on the modelling of ionic conductivity by a modified William Landel Ferry equation [7], the evolution of the coefficient of thermal expansion of a dicyanate ester thermosetting polymer has been evaluated during cure reaction, from temperature scanning dielectric spectroscopy experiments coupled to temperature modulated DSC experiments.

The absolute values of the CTE before reaction and after complete reaction are in agreement with experimental measurements. Moreover, the evolution of CTE with cure reaction is consistent with the knowledge of thermosetting polymers physico-chemistry, with in particular a evident change of behaviour through the gelification of the system.

These results suggest that the estimation method used may be an important tool for further studies about the evolution of the CTE of thermosetting polymers during cure reaction. Such a method could be easily implemented using the emerging temperature modulated dielectric spectroscopy technique [16].

Table 2
Calculated and measured values of CTE for uncured and fully cured states

Cure conversion degree (%)	Calculated CTE (ppm)	Measured CTE (ppm)
0 (Uncured)	640–700	660
100 (Fully cured)	320–410 (rubber)	180 (glass)–500 (rubber)

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