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Critique of dielectric cure monitoring in epoxy resins – Does the method work for commercial formulations?

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ABSTRACT

Dielectric techniques can be used as an in situ monitor of resin cure. This study reports measurements on two commercial resin formulations and aims to establish the extent to which identifiable turning points in the dielectric behaviour are dependent of the formulation used. Complementary curometer and differential scanning calorimetry data are used to monitor the progress of cure and are compared with the dielectric data. System [A] is a simple epoxy amine system, whilst system [B] is a blend of both epoxy and amine resins. It is clear that without calibration of the dielectric data against other methods it is difficult to unambiguously derive absolute cure information on a system not previously studied. However, dielectric data does allow identification of the points at which gelation and vitrification occur and demonstrates its utility as an in situ monitoring method for the cure process.

1. Introduction

Optimisation of the state of cure in situ is very important in the fabrication of adhesive bonded structures, coatings and composite structures. The thermal mass of the substrate and the influence of fillers can significantly influence the magnitude of the temperature rise produced through the reaction exotherm and hence the degree of cure achieved. In autoclave fabrication of composite structures, it is important to know when pressure should be applied to consolidate a moulding or aid the creation of a uniform adhesive bonded structure. Application of pressure too early in the cure cycle, when the resin is in a low viscosity state, can lead to thinning of a joint or the creation of resin rich and resin depleted areas in a composite. If the pressure is applied too late, then compaction will not occur and voiding may result.

The use of dielectric spectroscopy in cure monitoring of epoxy resin systems has been explored by a number of researchers [1–15], and involves monitoring changes in the dielectric permittivity ε'(ω) and dielectric loss ε"(ω) as cure proceeds. In previous studies, the cure of epoxy resins with various aliphatic diamines [7–10], triethylenetetramine [11], aromatic diamines [12] and mixtures containing a toughening agent [13,14], have been reported. Cessation of ionic conduction is an indication of gelation and dipole relaxation can be used to follow the growth of the epoxy network. In many cases the dipole relaxation processes retain their original shape but shift in frequency as the matrix changes from a gel to a glass [15–17].

Viscosity is the primary physical property which changes during cure and reflects the topography of the growing matrix and influences both ionic mobility and dipole relaxation rates [18]. In general, it is only once the molecular weight of the polymer entities are greater than 10k that there is a significant change in the ion mobility and ionic conduction is observed to cease. Ion conduction is sensitive to the local viscosity in the resin and reflects the growth in topography as cure proceeds. Further reductions in the dielectric loss and permittivity allow vitrification to be identified and are sensitive to the local chain mobility and hence degree of cure of the resin.

This study explores the cure characteristics of two commercial adhesive systems. Unlike the cure systems studied previously, these formulations contain components with a variety of different functionalities, designed to enhance the rate of cure and improve the final mechanical properties of the resin matrix. The different reaction rates will influence the cure process and the topography created as a function of time and this is reflected in the path by which gelation and vitrification are achieved.

Comparison of the data from these two very different systems and correlation of results obtained from other techniques allows a better understanding of the dielectric method as an in situ monitor of the cure process.

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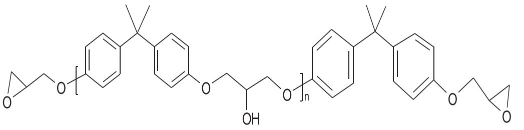
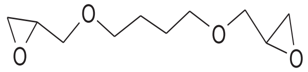
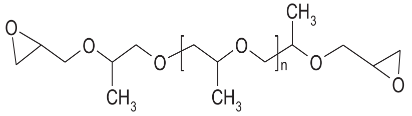
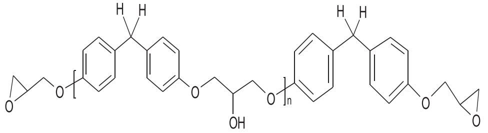
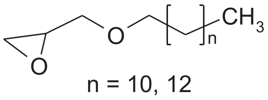
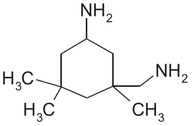
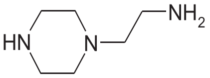
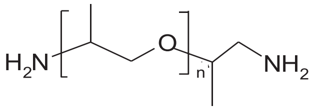
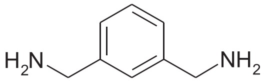
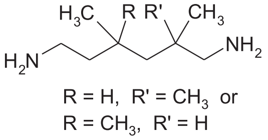
Table 1
Epoxy resin and amine hardeners used in the formulations studied.

bisphenol A-(epichorohydrin); epoxy resin (no. av. molecular wt<700) DEGBA	
1,4-bis(2,3-epoxypropoxy) butane BDGE	
diglycidylether of polypropyleneglycol PPGDGE	
diglicidylether of bisphenol F DGEBF	
C12/C14 alkylglycidylether	
3-aminomethyl-3,5,5-trimethylcyclohexylamine Isophoronediamine	
2-piperazin-1-ylethylamine	
polypropylene glycol bis (2-aminopropyl ether) Jeffamine D	
m-phenylenebis (methylamine)	
2,2,4(2,4,4)-trimethyl-1,6-hexanediamine -TMHDA	

2. Experimental

2.1. Materials and cure characteristics

The chemical structures of the components used are summarised in Table 1. The formulations contained various amounts of epoxy and hardener components, adjusted to achieve different initial viscosities, pot life, cure rates and mechanical properties in the cured resin. In both cases, cure was carried out at the stoichiometric ratios of epoxy and hardener. Small amounts, typically < 0.5 w/w% of additives; 4-tert-butyl phenol, benzyl alcohol and petroleum solvent were present to adjust the viscosity or catalyse the reaction [19]. The two formulations studied are summarised in Table 2.

Both systems are based on bisphenol A-(epichlorohydrin) which has an ‘n’ value of ~1.3 and are formulated to be close to stoichiometric ratios of epoxy and hardener. System (1) has a pot life of *ca.* 60 minutes at 20 °C and was studied at 25 °C, 30 °C, 35 °C, 40 °C and 45 °C. System (2) is designed to be used between 15 and 25 °C with a pot life

Table 2
Formulations used in this study.

Epoxy	wt%	Hardener	wt%
System (1)			
DGEBA	80	isophoronediamine	85
PPGDGE	20	benzyl alcohol	15
System (2)			
DGEBA	70	isophoronediamine	40
DGEBF	20	2-piperazin-1-ylethylamine	40
C12/C14 alkylglycidylether	7.5	Jeffamine D	17
BDGE	1.5	m-phenylenebis (methylamine)	1.5
		2,2,4(2,4,4)-trimethyl-1,6-hexanediamine -TMHDA	1.5

of 87 minutes at 15 °C; 70 minutes at 20 °C; 56 minutes at 25 °C; and 45 minutes at 30 °C. Isothermal cure was carried out at 40 °C, 50 °C, 60 °C, 70 °C and 80 °C.

2.2. Rheology curometer data

The Strathclyde vibrating curometer has been described previously [20–23] and was calibrated using liquids of known viscosity. The reaction mixture was contained in a glass vial (10 mm diameter) and filled to a depth of ~10 mm and heated in a stirred thermostated oil bath. The temperature was monitored with a thermocouple placed in the vial. The amplitude and phase outputs of the linear variable differential transformer (LVDT) operating at 2 Hz was recorded as a function of time using Picolog software. The data were converted into the shear viscosity using Origin software [20–23]. Consistency of the data was checked by achieving at least two coincident traces for each cure temperature.

2.3. Differential scanning calorimetry (DSC)

Isothermal DSC traces obtained using a TA Q1000 Differential Scanning Calorimeter were used to obtain the reaction exotherm and degree of conversion as a function of time [24–27]. Hermetic sealed aluminum pans containing ~3–6 mg of epoxy-amine mixture were referenced against an empty pan for the cure measurements. The calorimeter was purged with nitrogen gas at 20 ml min^{-1}. The reaction exotherm was established using dynamic scans which were performed by firstly equilibrating the pans at −50 °C, holding for 1 min and then ramping at 10 °C min^{-1} to 250 °C. Three measurements were carried out to determine the total reaction exotherm. Isothermal measurements allowed the degree of conversion as a function of time to be determined. Pans initially equilibrated at −50 °C, were held for 1 min and then ramping at 10 °C min^{-1} to the required cure temperature and the degree of conversion as a function of time measured. The total elapse time between mixing and isothermal measurement starting was ten minutes. Data analysis was carried out using TA Universal Analysis 2000 software.

2.4. Dielectric spectroscopy

The cure process was monitored using a Novotronic dielectrics spectrometer equipped with a custom made disposable cell [7–15]. Two copper etched patterned electrodes, separated using a PTFE spacer formed the cell which contained ~3 g of resin mixture and

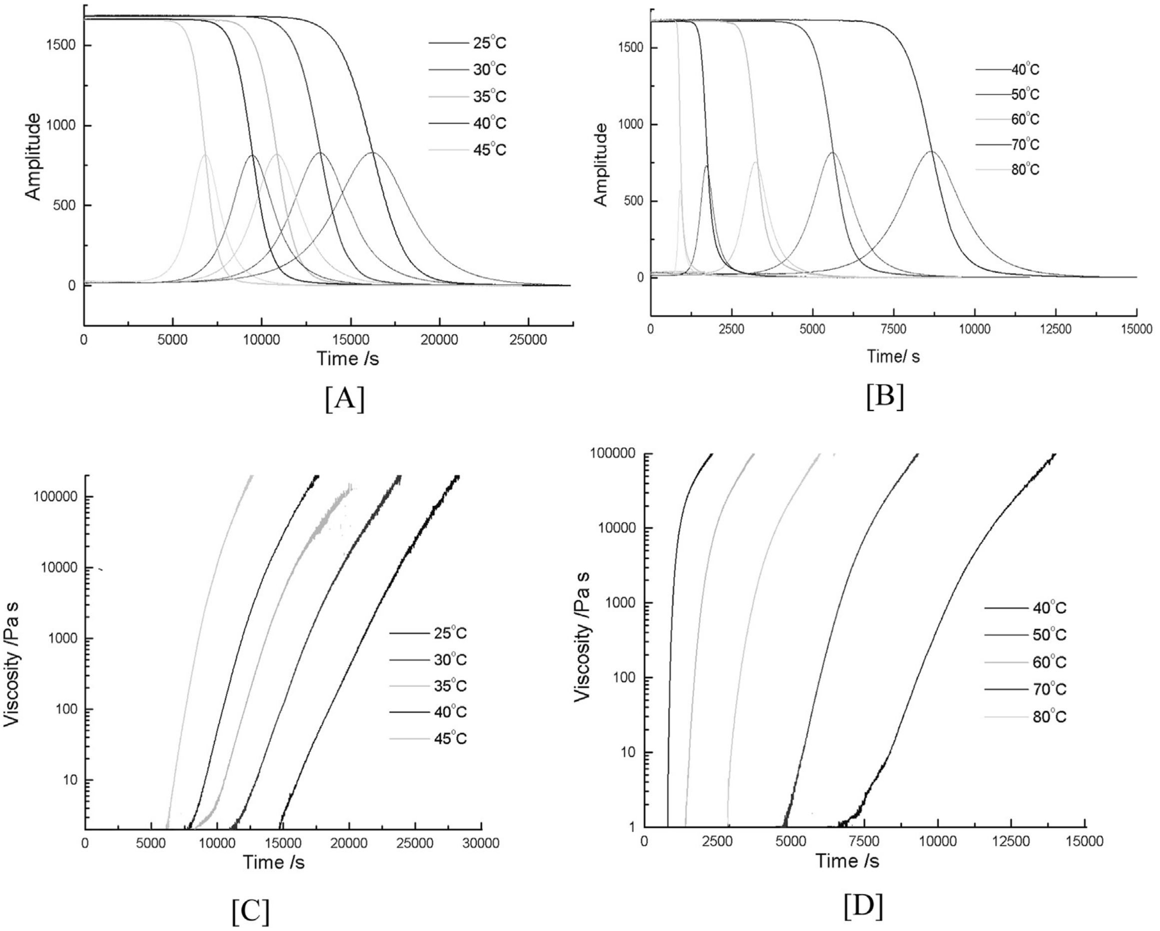


Fig. 1. Amplitude profile plots against cure time for System (1) – [A] and System (2) – [B] and Viscosity profile plots against cure time for System (1) – [C] and System (2) – [D].

was thermostated in a modified Linkam thermostatic cell holder. The WinData software package was used to obtain the dielectric permittivity [ε'] and loss [ε"] between 1 Hz and 1 MHz at pre-determined time intervals and the measurements took 2–3 min per scan to scan the frequency range. The initial time interval between successive measurements was set at 5 min. As the cure proceeded the interval between measurements was increased on a logarithmic scale. For each time interval measured, a two-dimensional plot of the real or imaginary permittivity against the frequency was produced using Origin software.

3. Results and discussion

This paper attempts to establish the extent to which dielectric NDT data can be used quantitatively to monitor the cure in complex resin systems. The points at which gelation and vitrification are observed by different techniques is sensitive to the way in which growth of the topography of the network is occurring [28–31]. The aim of this paper is to determine the extent to which dielectric measurements can unambiguously characterize the cure process and determine whether ancillary data is required.

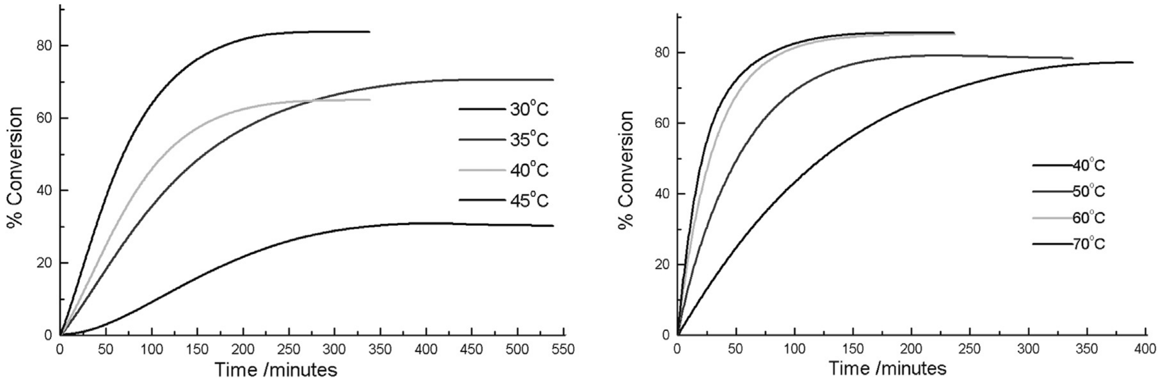
3.1. Curometer measurements

Viscosity is the principle property which changes during cure and curometer measurements were performed on both systems studied. The real and imaginary amplitudes obtained from the LVDT, Fig. 1A & B and the corresponding calculated viscosities, Fig. 1C & D were used to determine the gelation and vitrification times. System (1) consists of DGEBA diluted with a flexible aliphatic diepoxy PPGDE and cured with isophoronediamine and benzyl alcohol as an accelerant [19]. Measurements were performed at 25 °C, 30 °C, 35 °C, 40 °C and 45 °C. At 25 °C, Fig. 1C the viscosity maintains a low level for the first 6500 seconds, then grows in a logarithmic fashion to the vitrification point.

Raising the cure temperature shortens the time before the viscosity is observed to rise and the plots develop curvature once the viscosity has exceeded a value of 10^4 Pas. The vitrification is best identified as the point at which the paddle ceases to move and is indicated by the amplitude becoming zero, Fig. 1A. Gelation occurs when the viscosity reaches a value of 10^4 Pas and is coincident with the falling amplitude of oscillation crossing the center of the phase amplitude peak, Fig. 1A. In the initial stages of cure, the primary amine will react and increase its molecular weight and hence viscosity. The entities created will initially be low molecular weight linear molecules and have low viscosity. Reaction of the secondary amine generated by the initial reaction will produce branched chain structures which initially will not significantly increase the viscosity but eventually will form the network associated with vitrification. As the reaction proceeds cyclization can occur but the structures formed will also not significantly increase the viscosity. It is only later in the reaction that networks are developed, the viscosity will rise and gelation occurs. Further reaction will increase the extent of crosslinking and rigid matrix and ultimately a glass is formed. The primary amine reaction is an order of magnitude faster than that of the secondary amine reaction. The presence of the benzyl alcohol will aid the etherification reaction once secondary amine has been generated and help transformation of the gel to a glass. The activation energy (E_a) calculated from Arrhenius plots of the 10k Pas point on the viscosity curve gave E_a (gelation -viscosity)=32.8 ± 2.0 kJ mol^{-1}. The E_a (gelation – peak maximum) obtained by plotting the variation of the peak maxima gave a value of 32.5 ± 0.5 kJ mol^{-1} and plotting the point where the amplitude becomes zero gave E_a (vitrification)=26.8 ± 5.0 kJ mol^{-1}. These values are comparable with those reported by other workers [29–32]. The cure in this system is fairly simple and once reaction has started moves smoothly from the creation of linear entities through the generation of chain branches to network formation, gelation and finally to vitrification.

System (2) is a typical commercial formulation composed predominantly of DGEBA and DGEBF with a small amount of BDGE and C12/C14 alkylglycidyl ether, which has one epoxy group and acts as a reactive diluent, chain stopper and plasticizer. The blend of DGEBA with DGEBF helps lower the viscosity of the initial mixture. The C12/C14 alkylglycidyl ether helps to develop a smooth surface. Isophoronediamine and 2-piperazin-1-ylethylamine form the major part of the hardener. Jeffamine D which has a flexible chain between the primary amine groups, *m*-phenylenebismethylamine and trimethylhexane-1,6-diamine makes up the remainder of the hardener formulation. Small amounts of 4-*tert*-butylphenol act as a catalyst for the reaction. Real and imaginary amplitudes plots measured at 40 °C, 50 °C, 60 °C, 70 °C and 80 °C, Fig. 1B and viscosity plots, Fig. 1D were obtained. The viscosity curves are similar to those for system 1, except that at 40 °C there is initially significant curvature in the viscosity plot and also after gelation. At higher temperatures the initial curvature is absent but is still a feature post gelation. Both the epoxy entities and the amines will have different reactivity's and hence the growth of the initial polymer entities and formation of the network will depend on factors such as diffusivity and reactivity. The gelation and vitrification times were used to determine the activation energies; E_a (gelation - viscosity)=52.3 ± 2.0 kJ mol^{-1}, E_a (gelation – peak maximum)=52.2 ± 0.5 kJ mol^{-1}, E_a (vitrification)=43.7 ± 5.0 kJ mol^{-1}.

The curometer curves for both system are similar but do reflect difference in the pathways followed by the two systems. Whilst the viscosity data gives a clear indication of the progression of cure it is difficult to incorporate the method into practical molding equipment.



[A] [B]

Fig. 2. DSC conversion curves for system (1) - [A], and system (2) - [B].

Table 3
Final conversion values and rates of reaction calculated for system (1) and (2).

Cure Temperature /°C	Final % Conversion	Rate /min^{-1}	Glass transition temperature T_g °C
System (1)			
30	30.3	0.00717	33
35	70.5	0.00858	40
40	64.9	0.01369	52
45	83.8	0.0153	51
System (2)			
40	77.1	0.00944	50
50	78.4	0.02063	61
60	85.1	0.03148	70
70	85.5	0.03726	78

3.2. *Differential scanning calorimetry study*

DSC measurements of the reaction isotherm allow the degree of conversion to be mapped as a function of time and temperature, (Fig. 2). The method cannot be used in situ and hence is limited to evaluation of the cure process for the resin and does not allow the effects of substrate on the cure process to be investigated. The rates of reaction can be calculated using the Sigmoidal Boltzmann Eq. (1):-

$$y = \frac{A_1 - A_2}{1 + e^{(x-x_0)/dx}} + A_2 \tag{1}$$

where A_1 is the initial y value, A_2 is the final y value, x_0 is the centre (point of inflection) and dx is the width of the curve (the change in x corresponding to the most significant change in y values).

The reaction rate was found for each isothermal cure temperature by taking the reciprocal of the dx value. The average total heat of reaction was obtained from three dynamic scans and gave a value of 383.7 ± 21.3 J g^{-1} for system 1. Isothermal scans were carried out at 30 °C, 35 °C, 40 °C and 45 °C and the conversion plot produced, Fig. 2A. The rates of reaction were calculated using Eq. (1) and are listed in Table 3. Using these data an Arrhenius plot was used to obtain an activation energy of 43.9 ± 2.1 kJ mol^{-1}. This value is higher than that obtained from viscosity data but is dominated but the initial slope of the conversion plot. As indicated above, the viscosity is insensitive to the initial stages of the reaction and it is only once the molecular weight has reached a value of ~1–10 k that measurable effects are observed. This difference over which the rate of reaction is analysed in part explains the observed difference in values determined.

Dynamic scans were performed on the cured samples to determine their glass transition temperature - Tg. The Tg values, Table 3, are slightly higher than the temperature used in the cure and this behaviour is typical of many epoxy resin systems.

Dynamic scans on system (2) gave a total heat of reaction 476.7 ± 7.2 J g^{-1} which was significantly higher than that obtained for system 1 and reflects the presence of catalysts on the cure process in system 2. Isothermal scans were carried out at 40 °C, 50 °C, 60 °C and 70 °C and produced the conversion plot, Fig. 2B. The degree of conversion and reaction rates were calculated, Table 3 and used to construct an Arrhenius plot from which a value of the activation energy of 40.9 kJ mol^{-1} was obtained which is similar to that obtained for system (1) but lower than that obtained from the viscosity data. The T_g values similar to system 1 are typically 10 °C higher than the cure temperature, Table 3.

3.3. *Dielectric analysis*

In principle, dielectric measurements can be performed in situ in a fabrication mould and it is therefore of interest to understand at what stage in the cure process certain changes in the dielectric properties of the curing mixture occur and how these are related to the processes detected by the other methods. Ideally the dielectric NDT method could be applied without prior knowledge of the cure behaviour and in this paper were are testing this hypothesis.

3.3.1. *System (1)*

Isothermal cure studies were carried out at 25 °C, 30 °C, 35 °C, 40 °C and 45 °C and the data obtained at 25 °C is shown in Fig. 4 and illustrates that obtained at the other temperatures.

The dielectric spectrum of the uncured resin is characteristic of a low molecular weight freely rotating dipolar liquid reflected in a high value of the permittivity (ε') and has a value of approximately 8, identified by a plateau value between 1 Hz and ~100 kHz. Initially there is an additional contribution to ε'(ω) at lower frequencies, below 100 Hz, attributed to ionic mobility and blocking electrode effects, Fig. 3A. As the cure temperature is changed the rate at which the curves move and their values will alter. The epoxy resin contains chloride ions as a contaminant arising from the uses of epichlorohydrin to create the epoxy group. Chloride ions are free to migrate towards the positive electrode and gives rise to ion conduction losses evident in the ε"(ω) plot, Fig. 3B. If the conduction process is inhibited, either by blocking electrodes or the presence of heterogeneity, then a contribution to the dielectric permittivity ε'(ω) can be observed. This process can be ascribed to Maxwell Wagner Sillers losses [32–34] and has a relaxation rate τ_{MWS}. As the cure proceeds, the viscosity of the liquid will increase

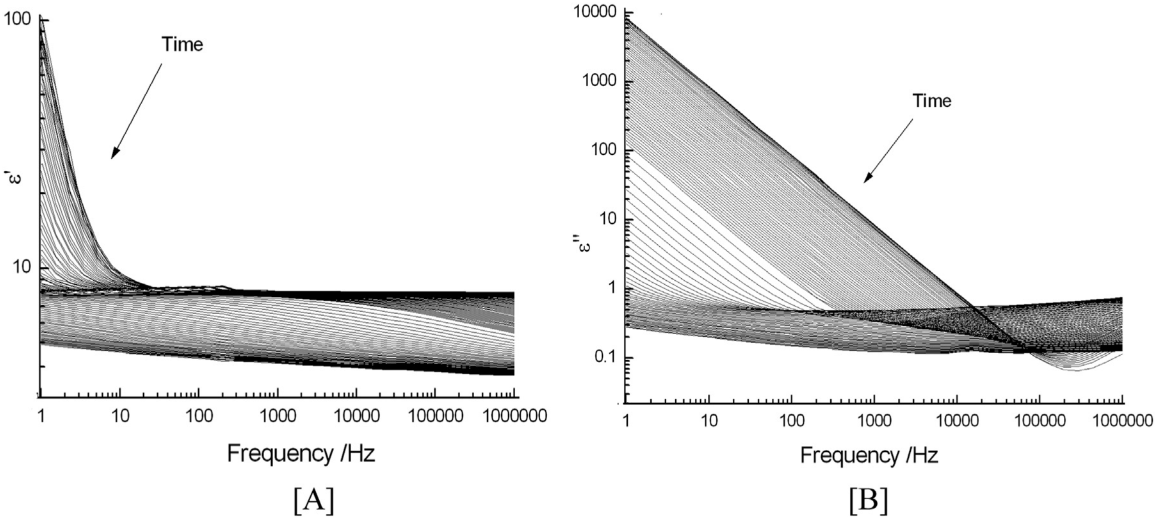


Fig. 3. Variation of the dielectric permittivity ε'(ω) and loss ε"(ω) as a function of cure time for system (1) at 25 °C.

slowing down the rate of motion of the ionic impurities and the low frequency amplitude for both ε’(ω) and ε”(ω) are reduced. A plateau value in ε’(ω) is observed reflecting the rotational dipole processes of the partly cured resin. The initial ε”(ω) plot, Fig. 3B, is dominated by motion of the ionic impurities and is characterised by its 1/(ω) dependence. The initial decrease in the 1/(ω) dependence of ε”(ω) in principle correlates with the increase in viscosity as cure proceeds, Fig. 3B. The dielectric permittivity and loss can be expressed by Eqs. (2) and (3):-

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_1 - \varepsilon_2}{1 + \omega^2\tau_{MW}^2} + \frac{\varepsilon_2 - \varepsilon_\infty}{1 + \omega^2\tau_{dipole}^2} \tag{2}$$

and

$$\varepsilon''(\omega) = \varepsilon_\infty + \frac{(\varepsilon_1 - \varepsilon_2)\omega\tau_{MW}}{1 + \omega^2\tau_{MW}^2} + \frac{(\varepsilon_2 - \varepsilon_\infty)}{1 + \omega^2\tau_{dipole}^2} + \frac{\sigma}{\omega}$$

MWS losses dipole relaxation ionic conduction (3)

where ε_1 is the limiting low frequency value of the dielectric permittivity, ε_2 is the intermediate value and reflects the amplitude of the dipole relaxation process and has a value of ~8 and ε_∞ is the high frequency limiting value of the permittivity and has a value of ~3.5 at 30 °C. These values will change with the cure temperature and the formulation studied. The relaxation frequency for the blocking electrode process -τ_{MW} is located at < 0.1 Hz, whereas the τ_{dipole} is initially relaxing at a frequency above 10 MHz. As cure proceeds the viscosity increases and ionic conduction and associated blocking electrode polarization processes disappear. Increasing the molecular weight slows down the dipole relaxation and it moves into the window of the dielectric measurements. At the end of the cure process the main dipole relaxation will have ceased and a glass is created – vitrification has occurred. However there is always the possibility of dipolar relaxation processes remaining active in the glass state and associated with rotation of OH groups and similar small molecule entities.

The point at which gelation is observed depends upon the frequency of observation as seen in Fig. 3B, indicated by the point at which the curves dip through a minimum before increasing as a consequence of the slowing down of the dipole relaxation. The time at which this minimum occurs is indicative of gelation. The subsequent changes in the dielectric spectrum are associated with dipole relaxation and reflect the constraints on the matrix as the resin vitrifies and passed through its T_g. To characterise the cure process plots were generated of the dielectric data at 2 Hz for the isothermal cure of the system 1 was plotted against time, (Fig. 4).

The initial high values of ε”(ω) are associated with blocking electrode effects and disappear once the system has passed through its gelation point. The ε’(ω) shows a similar drop however gelation is not as clearly defined. The point of vitrification is less easily identified in both the ε” and ε’ plots. The values of ε’(ω) are higher than would be expected for a cured epoxy resin and indicate that there still remains a significant amount of dipolar activity consistent with the matrix being under cured or plasticised. The critical point for gelation as indicated by the loss of the 1/ω dependence in the ε” versus time plot, (Fig. 4A) are obtained by extrapolation of the curves to the base line. Vitrification is indicated by the cessation of dipole activity when ε’reaches an asymptotic value and is associated with the T_g. Analysis of the data gives the turning points Table 4. At lower temperatures, the cure was very slow and as a consequence it is difficult to identify the precise time at which vitrification occurs. At the higher temperatures, the analysis becomes easier and more precise values can be determined. The values of ε’(1) and ε” are estimates respectively of gelation and ε’(2) of vitrification. The values of ε” are longer than those for ε’(1) as they are an extrapolation to the time axis and more realistic values would be obtained if time to reach a nominal value of ~10 were used. Clearly the conductivity depends on the level of the impurities in the epoxy resin and it is difficult to use absolute values to determine turning points, however the trends are consistent with the growth in the resin network.

The activation energy using each of the turning points can be used to create an Arrhenius plot from which the following values are obtained: E_a (ε”)=31.1 ± 4 kJ mol^{-1}, E_a (ε’(1))=36.6 ± 4 kJ mol^{-1}, E_a (ε’(2))=16.4 ± 7 kJ mol^{-1}. The last value, E_a (ε’(2)) has a magnitude which is consistent with the motion of a labile dipole and reflects the under cured nature of the resin.

3.3.2. System (2)

This system contains a blend of two aromatic epoxy resins together with a bifunctional aliphatic and a mono-functional chain stopper-plasticizer. The amine hardener contains isophoronediamine in common with system (2) but also contains 2-piperazin-1-ylethylamine, Jeffamine D and small amounts of m-phenylenebis(methylamine) and trimethylhexane-1,6-diamine making the overall cure a complex process. The reactivity's of the species present are very different. Dielectric measurements were performed at 40 °C, 50 °C, 60 °C, 70 °C and 80 °C and traces for the 40 °C cure are presented in (Fig. 5). However the plots do not look significantly different from those for the simpler system (1).

The change in the real and imaginary permittivity respectively at 2 Hz measured throughout the cure process under isothermal conditions are presented in Fig. 6.

Analysis of the data provides an estimate of the turning points as indicated in Table 4. The activation energy obtained from the data using Arrhenius plots were as follows: E_a (ε”)=27.5 kJ mol^{-1}, E_a (ε’(1)) =40.8 kJ mol^{-1} and E_a (ε’(2))=41.3 kJ mol^{-1}. Despite the complexity of the polymerization process the curves are smooth and can be interpreted in terms of clear turning points for the polymerization.

Using the viscosity and ε”(ω) time curves it is possible to explore that way in which the ionic conductivity relates to the viscosity, Table 5.

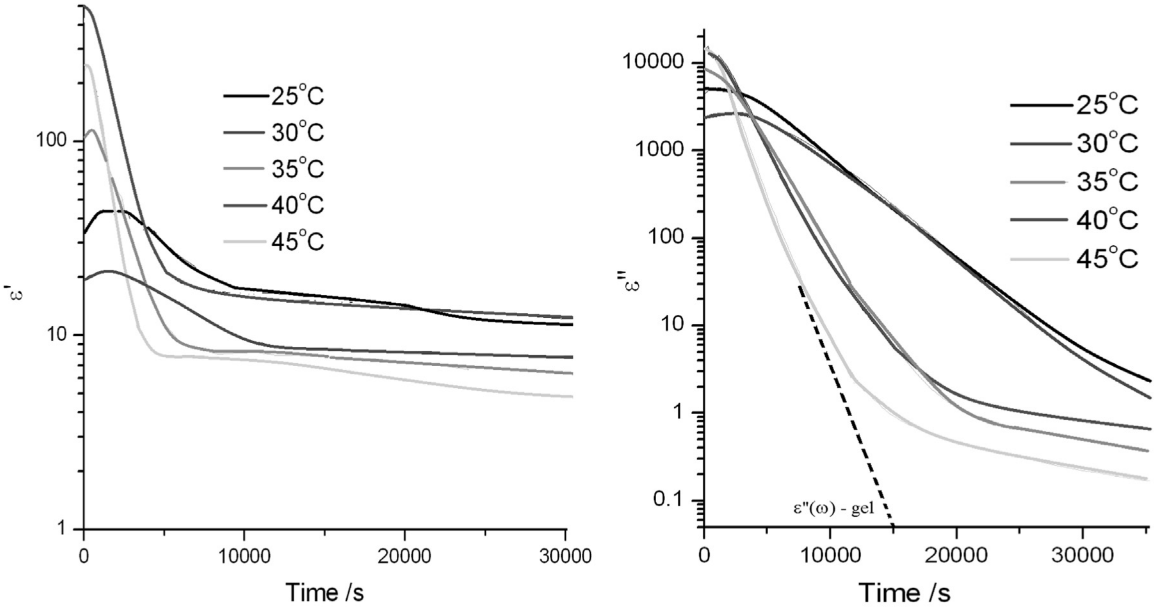
For system (1) the value ε”(ω) decreases as the viscosity increases. However the variation is not completely smooth apparently increasing at 40 °C before once more falling at 45 °C. For system (2) the reverse effect is observed, the value of ε”(ω) decreasing as cure proceeds but increasing as the temperature of cure is increased. The ε”(ω)=σ/ω term is associated with the ionic mobility and considered to be proportional to the inverse of the viscosity. The ions present in the system will depend on the formulation and will consist of chloride and protons created by proton transfer from an accelerator such as benzyl alcohol or 4-tertbutyl phenol. The observed increase in the number of ions and conductivity with temperature is a consequence of the dissociation of the accelerant, but their mobility can be influenced by the polar entities created during the cure process. It is clear that changing the formulation has changed the profile of the cure as indicated by the time dependence of the 2 Hz values of ε’(ω) and ε”(ω).

It is undesirable to require a knowledge of the number and dissociation behaviour of the charge carriers as this will vary from batch to batch and reflects the extent to which the resin has been purified after its synthesis. To explore the possible correlation of ε”(ω) against viscosity the data at 2 Hz, are plotted in (Fig. 7). The plots show that ionic mobility is changing as the viscosity increases but different cures are obtained for each temperature The ion conductivity term characterised by its 1/ωε”(ω) dependence is often directly correlated with the viscosity as follows:

$$Ion\ \ vis\cos ity{\sim}1/\sigma{\sim}bulk\ \ vis\cos ity \quad [\Omega .\ m] \tag{4}$$

It is evident that the data does not reduce to a single curve and reflects the differences in the nature of the impurities present and their ionic character introduced and the effects of change in cure temperature. There is a general trend which in principle indicates that the process of cure can be monitored by observation of the change in ε”(ω) with time, but illustrates the fact that it is not possible to use values for ε”(ω) to estimate the viscosity.

The interaction of the ions with the matrix and the level of conducting species will be higher as the temperature is increased is illustrated by system 2, Fig. 7B. However, system (1) shows markedly



[A] [B]

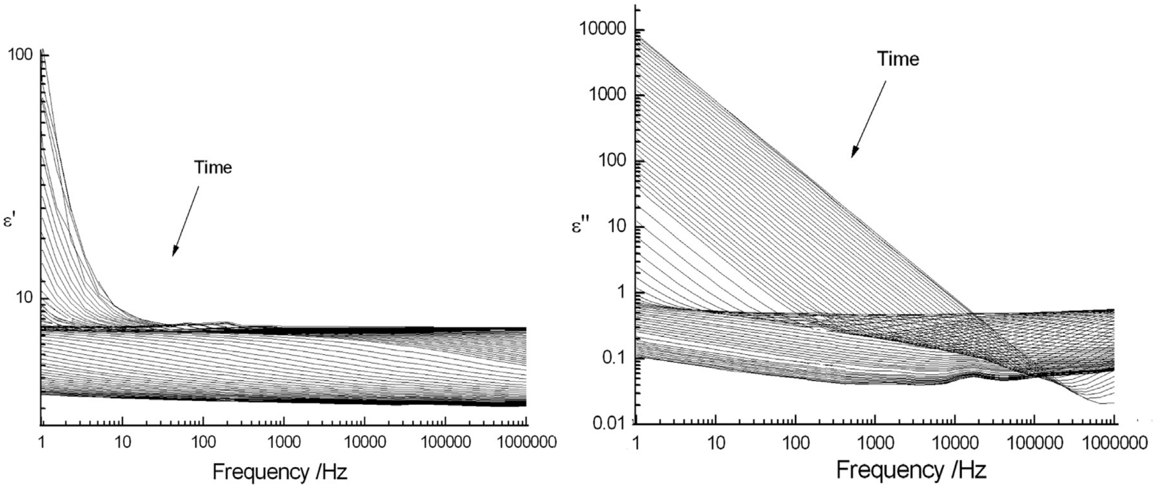
Fig. 4. Plot of the variation of the real permittivity [A] and loss [B] at 2 Hz as a function of time and temperature for system (1).

Table 4
Turning points for system 2 (times in s).

Cure Temperature /°C	ε'(1) /s	ε'(2) /s	ε" /s
System (1)			
25	10000	23000	> 40000
30	9000	23000	> 40000
35	6000	21000	22000
40	5500	19000	20000
45	4000	15000	15000
System (2)			
40	6000	16000	15500
50	3000	11000	10000
60	2050	7000	7500
70	1500	3500	6000
80	1000	3000	4500

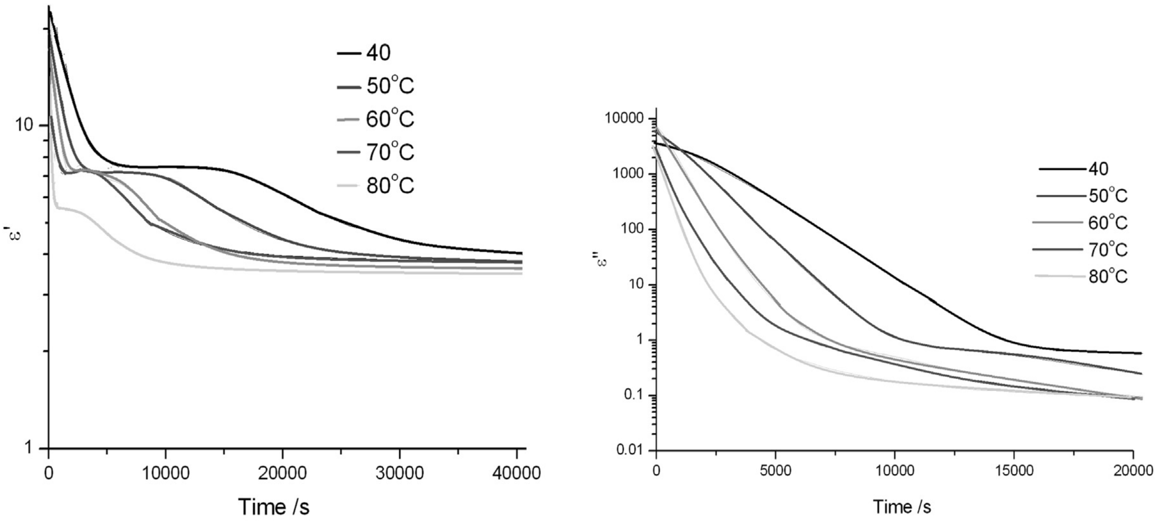
different behaviour, the initial conductivity being high and then decreasing with cure temperature before once more rising similar to system (2).

In principle, the changes in ε'(ω) should reflect the extent of dipole activity and hence should decrease with the extent of cure becoming essentially equal to ε_∞ once full cure has been achieved. However a detailed study of the dielectric characteristic as a function of temperature indicates that there still remains a small dipolar relaxation consistent with the cure process creating OH groups which are still active in the glassy state. Since the particular cure reaction will create different types of groups in the glass; some of the OH groups being involved in etherification reactions etc. the final dipolar activity will also be dependent on the cure process. The value of ε_∞ is influenced by the density of the matrix formed and this is influenced by the nature of the network formed and can be estimated using Cole-Cole plots. Using the data from Figs. 4 and 6 gave values of ε_∞ respectively of 3.3 and 3.5 for system (1) and (2) the calculated degrees of conversion can be



[A] [B]

Fig. 5. Variation of the dielectric permittivity ε'(ω) and loss ε"(ω) as a function of cure time for system (2) at 40 °C.



[A] [B]

Fig. 6. Plot of the time-temperature dependence of ε'(ω) and ε"(ω) at 2 Hz for system (2).

Table 5
ε"(ω) values as a function of viscosity (Pas) as a function of temperature and cure.

Temp. °C	10 Pas	100 Pas	1000 Pas	10000 Pas
System (1)				
25	180	100	40	11.5
30	120	110	102	70
35	40	11.5	10.2	5
40	80	40	11	10
45	60	20	10.5	6
System (2)				
40	35	20	10.5	4.5
50	45	30	17	6
60	120	70	40	10
70	170	100	70	30
80	300	160	130	100

obtained using

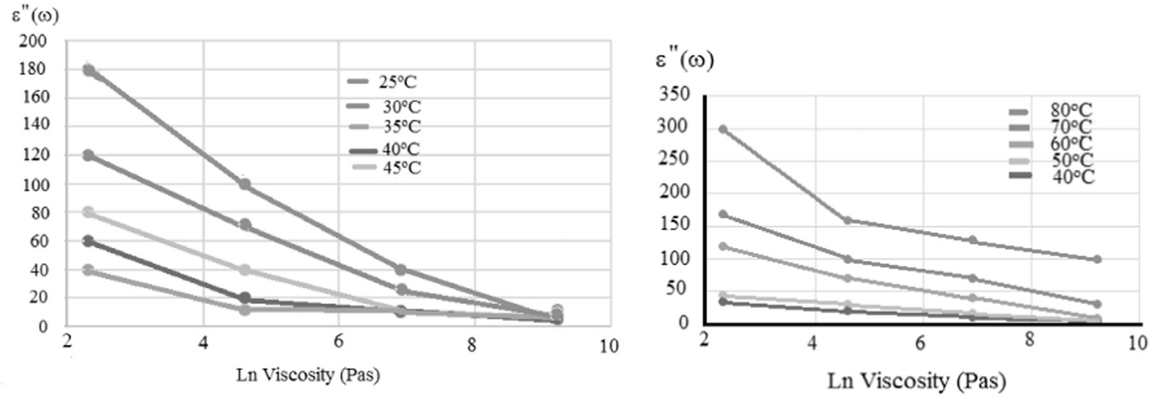
$$\textit{Degree of conversion} = 1 - \frac{\varepsilon_2^* - \varepsilon_\infty}{\varepsilon_2 - \varepsilon_\infty} \tag{5}$$

where ε_2^* is the asymptotic values of ε(ω) on the completion of the cure reaction,ε_1 is the initial value of the real permittivity after the conductivity loss has been quenched but before the transformation from gel to glass has started and ε_∞ is the infinite value obtained from Cole-Cole plots. The degree of conversion calculated using the data from Fig. 4A are presented in (Table 6). At low cure temperatures where the degree of cure is low the values obtained from the dielectric analysis are significantly lower than those obtained by DSC measurement as illustrated in system 1. However for higher degrees of cure the agreement is much better as illustrated for the higher temperature cure for system 1 and those measured for system 2.

The principle problem with this analysis is that the estimation of the value of ε_∞ requires dielectric measurements as a function of frequency on the complete cured resin and small changes in the value used can introduce a significant level of error into the calculations.

4. Conclusions

Measurement of the profile of the variation of ε"(ω) with time provides a method of identification of gelation however it appears significantly more difficult to correlate absolute values of ε"(ω) with values of the viscosity. The ability to use the dielectric method to aid cure monitoring requires calibration of the dielectric cure curves with the specific viscosity curves measured at the cure temperature. Because of the variation in the chemical nature of the network formed it is not possible to use residual values of ε'(ω) without calibration using a method such as DSC to determine the degree of conversion of resin to matrix and a knowledge of ε_∞ for a particular resin mixture. Estimates



[A] [B]

Fig. 7. Plots of ε"(ω) values against ln (viscosity) for system (1)-[A] and system (2)- [B] as a function of temperature.

Table 6
Calculation of the degree of conversion using dielectric permittivity data.

System (1) $\varepsilon_\infty=3.3$				
Temperature °C	30	35	40	45
ε_2^*	10.1	8.0	6.2	4.8
ε_2	11	9	8.5	7.5
% conversion	11	47	65	80
% conversion DSC	30	70	64	83
System (2) $\varepsilon_\infty=3.5$				
Temperature °C	40	50	60	70
ε_2^*	4.2	4.0	4.0	3.8
ε_2	7.5	7.3	7.2	7.2
% conversion	79	85	84	90
% conversion DSC	77	78	85	96

of ε_∞ can be made using Cole-Cole plots but this will require broad band dielectric measurements of the cured resin and calibration against DSC and density data. The dielectric method can however be used in situ and hence provides a useful method for cure monitoring in real moulding situations.

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