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Real-time dielectric studies of network formation in thermally activated epoxy–amine and isocyanate–triol systems

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Dielectric measurements are reported on the changes that occur in the nature of the dipole relaxation processes during cure of an epoxy–amine and a diisocyanate—triol system. The epoxy resin forms a vitrified solid in the final cured state, whereas the urethane retains its elastomeric properties. The initial behaviour for the epoxy resin is dominated by ionic conduction processes. Subtraction of the conductivity contribution reveals a dipolar relaxation process, which is analysed using the Havriliak–Negami (HN) equation. The characteristic exponent $1-n$ of the HN equation changes in a similar manner to that found with other epoxy–amine systems. However, the dipolar process in the urethane occurs at very high frequency and a different form of the $1-n$ dependence is observed. Sensitivity of the dielectric method for the detection of vitrification and gelation is critically assessed. If the vitrification is allowed to occur, then detection of a gel point may not necessarily be inferred from the dielectric data.

(Keywords: dielectric relaxation; network formation; thermal curing)

INTRODUCTION

An extensive literature exists on use of dielectric monitoring of the cure of thermosetting materials and, in particular, epoxy resins. Senturia and Sheppard[1] summarize the typical behaviour accompanying cure and have considered its molecular origins. The measured dielectric loss factor ϵ'' is generally represented by the sum of two components:

$$\epsilon'' = \epsilon''_{\mathrm{d}} + \sigma/(\epsilon_0\omega) \qquad (1)$$

a dipolar (ϵ''_{d}) and a conduction contribution, where σ is the d.c. conductivity, ϵ_0 is the permittivity of free space and ω is the angular frequency. Recently the validity of the method for determination of the gel and vitrification points has been extensively discussed[2–5]. Variation of the conductivity and locus of the dipolar loss with time reflects the influence of the local environment on the ability of a dipole to relax as cure occurs. Gelation is analogous to the temperature dependence of the dipole relaxation of an amorphous solid near to its glass transition temperature (T_{g})[4–6] and the analysis used is based on the assumption that the same factors influence cure and the glass transition process[7]. The phenomenological equations used to describe the curing-time dependence of the complex permittivity vary with temperature and conditions used in the cure process[8,9]. The chemical structure of the species involved in the curing process is rarely discussed specifically. This paper presents data on two very different systems: an epoxy–amine system, which cures to an amorphous glass, and a urethane, which cures to an elastomer.

EXPERIMENTAL

Materials

Epoxy resins. The mixture was prepared by mixing at room temperature a 1:1 stoichiometric mixture of the diglycidyl ether of bisphenol A (DGEBA) obtained from Dow Chemical Co. (DER 332), with diethylenetriamine (DETA) obtained from Aldrich Chemical Co. The DGEBA was accurately weighed into a glass vial with an appropriate amount of DETA. The sample was stirred thoroughly and degassed for about 10 min, at which point the hardener was completely dissolved and a clear homogeneous mixture obtained. Cure was carried out at 298 K.

Urethane. The urethane was produced by reaction of polyoxypropylated triol (OPT) with hexamethylene diisocyanate (HMDI); both compounds were obtained from Aldrich Chemical Co. The OPT has a molar mass of 722 g mol^{-1} and that of the HMDI is 168 g mol^{-1}. Reaction was achieved by the addition of 2×10^{-3} g of

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dibutyltin dilaurate per gram of reactant and cure was carried out at 298 K. The functionalities were determined to be 3 and 2 respectively for the OPT and HMDI using standard methods[10,11]. A stoichiometric ratio $r = 0.55$, defined as the initial ratio of the concentrations of isocyanate (NCO) to hydroxyl (OH) groups, was used to avoid complete gelation of the sample.

Dielectric measurements

Epoxy resin system. Cure of DGEBA/DETA was carried out using a Solartron 1250 frequency response analyser operating over the frequency range of 10^{-1} to 63×10^3 Hz, which at a data collection rate of 30 points per decade takes approximately 1 min to execute a frequency sweep. The cell was constructed from two pre-etched copper electrodes of 1 cm^2 active area mounted on a fibreglass base. The uncured resin mixture was injected into the cell and the whole assembly placed in an Oxford Instruments cryostat (DN1704)[12].

Urethane system. Relaxation of the molecular dipoles in this case occurs above 10^5 Hz at room temperature. Using a Hewlett-Packard 8753A network analyser, the frequency range from 300 kHz to 3 GHz can be investigated. The sample cell was thermostatted at 293 K and constructed from a 50 Ω gold-plated coaxial transmission line surrounded by a glass thermostatting jacket[13].

RESULTS AND DISCUSSION

Epoxy resin

The real and imaginary parts of the complex permittivity, $\epsilon'(\omega)$ and $\epsilon''(\omega)$ (*Figure 1*), were obtained at various times during the cure for DGEBA/DETA. the low-frequency part of the dielectric loss spectrum $\epsilon''(\omega)$ in the early stages of the cure exhibited a $1/\omega$ dependence. Similar behaviour has been observed by many workers[1-6] and can be attributed to a combination of ionic conductivity and blocking electrode effects. The parallel-plate structure of the cell allows generation of a double layer at the electrodes and observation of a *blocking electrode effect*. Epoxy resins are synthesized from epichlorohydrin, and low levels of chloride, sodium and hydrogen ions are present in the epoxy resin component. As the molar mass of the polymer increases, so does the viscosity, and a corresponding reduction in the amplitude of the low-frequency loss process is observed. Reduction in the amplitude is consistent with an increased microscopic viscosity but is *not* uniquely connected to the changes in the macroscopic viscosity.

A number of methods have been proposed for the subtraction of the conduction and blocking electrode effects[14-17]. If the process is only associated with ionic conduction then a $1/\omega$ component can be subtracted. Alternatively, the electrical modulus approach can be used, in which the complex modulus $M^* = 1/\epsilon^*$ is computed, where:

$$M' = \frac{\epsilon'}{(\epsilon')^2 + (\epsilon'')^2} \qquad M'' = \frac{\epsilon''}{(\epsilon')^2 + (\epsilon'')^2} \qquad (2)$$

The modulus analysis (*Figure 2*) allows identification of the point at which the contributions from ionic conduction and blocking electrodes become undetectable. associated with the microscopic viscosity being sufficiently high as to inhibit ion migration between electrodes. It is correct to associate a decrease in the loss at low frequency with an increase in the viscosity, but there is no direct connection between it and formation of the gel network. An increase in the local viscosity is a direct consequence of the formation of a network topography[7]. The nature of the interfacial polarization process would lead to the prediction that, as the conductivity decreases, so the frequency of the process would move to lower frequency, as would appear to occur from *Figure 2b*. However, the change of thickness of the double layer associated with the blocking electrode effects would also lead to a shift of the process to higher frequency, making further analysis of the shift in the relaxation unreliable. Loss in amplitude is more clearly connected to an increase in the viscosity and to the gelation process.

Subtraction of the lower-frequency process reveals clearly a dipolar process, which moves to lower frequency as cure proceeds. This feature occurs above the frequency range of the measurements in the very initial stages of cure and is associated with dipole motion

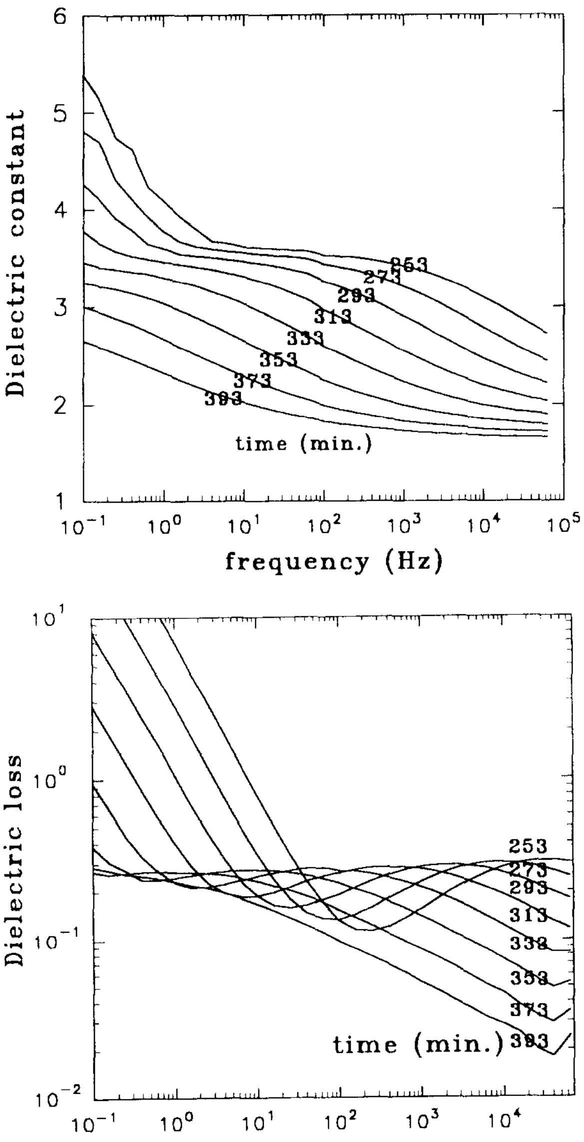


Figure 1 Variation of (a) the real (ϵ') and (b) the imaginary (ϵ'') parts of the dielectric constant with time for DEGBA/DETA cured at 298 K

of the components of the curing polymer (*Figures 1a* and *1b*). In the uncured resin the dipole activity arises from the amine, bridging ether and epoxy ring groups. Rotation of the molecule will completely relax the dipole orientation and occurs relatively easily in the low-viscosity state. After coupling, the epoxy ring is converted into a hydroxyl group and one of the NH bonds is lost. The changes in the dipolar components are illustrated in *Scheme 1*.

Increase in the molar mass will reduce whole-molecule rotation and relaxation will occur by reorientation of the chain between the two phenyl groups, leading to cooperative motion of the hydroxyl, ether bridge and amine bridge groups. Gelation is associated with the development of a high-molecular-weight matrix and observation of viscoelasticity at low frequency. In practice, the additional cooperative relaxation will broaden the relaxation process towards lower frequencies. In such a structure the component of the dipole that lies along the chain direction can only be relaxed by either whole-molecule rotation or normal-mode motion[16,17]. The dipolar components are shown in *Scheme 2*.

Cooperative rotational motion of a segment of the chain backbone is closely associated with the glass transition process[18] and may be described by the Havriliak–Negami equation[19]:

$$(\epsilon^* - \epsilon_\infty)/(\epsilon_0 - \epsilon_\infty) = \left[1 + (i\omega/\omega_g)^{1-\alpha}\right]^{-\beta} \qquad (3)$$

where ω_g corresponds to the frequency of the glass transition process, $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$ is the dielectric increment associated with the relaxation, and ϵ_0 and ϵ_∞ are respectively the dielectric constants at low and high frequency. The exponents α and β are characteristic parameters of the relaxation process and are indicative of both the number of different types of process and the width of distribution of each process contributing to the observed relaxation feature. In the case of a simple molecule undergoing free rotation, the process would approximate to a simple Debye relaxation with $\alpha = 0$ and $\beta = 1$. However, in the case of most polymeric materials, restrictions on the nature of the chain relaxation processes lead to asymmetry of the spectrum.

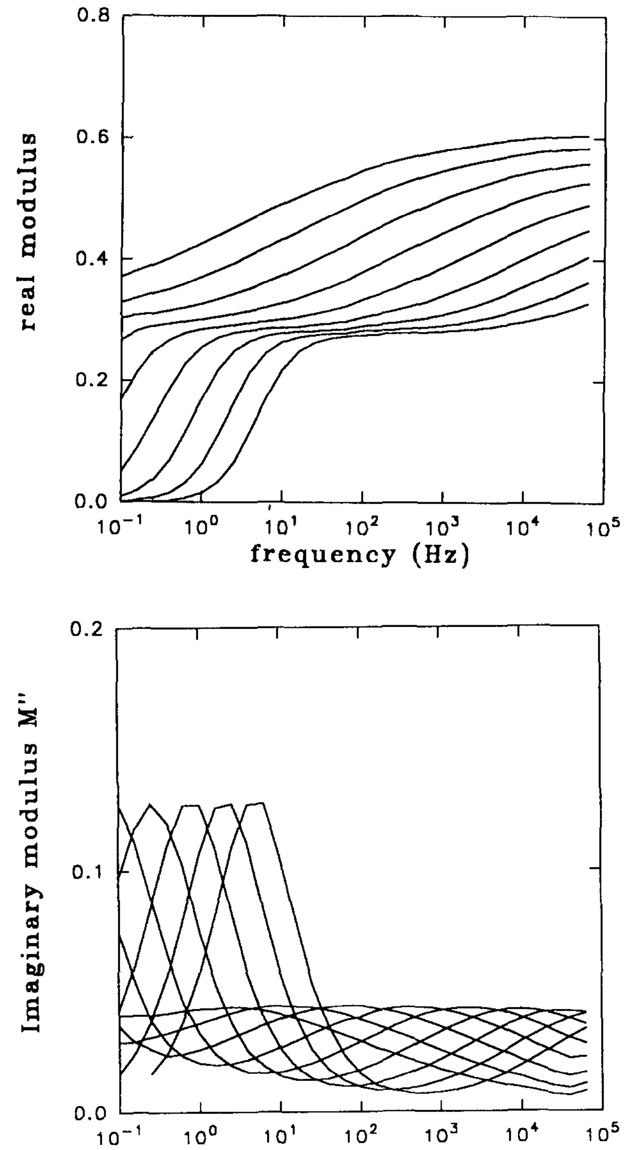
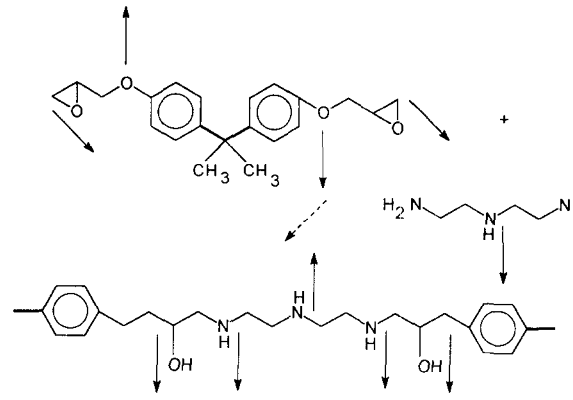
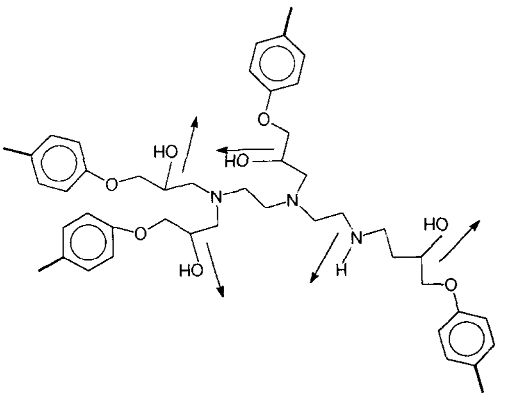


Figure 2 Variation of (a) the real (M') and (b) the imaginary (M'') parts of the modulus of the dielectric data for DEGBA/DETA at 298 K



Scheme 1 Initial stages of reaction for the epoxy resin system. The full arrows indicate dipoles that can contribute to the relaxation process



Scheme 2 Intermediate stages of cure for the epoxy resin system. The full arrows indicate dipoles that can contribute to the relaxation process

The data may thus be analysed assuming two frequency domains separated by ω_g and corresponding to: $\epsilon'' \propto \omega^m$ for $\omega/\omega_g \ll 1$ with $m = 1 - \alpha$, and $\epsilon'' \propto \omega^{n-1}$ for $\omega/\omega_g \gg 1$ with $1 - n = \beta(1 - \alpha)$. The exponents m and n can be determined from fitting the data using the Havriliak–Negami equation. The results of this analysis are presented in *Table 1* and their variation with cure time illustrated in *Figure 3a*.

Table 1 Results of the Havriliak–Negami fit of the experimental data for DGEBA/DETA cured at 298 K

Time (min)	ϵ_0	ϵ_∞	f_c (Hz)	m	β	$1 - n$
273	3.54	1.77	2500	0.55	0.48	0.27
293	3.56	1.75	508	0.50	0.53	0.27
313	3.52	1.77	115	0.48	0.59	0.28
333	3.58	1.74	26	0.46	0.65	0.30
353	3.42	1.72	5	0.45	0.72	0.32
373	3.38	1.67	1	0.42	0.77	0.32

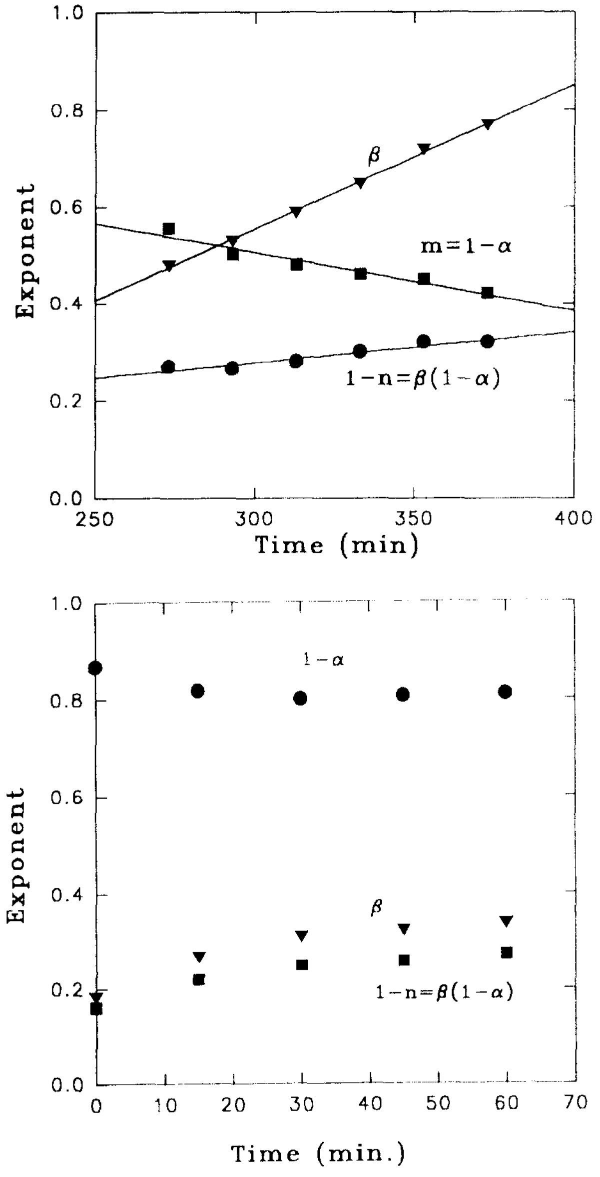


Figure 3 Variation of the exponents m and $1 - n$ of the Havriliak Negami equation during cure for (a) DEGBA/DETA and (b) HMDI/OPT at 293 K

The dipole process appears in the frequency window 10^{-3} to 10^5 Hz only after gelation, estimated from viscoelastic measurements to be 200 min, has occurred. In the gel phase, the value of $1 - n$ increases slightly from 0.27 to 0.32 and no plateau value is reached, indicating that the changes in the process are continuing up to the point where dipolar relaxation is occurring slower than 10^{-1} Hz. In DGEBA the phenyl groups can physically interact and this will lead to significant loss of mobility of the matrix and ultimately to vitrification.

Urethane system

In the urethane system relaxation occurs at frequencies in excess of 1 MHz and reflects the intrinsic mobility of this system in comparison to epoxy resins. Evolution with time of the real and imaginary components of the complex permittivity (*Figure 4*) is similar to that observed at lower frequency for the epoxy resin system. The HMDI and OPT are of sufficiently low molar mass to exhibit whole-molecule rotational diffusion as the preferred mechanism for dipole relaxation. However, as

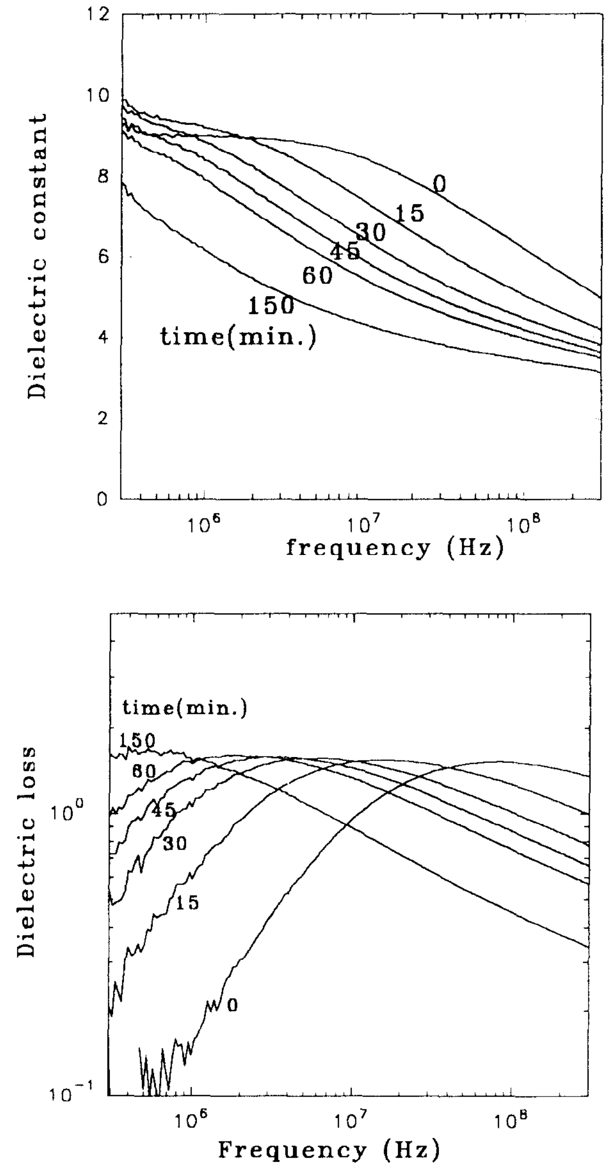
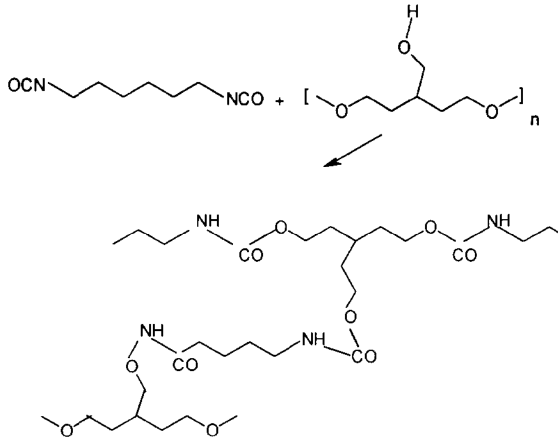


Figure 4 Variation of (a) the real (ϵ') and (b) the imaginary (ϵ'') parts of the dielectric constant with time for HMDI/OPT cured at 293 K



Scheme 3 The reaction in the urethane system

reaction (*Scheme 3*) proceeds, so segmental relaxation of the urethane group will replace the dominance of isocyanate and hydroxyl groups on the relaxation spectrum, reflected in the breadth of the relaxation feature.

The initial breadth of the peak is influenced by the differences in the rotational diffusion constants of the reactants, HMDI and OPT, and their dipole activities. As reaction proceeds the nature of the dipole is changed, reflected in both relaxation frequency and its amplitude. *Once 50% conversion has been achieved, the dominant dipole will be that of the urethane.* However, since this can itself become hydrogen-bonded to neighbouring groups, the final magnitude will reflect whether or not significant order has been generated in the system. In the present study the ratios were selected so as to retain an elastomer throughout the whole process. The shift with time of the dipole relaxation will reflect the constraints imposed on the dipole motion by chemistry occurring in its neighbourhood and effectively slowing the rotational process. An additional and constant contribution to the dipole activity will be the ether oxygen. It is well known that the dipole relaxation of polyethers involves dipole components both perpendicular to and along the chain axis. The dominant relaxation is of the component perpendicular to the axis; however, in certain cases the component along the axis has been shown to demonstrate characteristics of the normal-mode spectrum of the polymer in solution[17,18]. The observed spectrum will contain components associated with all the active dipoles and their resolved components. Changes in the breadth of the spectrum therefore reflect the change in this distribution as well as the influence of the local environment. In the case of the urethanes, the final material is an elastomer, and therefore the vitrification processes observed with epoxy resins are not observed in this case. Hence at the latter stages of the cure, the dipole process still lies in the MHz region.

Changes in the high-frequency relaxation behaviour of the urethane system resemble closely that of the epoxy resins. The exponent $1-n$ (*Table 2* and *Figure 3b*) increases rapidly in the early stages of cure from 0.15 to 0.28 and then remains constant between 60 and 150 min, although the reaction is still proceeding.

In order to determine whether the exponent $1-n$ remains constant in the gel phase, an experiment was carried out on a mixture with stoichiometric ratio $r = 1$ at 283 K. The relaxation process appears in the experimental window only at the end of the reaction. A value of $1-n = 0.35$ was obtained, which indicates that the exponent increases in the gel phase as in the case of DGEBA/DETA systems.

Table 2 Results of the Havriliak–Negami fit of the experimental data for HMDI/OPT cured at 293 K

Time (min)	ϵ_0	ϵ_∞	f_c (MHz)	m	β	$1-n$
0	9.05	1.45	21	0.80	0.30	0.25
15	9.45	1.90	4.51	0.80	0.32	0.26
30	9.85	2.15	1.92	0.72	0.38	0.27
45	9.95	2.26	1.065	0.72	0.39	0.28
60	10.10	2.35	0.579	0.72	0.40	0.29
150			–	–	–	0.29

CONCLUSIONS

From these studies the dielectric behaviour is consistent with the concept that the dipole relaxation is initially controlled by the microviscosity, which is for a simple liquid equivalent to the low-frequency Newtonian limiting value. However, as the cure process proceeds, the relaxation of the dipoles, whilst still being sensitive to the microscopic viscosity, no longer will reflect the whole-molecule motions of the growing cluster but reflect segmental motion of the chain element of which they are a part. Changes in the relaxation-time distribution reflected in the parameter $1-n$, relative to the high-frequency part of the spectrum, are indicative of a complex interplay of effects associated with transformation of the molecular dipole as a consequence of reaction and the effect of cluster growth on the microviscosity influencing rotational motion. As pointed out recently in the literature, it must be emphasized that the dipole relaxation senses the local intra- and intermolecular potentials and hence network formation, which primarily leads to development of viscoelastic elements in the spectrum that are not directly sensed by the dipole probe. It is important, however, to realize that the component along the chain axis is sensitive to this latter effect and is reflected in the distribution of the observed processes. Thus the parameter $1-n$ does reflect these changes, but not necessarily in a direct way.

This paper emphasizes that, in order to understand the observed changes, it is *essential* to consider the nature of the species producing the relaxation and not follow the custom of ignoring the chemical processes that are occurring.

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