Dielectric Study of Epoxy Vitrification: Does a Percolation Model Apply?

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ABSTRACT: Dielectric measurements were performed during the cross-linking reaction of an epoxy/amine system. Two transitions are successively crossed: the gelation which is a transition of connectivity and the vitrification which is a transition of mobility. It is found that dielectric measurements are insensitive to gelation but nevertheless are a powerful method of investigation for the vitrification process. This latter transition is interpreted as a percolation of growing vitreous domains.

Introduction

The gelation transition occurs when the increase of connectivity between monomers leads to an infinite macromolecule. This transition is widely studied, and among the various theoretical models proposed to describe this critical phenomenon, the percolation approach seems to be the most appropriate.[1] On the other hand, the glass/liquid transition, which occurs with increasing temperature, is described by some authors[2-4] in terms of a mobility or a free volume percolation. As the temperature increases, mobility islands grow and the material becomes liquid when these islands percolate.

In the case of many cross-linking systems, the increasing connectivity decreases the local mobility of the polymer and leads to an increasing glass transition temperature of the material. Therefore, depending on the temperature and on the frequency of investigation, the material transforms from a liquid or rubber state (depending on the degree of connectivity) to a vitreous state, without changing the temperature. Until now, this vitrification process was studied from molecular relaxation point of view,[5] and this paper attempts to apply the percolation model in this context.

Experimental Section

Materials. The investigated epoxy/amine system was diglycidyl ether of Bisphenol A (DGEBA) which is cross-linked by diaminodiphenyl sulfone (DDS). DGEBA was purchased from Dow Chemical (DER 332), and DDS was purchased from Fluka Chemical Co. The required amount of resin (DGEBA) was accurately weighed into a glass vial and the appropriate amount of hardener (DDS) added. The vial containing the sample was stirred and degassed for about 7 min, at which point the hardener had dissolved and the mixture appeared homogeneous. The advancement of the chemical reaction after dissolution was determined by differential scanning calorimetry (DSC) and was found to be less than 5%. In this study, the epoxy/amine systems were prepared in a 1:1 stoichiometric ratio, without catalyzer or solvent, and the chemical reaction is only induced by the temperature.

Dielectric Measurements. Measurements were performed using a SOLARTRON 1250 frequency response analyzer operating over a range from 10^{-1} to 6×10^5 Hz. The frequency range can be covered by 30 data points, and the collection time was approximately 1 min. This collection time is sufficiently short to approximate a set of data as an instantaneous snapshot of the dielectric properties of the material. A cell was designed which consisted of two preetched copper electrodes of a 1-cm^2 active area mounted on an epoxy glass fiber base. This design generates a three-electrode system and was placed in an Oxford Instrument cryostat (DN1704). The space between the electrodes was maintained constant with a copper spacer, and the electrodes and spacer were soldered together to form a seal around three edges. The resin to be studied was injected as a liquid into the cell, with capillary action ensuring that the cell was completely filled. The electrodes are in good thermal contact with a copper block which was used to maintain the temperature of the sample as required for isothermal cure studies.

The method used for the dielectric measurements was described elsewhere.[6] The experiments were performed isothermally in a temperature range from 120 to 170 °C.

Experimental Results

The calculated real and imaginary parts of the complex permittivity, $\epsilon'(\omega)$ and $\epsilon''(\omega)$ respectively, are most conveniently presented in the form of three-dimensional plots (Figure 1). The dielectric data may be subdivided into two regions: the first corresponds to the low-frequency part of the spectrum at the beginning of the chemical reaction and the second to the higher-frequency part of the spectrum for the longer cure time.

At short cure time and low frequency, an important ionic conductivity process is revealed by dielectric loss varying as $1/\omega$. Classically the epoxy resin synthesis comes with H^+Cl^- apparition, which is neutralized afterward. These ions remain in the medium at a constant concentration during the cross-linking reaction, and their migration induces a loss current increasing with decreasing frequency. Progressively, with increasing viscosity, this ionic conductivity tends to vanish. Examination of the real part of the dielectric permittivity indicates that this region contains not only a large conduction loss but also a large relaxation process (Figure 1). This process is very much larger than would be expected for a simple dipolar relaxation process and may therefore be connected with the high ionic conductivity of the material and a possible interfacial polarization. These two processes mask the possible manifestation of the sol/gel transition which occurs during this time period as was shown in previous rheological studies.[7] However, their interpretation needs further experiments to be elucidated and will be developed in another paper.

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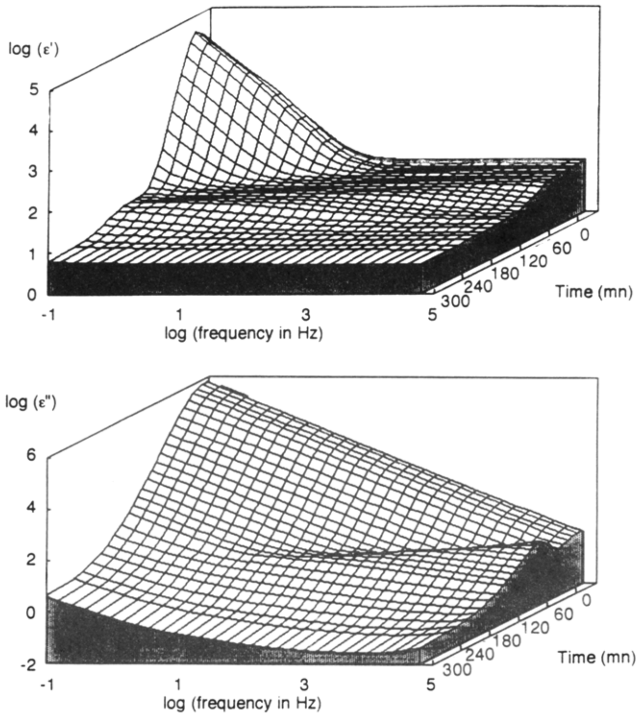

Figure 1. Three-dimensional representation of dielectric spectra during the cure of DGEBA–DDS at 150 °C.

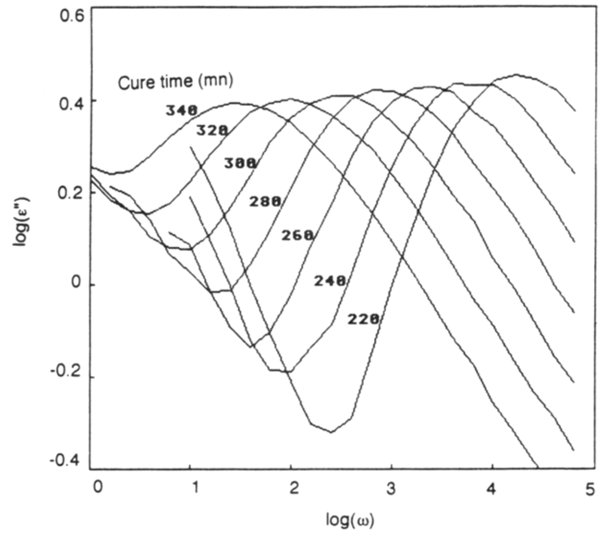

Figure 2. Evolution of α-relaxation spectra (after subtraction of direct current conductivity) during the cure at 130 °C.

At longer cure time another relaxation process appears from the high-frequency part of the frequency window. This process is more particularly studied in this work. This part of the dielectric spectrum can be associated with a dipolar relaxation. It corresponds quite well to the α-relaxation spectrum of the epoxy resin DGEBA described in the literature.[8,9] This relaxation is the manifestation of the vitrification in the frequency domain. So, during the course of the chemical reaction which leads to the network formation, the increasing glass transition temperature of the system would manifest itself by a decreasing relaxation frequency ω_g. This is effectively observed in Figure 2, where the frequency ω_g is shown to decrease by more than 3 decades as the cross-linking reaction proceeds. It is important to emphasize that the variation of the frequency ω_g, corresponding to the high-frequency limit of the viscoelastic domain, has an influence on the viscoelastic properties near the sol/gel transition. This problem is widely discussed in another paper.[10]

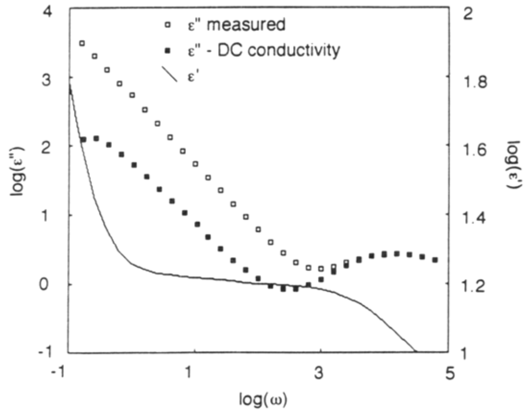

Figure 3. Example of subtraction of the direct current conductivity from the dielectric loss measured at 150 °C after 120 min of cure.

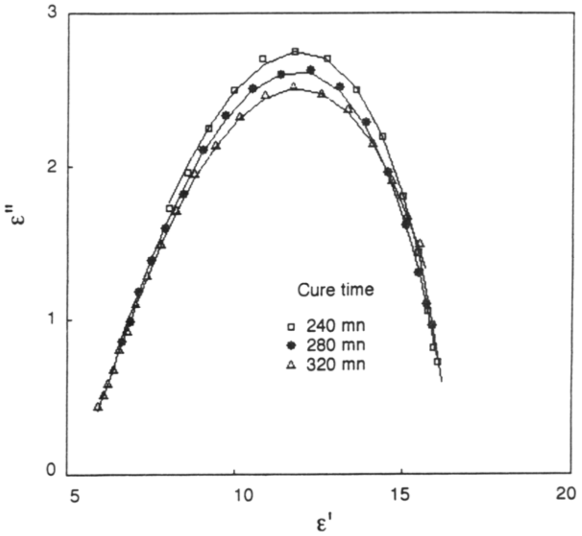

Figure 4. Example of Cole–Cole representation of the α-relaxation spectra obtained during the cure of DGEBA–DDS at 130 °C (points correspond to experimental data and lines to best fits).

During the earlier stage of cure, this α-relaxation process overlaps with the ionic conductivity discussed above and it is necessary to subtract this contribution before analyzing the dipolar relaxation spectrum (Figure 3).

A Cole–Cole representation of the data (Figure 4) clearly shows a dissymmetry between the low- and high-frequency parts of the relaxation spectrum. The symmetric situation corresponds to a semicircle Cole–Cole plot which would be obtained for Debye's liquid. Here, the Cole–Cole representations are not symmetric, and moreover, during the cure, the evolution of each part of the spectrum is quite different. To describe the data, the low- and high-frequency limits of the relaxation spectrum are usually fit to the forms[11]

$$\epsilon'' \sim \omega^{m} \qquad \text{for } \omega/\omega_g \ll 1$$

$$\epsilon'' \sim \omega^{n-1} \qquad \text{for } \omega/\omega_g \gg 1 \qquad (1)$$

where m and n are two exponents which must be determined from fitting the data. To determine precisely the value of these exponents, the data were fitted by numerical method using the Havriliak and Negami phenomenological equation[12]

$$(\epsilon^* - \epsilon_\infty)/(\epsilon_s - \epsilon_\infty) = [1 + (i\omega/\omega_g)^{1-\alpha}]^{-\beta} \qquad (2)$$

Table I
Results of the Havriliak and Negami Fits of Experimental Data

	time (min)	log ϵ_∞	log ϵ_s	log ω_g (Hz)	$m = 1 - \alpha$	β	$1 - n = \beta(1 - \alpha)$
120 °C	270	4.25	15.0	3.56	0.79	0.42	0.33
	300	4.66	14.9	3.12	0.74	0.50	0.37
	330	4.79	15.0	2.66	0.68	0.57	0.38
	360	4.85	15.0	2.16	0.64	0.61	0.39
	390	4.78	15.1	1.60	0.61	0.63	0.38
	420	4.76	15.3	1.04	0.58	0.65	0.38
	450	4.72	15.8	0.40	0.55	0.66	0.36
130 °C	220	5.11	16.4	3.83	0.78	0.47	0.37
	240	5.05	16.5	3.38	0.75	0.47	0.36
	260	5.28	16.4	2.99	0.72	0.53	0.38
	280	5.28	16.5	2.54	0.69	0.54	0.37
	300	5.33	16.7	2.12	0.65	0.59	0.38
	320	5.33	17.0	1.65	0.61	0.62	0.38
	340	5.35	17.1	1.19	0.59	0.64	0.38
140 °C	165	5.17	16.2	3.91	0.78	0.46	0.37
	180	5.29	16.3	3.53	0.72	0.54	0.39
	195	5.47	16.3	3.15	0.68	0.61	0.41
	210	5.55	16.5	2.69	0.64	0.64	0.41
	225	5.51	16.9	2.21	0.60	0.68	0.41
	240	5.44	17.1	1.68	0.57	0.67	0.38
	255	5.51	17.7	1.21	0.53	0.76	0.40
	270	5.49	18.4	0.72	0.48	0.85	0.40
150 °C	120	5.20	16.0	3.83	0.72	0.54	0.39
	130	5.70	16.1	3.48	0.67	0.65	0.44
	140	5.64	16.2	3.06	0.64	0.67	0.43
	150	5.60	16.4	2.60	0.60	0.69	0.42
	160	5.63	16.7	2.12	0.58	0.71	0.41
	170	5.52	17.1	1.58	0.56	0.69	0.39
	180	5.54	17.4	1.08	0.54	0.71	0.39
160 °C	110	4.52	14.3	3.81	0.72	0.50	0.36
	120	4.77	14.3	3.30	0.69	0.55	0.38
	130	5.00	14.6	2.81	0.63	0.64	0.40
	140	5.00	14.9	2.20	0.60	0.65	0.39
	150	4.99	15.2	1.57	0.58	0.65	0.37
	160	4.95	15.6	0.94	0.56	0.66	0.37
170 °C	80	4.98	14.9	4.19	0.71	0.56	0.40
	90	5.21	15.0	3.55	0.66	0.62	0.41
	100	5.37	15.5	2.90	0.58	0.73	0.42
	110	5.40	16.0	2.15	0.54	0.77	0.42
	120	5.35	16.6	1.29	0.53	0.73	0.39

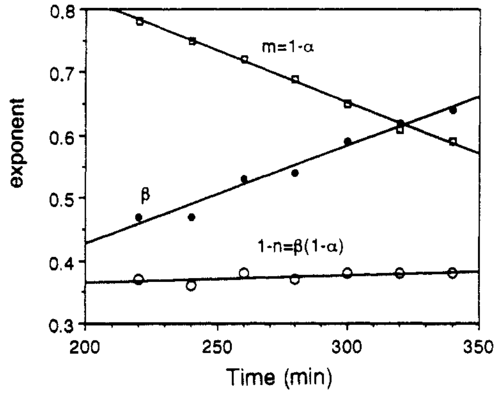

Figure 5. Variation of the exponents m and $1 - n$ during the cure of DGEBA-DDS at 130 °C.

where ϵ^* is the complex permittivity, and ϵ_∞ and ϵ_s are the dielectric constants at infinite frequency and zero frequency, respectively. This expression describes both the low- and high-frequency parts of the relaxation spectrum. The two limits of this equation are

$$\epsilon'' \sim \omega^{1-\alpha} \quad \text{for } \omega/\omega_g \ll 1$$

$$\epsilon'' \sim \omega^{-\beta(1-\alpha)} \quad \text{for } \omega/\omega_g \gg 1 \qquad (3)$$

The fit was driven simultaneously for the five parameters of the Havriliak and Negami equation. The results are reported on Table I. Figure 5 shows an example of the variation of the exponent $m = 1 - \alpha$ and $1 - n = \beta(1 - \alpha)$. While $1 - n$ is rather constant between 0.3 and 0.4, m decreases continuously during the cure.

Discussion and Conclusion

The values and the evolutions of the exponents n and m can be simply interpreted. In order to describe the dielectric behavior of many heterogeneous materials having a more or less granular structure, some authors[13-15] suggested that the high-frequency part of the spectrum reflects the cooperative motions inside a grain, while the low-frequency part reflects their interactions. In addition, if the percolation model is used to describe the glass transition in the case of polymers,[2-4] it is possible to imagine that a grain will correspond to a correlation volume of the dipolar motions and that the high-frequency part of the spectrum is an indication of the self-similar nature of these percolation clusters. In this approach, the predicted value of the exponent governing this part of the spectrum is $1 - n = 0.3$ ($n = 0.7$),[16,17] in agreement with our experimental results. In this framework, it is important to note that this predicted value of the exponent was verified for gelation in the same chemical system investigated by rheological measurements.[18]

The evolution of the exponent m, which governs the low-frequency behavior, may be interpreted as a continuous crossover from Debye's liquid ($m = 1$) to a vitreous solid, zero being the value of m for a perfect solid without any relaxation process.[13]

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