

Evolution of Ion Mobility in Cured Epoxy-Amine System as Determined by Time-of-Flight Method

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ABSTRACT: The concept of the time-of-flight (TOF) method for the determination of ionic carriers' mobility is presented. This method is used for the model system, the properties of which (including viscosity) change with time: the isothermally cured epoxy-amine system. It is demonstrated that the form of the TOF current signals depend on the material of the electrodes. The Cu, Ag, Al, and Au electrodes were tested; of these, the Cu and Au electrodes have yielded the most distinct TOF signals and therefore were chosen for further experiments. The investigated samples were placed between parallel electrodes with guard rings distanced with polyethylene terephthalate (PET) films of different thickness (0.02–0.2 mm). According to the predictions, it was found that the TOF of the ionic carriers increases with an increase of the distance between the electrodes (for constant electric field) and decreases with an increase of the electric field (for constant distance). The series of measurements performed for the well-known epoxy resin system diglycidylether of bisphenol A with diamino-4,4'-dimethyl-3,3'-dimethyldicyclohexylmethane, isothermally cured at different temperatures, have confirmed that in a course of the curing, below the gelation, the conductivity decreases following the decrease of the ionic mobility due to the viscosity increase during the reaction. However, with an advancement of reaction, deviations from that linear relationship are observed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1143–1150, 1997

Key words: ionic carriers mobility; ion conductivity; time-of-flight of ionic carriers; direct-current measurements; epoxy-amine system under isothermal curing

INTRODUCTION

The ability to predict and monitor polymer-processing operations is an important aspect in the development and control of polymer material fabrication. The epoxy resins provide a unique combination of properties, making them one of the most important polymer groups that have a wide range of applications where a high performance in terms of resistance to chemical, mechanical, and electri-

cal properties is required. The uncured epoxies are thermoplastic, but they can be transformed into an insoluble and infusible form by three-dimensional crosslinking as an effect of complex chemical reactions between the functional groups of the resin and the hardener occurring at adequate temperature. These processes are accompanied by changes of the physical properties of the system connected with phase transitions: gelation and/or vitrification. An important problem is the determination of the viscosity of the reacting system *in situ*, as a function of curing time and temperature, because direct, on-line measurements of viscosity are usually not possible.

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In recent years, electrical techniques, like microdielectrometry,^{1–7} have attracted increasing interest because they allow continuous monitoring of the advancement of reaction of the curing resin in a nondestructive way. These methods are already used in the plastic industry. In order to generalize these methods for the different kinds of resins and for different processing techniques, it is important to understand the physical basics of the observed phenomena during the curing process.

In a polymer system, viscosity and ion conductivity are macroscopic and microscopic properties, respectively, that characterize chain segment mobility and ion mobility. In general, an inverse proportionality between viscosity and ion conductivity is assumed^{2,7–9}; however, the studies performed so far on the ion conductivity of polymer systems undergoing phase transitions^{2,3,5,6,8–11} do not allow the development of the relationships between ion conductivity, viscosity, and changes in the polymer system.

The ionic conductivity is determined by a concentration of ions and their mobility. It is known that these quantities can be influenced by the chemical structure of polymers, by incorporated salt species, and in the solid state, by morphology, for example, the degree of crystallinity.^{12–15} It was claimed several times that close correlations have been found between the evolution of the ionic conductivity and an advancement of the network formation during the resin cure, allowing the occurrence of gelation and/or vitrification to be determined.^{16–18} However, it is still not well recognized how variables such as polymer structure, polymer chain length, and crosslinking density affect the ion mobility and the ion concentration, and therefore, the ion conductivity. In particular, it is difficult to explain how the occurrence of the gelation, influencing the macroscopic viscosity, may affect the ionic conductivity that is dependent on local, microscopic viscosity.

In order to gain a fundamental understanding of the correlation between electrical and chemorheological phenomena, the mechanism of ionic conduction in reactive polymers has to be clarified. It means that not only the changes of the conductivity but also the evolution of fundamental physical quantities, concentrations and origin of mobile ions and their mobility, have to be investigated. There are relatively few published results on ionic mobilities in polymers in general. This article describes the first attempt on the direct

measurements of the evolution of ionic mobility in a course of resin curing by means of the time-of-flight (TOF) method.

EXPERIMENTAL

TOF Concept

The ionic mobility can be evaluated from direct-current (dc) measurements on the cell with ion-blocking electrodes. The dc voltage (U) is initially applied to the cell in one direction for a long time in order to accumulate all mobile ions in the vicinity of the electrodes. The polarity of the applied voltage is then reversed, and the flowing current is recorded. When the ionic carriers reach the opposite electrode, they will accumulate again near that electrode, leading to a decrease of mobile ionic carrier concentration and, consequently, to a decrease of the conduction current. If this decrease of current can be detected, it would allow one to determine an average TOF (τ) of ions over the sample thickness. Then, by taking into account the sample thickness (d), it will be possible to calculate the ion mobility (μ) from eq. (1):

$$\mu = \frac{d^2}{\tau U} \quad (1)$$

Measurement Technique

The measuring circuit consists of a Keithley 617 electrometer (Keithley Instruments, Inc., Cleveland, Ohio) with an incorporated voltage source, a PC computer for a data acquisition, storage, and handling, and a thermoregulated measurement oven (Fig. 1). Sandwich-type configuration of the sample was chosen for measurements, with two parallel plates with round electrodes ($\phi = 16$ mm) and with guard rings. The plates are distanced with PET film of different thickness (0.02–0.2 mm). The resin sample (which is a viscous liquid at the beginning) is placed between preheated plates and then put in the thermostated oven. Various metals were used as the material of the electrodes: Cu, Ag, Al, Au.

The voltage cycle used for the TOF measurements is presented in Figure 2(a). The current signals corresponding to this cycle are schematically presented on Figure 2(b).

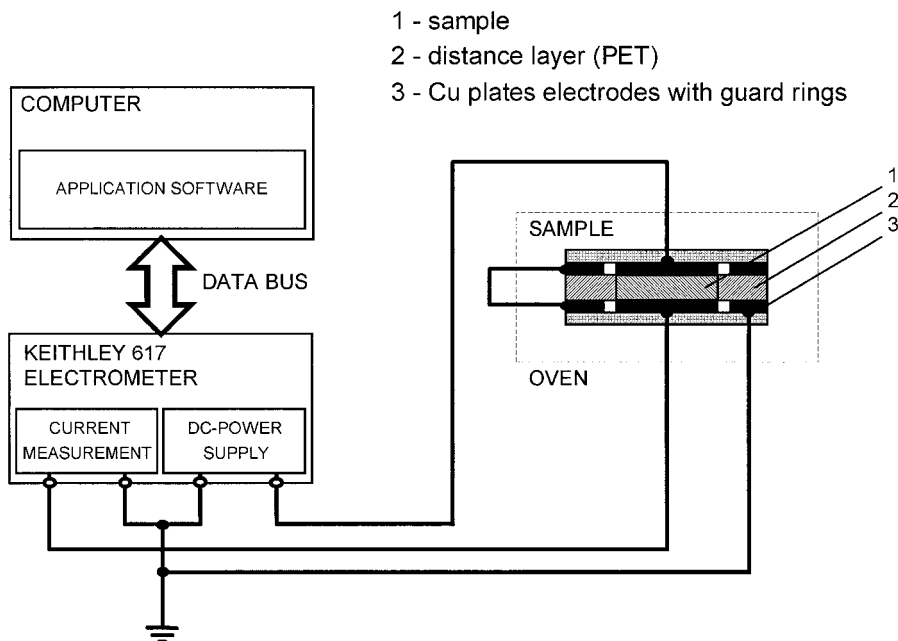


Figure 1 Schematic diagram of the TOF measurement circuit.

Materials

The measurement series have been done for a stoichiometric mixture of the epoxy resin system diglycidyl ether of bisphenol A (DGEBA) with diamino-4,4'-dimethyl-3,3'-dimethyldicyclohexylmethane (3DCM) isothermally cured at different

temperatures. The characteristics of DGEBA and 3DCM components are listed in the Table I.

The reactions occurring in the DGEBA-based epoxy-amine system during curing are shown schematically below²:

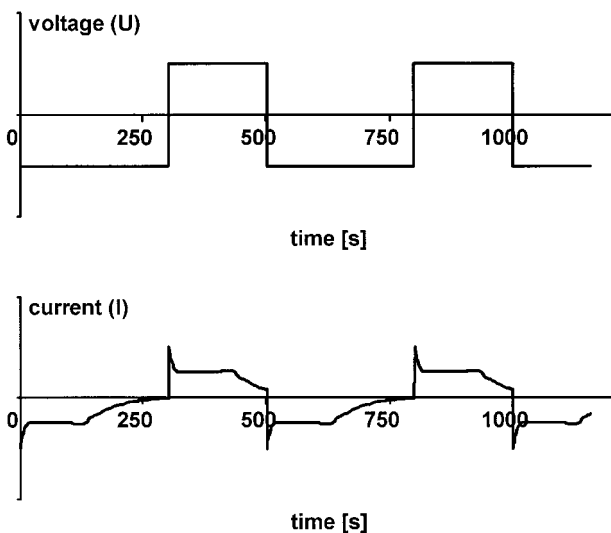
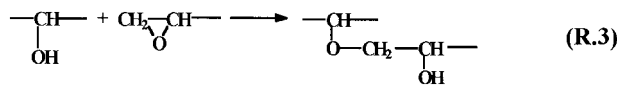
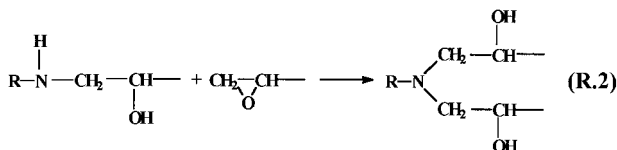
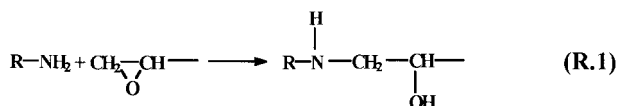
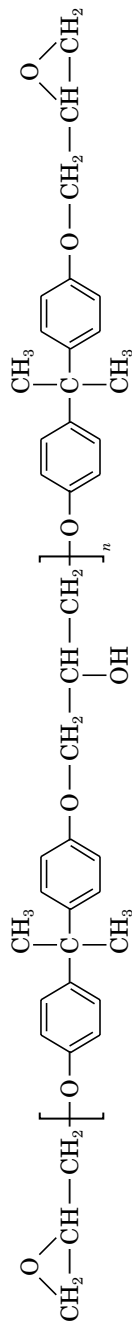
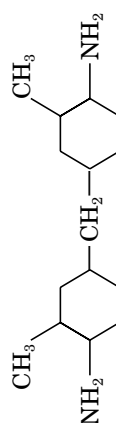


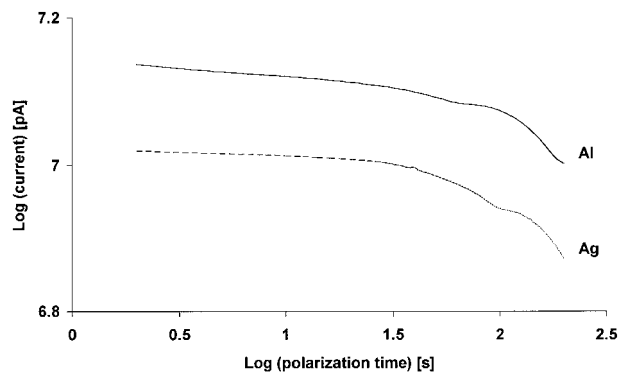
Figure 2 Scheme of (a) voltage and (b) current time dependences during the TOF measurements.

RESULTS AND DISCUSSION

In the early stage of curing, the reacting polymer is a viscous liquid. It is well known that in this case, the electrode-resin interface is usually electrochemically blocked at low voltages used for

Table I Characteristics of DGEBA and 3DCM Epoxy-Amine System Components

Monomer	Molar Mass (g/mol)	Functionality
 DGEBA ($n = 0.03$)	348	2
 3DCM	238	4

**Figure 3** The TOF current signals obtained for the DGEBA/3DCM system after 800 sec of isothermal curing at 70°C for Al and Ag electrodes ($d = 20 \mu\text{m}$, $V = 100 \text{ V}$).

AC and DC measurements.^{1,19} The applied electric field can polarize the electrodes by causing the accumulation of ion layers that can influence the interpretation of the measurement results. This effect is usually seen in the time-domain dielectric results, first of all in the permittivity data and especially in low-frequency regions.

The electrode polarization effect depends on the ratio of a sample thickness to a charge layer thickness and can be reduced to a nearly negligible value by increasing this ratio value. One can do that by increasing the electrode spacing or by decreasing the charge layer thickness by changing the material of the electrodes. On the other hand, one can enhance the electrode polarization effect by decreasing the ratio value, that is, by decreasing the electrode spacing or by increasing the charge layer thickness by changing the material of the electrodes.^{1,19}

Taking the above considerations into account, an influence of the material of the electrodes on the electrode polarization effects and on the TOF current signals has been investigated. The Cu, Ag, Al, and Au electrodes were tested in order to reveal the best ion-blocking materials for the TOF measurements of the investigated epoxy-amine system. For the Ag and Al electrodes, the current decreases monotonically and the $\log(I)$ versus $\log(t)$ plots yield curves without any distinct points that could be related to the TOF of ions (Fig. 3). This is an indication that these electrodes are insufficiently ion blocking for the mobile ionic species present in the medium. In the case of the Cu and Au electrodes, it was possible to find the experimental conditions (field strength,

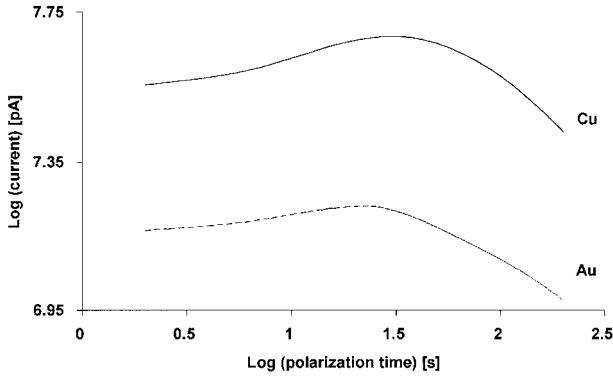


Figure 4 The TOF current signals obtained for the DGEBA/3DCM system after 800 sec of isothermal curing at 70°C for Cu and Au electrodes ($d = 20 \mu\text{m}$, $V = 100 \text{ V}$).

sample thickness, temperature) at which a distinct kink on the $i(t)$ curve and sometimes a maximum were observed (Fig. 4). Assuming that these electrodes are sufficiently ion blocking for the ionic carriers in the medium, this point can be regarded as the time when ionic carriers have reached the opposite electrode.

The appearance of a maximum in the TOF current signals can be rationalized as follows. Due to prolonged application of a polarizing field in the first step of the TOF experiment, the ions accumulate in the vicinity of the electrodes. This causes a decrease in the number of mobile ions in the bulk (clean-up effect) and a decrease of the internal electric field (space charge effect). After the reversal of the field polarity, the number of ionic charge carriers (n_i) in the bulk increases due to a release of the ions from the accumulated layer and the current also increases. Just after the ionic carriers reach the opposite electrode, the accumulation of ions begins again, resulting in a decrease in the number of carrier ions (n_i). Thus, the number of mobile ions in the bulk reaches a maximum at some time (τ), and therefore, the time dependence of the monitored current also shows a peak.¹²

The time τ after which the current reaches the maximal value can be taken as a measure of a mean value of the TOF of the ionic carriers between the electrodes. According to this concept of TOF, the time τ should increase with an increase of the sample thickness (for the same voltage) as the result of the increase of the distance that ions have to pass between the electrodes and the decrease of the electric field. Such an effect was ob-

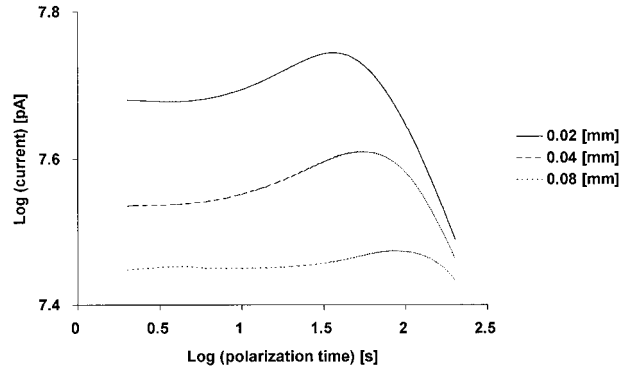


Figure 5 The TOF current signals obtained for the DGEBA/3DCM system after 300 sec of isothermal curing at 50°C for the different sample thicknesses indicated on the figure (Cu electrodes, $V = 50 \text{ V}$).

served in our experiments, as is shown in Figure 5. For the same reasons, the TOF of the ionic carriers should decrease with increasing electric field (for the constant distance layer). This effect is shown in Figure 6, confirming our interpretation of the TOF experiment results.

In the investigated DGEBA/3DCM resin system, it was found, as expected, that the ionic conductivity decreases with time of curing. The plot of the isochronal values of the current taken from the polarization signals of the TOF experiments (which can be taken as a measure of ionic conductivity) versus time is shown in Figure 7(c).

In order to compare the results of ionic current measurements with the results obtained from the measurements made using the other well-es-

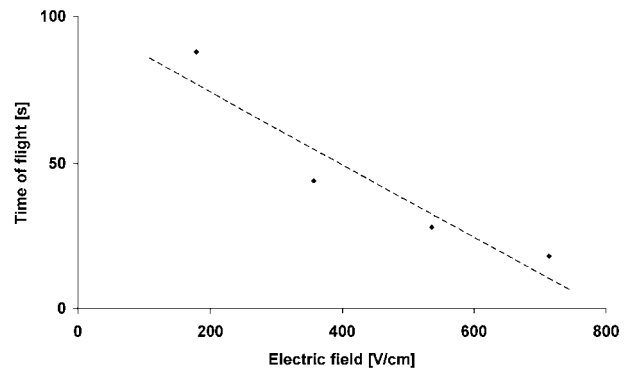


Figure 6 The TOF current signals obtained for the DGEBA/3DCM system after 800 sec of isothermal curing at 70°C for the different electric fields indicated on the figure (Cu electrodes, $d = 14 \mu\text{m}$).

lished technique, we have performed additional dielectric measurements. We have used a measurement set-up consisting of the Hewlett-Packard HP4284A LCR bridge and a sensor with interdigitated nickel electrodes (IDEX, supplied by Micromet Instruments Inc.). The permittivity and

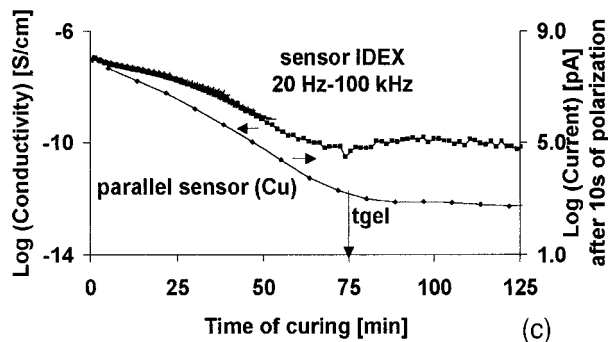
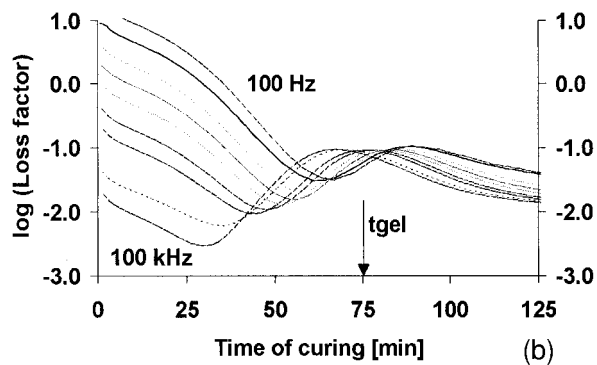
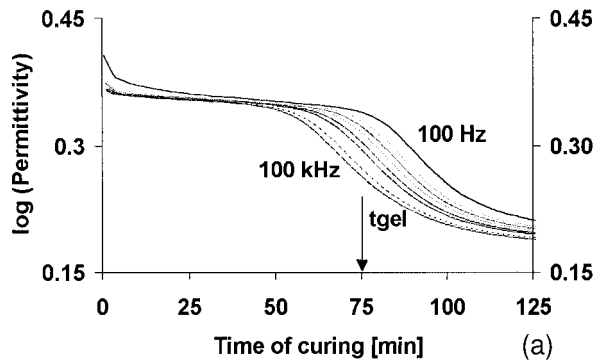


Figure 7 The dielectric properties of the DGEBA/3DCM system cured isothermally: (a) permittivity, (b) loss factor, (c) conductivity from the dielectric measurements (Ni electrodes IDEX sensor, 20 Hz–100 kHz, $V = 5$ V, 70°C), upper curve in panel c and ionic current values after 10 sec of dc polarization (Cu electrodes, $d = 14$ μm , $V = 50$ V, 70°C), lower curve in panel c.

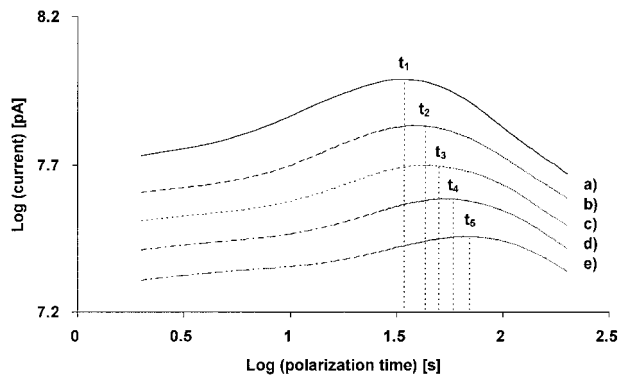


Figure 8 Evolution of the TOF current signals obtained for the DGEBA/3DCM system after (a) 800 sec, (b) 1,300 sec, (c) 1,800 sec, (d) 2,300 sec, and (e) 2,800 sec of isothermal curing at 50°C (Cu electrodes, $d = 20$ μm , $V = 100$ V).

the loss factor evolutions obtained from dielectrometry are shown in Figure 7(a) and (b), respectively, with indicated points of gelation determined by independent methods (differential scanning calorimetry, dynamical mechanical analysis (DMA)).^{20,21} The conductivity versus time calculated from the dielectric results is shown in Figure 7(c). The shape of this curve is similar to the shape of the current curve obtained from the dc measurements shown in the same figure, indicating that the TOF measurement conditions were correct.

According to our predictions, the TOF of ionic carriers should increase with an advancement of reaction. The reason is an increase of the medium viscosity in a course of curing. The higher the viscosity, the lower the mobility of the ionic carriers and the longer the time needed by them to reach the opposite electrode. The typical TOF current signals obtained for isothermal curing at 50°C after different times of curing are shown in Figure 8. The evolution of the ionic carrier mobility for two different temperatures of curing, calculated according to eq. (1), versus time of curing is shown in Figure 9. Unfortunately, when the resin was approaching gelation, the mobility decreased so strongly that the TOF became very long, exceeding the time of complete curing; therefore, it was not possible to follow the changes in the ion mobility above the gelation. The attempts to lower the sample thickness below 20 μm in order to attain shorter times of flight were unsuccessful. It was difficult to determine the point of TOF, proba-

bly because the two opposite electrodes were not strictly parallel and differences of a few micrometers for such small distances were not negligible and were causing broadening of the TOF signal. It was also not possible to perform the measurements at electric fields higher than $5 \text{ V}/\mu\text{m}$ (that is, at voltages higher than 100 V at $20\text{-}\mu\text{m}$ -thick samples).

The plot of $\log(I)$ versus $\log(t)$ gives an approximately straight line with a slope equal to -1 (Fig. 10), indicating linear relations between the ionic conductivity and mobility in this range of advancement of reaction, that is, before reaching the gelation point. However, with advancement of the reaction, deviations from the linearity are observed, especially at 70°C , suggesting some decrease in the concentration of mobile ions.

CONCLUSIONS

It is demonstrated that the concept of TOF can be applied for the determination of ion mobility in polymers and, in particular, for the determination of the evolution of the ion mobility in reactive polymer medium in a course of resin curing. The form of the TOF current signals depends on the materials of the electrodes. If the electrodes are sufficiently ion blocking, the monitored current increases and when the ions reach the opposite electrode, the current shows a peak at the point that determines the TOF of ionic carriers from one electrode to the other.

The ion mobility calculated from the TOF measurements decreases during the curing as a result

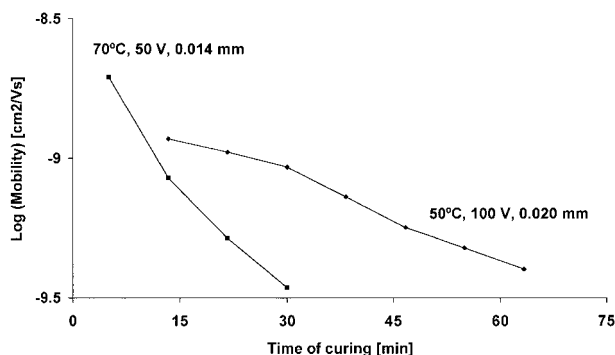


Figure 9 The ion mobility values versus time of curing in the TOF measurements obtained for the DGEBA/3DCM system cured isothermally at 50°C (Cu electrodes, $d = 20 \mu\text{m}$, $V = 100 \text{ V}$) and at 70°C (Cu electrodes, $d = 14 \mu\text{m}$, $V = 50 \text{ V}$).

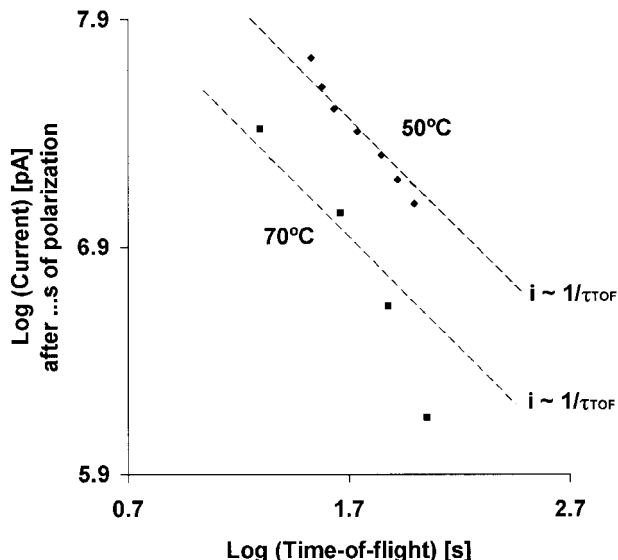


Figure 10 The plot of the ionic current values after 10 sec of polarization versus TOF τ for the DGEBA/3DCM system cured isothermally at 50°C (Cu electrodes, $d = 20 \mu\text{m}$, $V = 100 \text{ V}$) and at 70°C (Cu electrodes, $d = 14 \mu\text{m}$, $V = 50 \text{ V}$); the broken line indicates a slope of -1 .

of the viscosity increase of the medium. The relation between ion conductivity and ion mobility is inversely linear before gelation. Recent, preliminary studies on the evolution of ion conductivity and ion mobility by means of TOF experiments on less viscous, low- T_g epoxy-amine systems, diglycidylether of 1,4-butanediol (DGEBD) and 4,9-dioxa-1,12-dodecane diamine (4D), have shown that due to higher ion mobility, it is possible to perform the TOF experiments both before and after the gelation; the studies are in progress, and the results will soon be published.

REFERENCES

1. S. D. Senturia and N. F. Sheppard, Jr., *Adv. Polym. Sci.*, **80**, 1 (1986).
2. T. Koike, *J. Appl. Polym. Sci.*, **50**, 1943 (1993).
3. M. B. M. Mangion and G. P. Johari, *J. Polym. Sci. Polym. Phys.*, **29**, 1117 (1991).
4. C. G. Delides, D. Hayward, R. A. Pethrick, and A. S. Vatalis, *Eur. Polym. J.*, **28**, 505 (1992).
5. D. Kranbuehl, S. Delos, M. Hoff, and P. Haverty, *Polym. Eng. Sci.*, **29**, 285 (1989).
6. G. Boiteux, P. Dublineau, M. Fave, C. Mathieu, G. Seytre, and J. Ulanski, *Polymer Bull.*, **30**, 441 (1993).
7. G. Maistros, H. Block, C. Bucknall, and I. Partridge, *Polymer*, **33**, 4470 (1992).

8. J. Simpson and S. Bidstrup, *J. Polym. Sci. Polym. Phys.*, **33**, 55 (1995).
9. J. Simpson and S. Bidstrup, *J. Polym. Sci. Polym. Phys.*, **31**, 609 (1993).
10. A. MacKinnon, S. Jenkins, P. McGrail, and R. Pethrick, *Polymer*, **34**, 3252 (1993).
11. I. Alig and G. Johari, *J. Polym. Sci. Polym. Phys.*, **31**, 299 (1993).
12. M. Watanabe, K. Sanui, N. Ogata, F. Inoue, T. Kobayashi, and Z. Ohtaki, *Polym. J.*, **17**, 549 (1985).
13. M. Watanabe, M. Rikukawa, K. Sanui, and N. Ogata, *J. Appl. Phys.*, **58**, 736 (1985).
14. H. W. Starkweather, Jr. and P. Avakian, *Macromolecules*, **26**, 6217 (1993).
15. Y. Zheng and G. Wan, *J. Appl. Polym. Sci.*, **57**, 623 (1995).
16. Y. Deng and G. Martin, *Macromolecules*, **27**, 5141 (1994).
17. J. Mijovic, *Polym. Mat. Sci. Eng.*, **72**, 54 (1995).
18. F. Stephan, G. Boiteux, and G. Seytre, *Mater. Tech.*, **Novembre-Decembre**, 23 (1994).
19. D. R. Day, T. J. Lewis, H. L. Lee, and S. D. Senturia, *J. Adhesion*, **18**, 1 (1985).
20. D. Verchère, H. Sautereau, J. P. Pascault, C. C. Riccardi, S. M. Moschiar, and R. J. J. Williams, *Macromolecules*, **23**, 725 (1990).
21. Z. Cao, J. Galy, J. F. Gerard, and H. Sautereau, *Polym. Networks Blends*, **4**, 15 (1993).