Polymer Bulletin 30, 441–447 (1993)

Polymer Bulletin

Dielectric and viscoelastic studies of curing epoxy-amine model systems

Gisèle Boiteux[1,*], Pascal Dublineau[2], Michel Fève[3], Christophe Mathieu[1], Gérard Seytre[1], and Jacek Ulanski[4]

[1]Laboratoire d'Etudes des Matériaux Plastiques et des Biomatériaux, URA CNRS n° 507,
Université Claude Bernard Lyon I, F-69622 Villeurbanne Cedex, France
[2]AEROSPATIALE, F-92152 Suresnes Cedex, France
[3]Laboratoire des Matériaux Macromoléculaires, URA CNRS n° 507, Institut National des
Sciences Appliquées de Lyon, F-69621 Villeurbanne Cedex, France
[4]Polymer Institute, Technical University of Lodz, Lodz, Poland

Summary

The curing of different epoxy-amine model systems which present only gelification and/or vitrification processes has been followed with the evolution of their viscoelastic and electrical behaviours during the network formation. Some attempts are performed to correlate the significant evolution of the mechanical and electrical parameters with the physico-chemical changes of these well defined chemical systems during their hardening and complete curing.

Introduction

The curing of epoxy resin systems includes not only reaction kinetics but also gelation and network formation (1-4). Several chemorheological studies concerning reaction kinetics and rheology change have been done to follow the curing of epoxy resins (5-11). Recent advances (12-17) indicate microdielectrometry as a promising technique for such investigations. In a polymerizing mixture, the resulting complex permittivity is connected with two main microscopic mechanisms : ionic conduction and dipole motion whose contributions strongly depend on the frequency of the applied electric field.

Ionic mobility in curing systems is strongly affected by bulk viscosity and dipole response is related to segmental and side chain motions in the macromolecule. On the other hand, many well documented reasons exist for the difficulties in interpretating dielectric data.

Starting from these considerations, an accurate experimental analysis on different chemical systems has been established to clearly distinguish the two principal processes involved during the curing of thermosetting polymers : first the conversion of a sol to a gel (gelation) and the second, the conversion of the gel to a glassy state (vitrification). For this purpose, we perform measurements with a mechanical technique (viscoelasticimetry) and a electrical techniques (microdielectrometry and dc measurements) on well-defined epoxy/amine model systems where the gelation and/or the vitrification processes are distinct.

Experimental

Materials

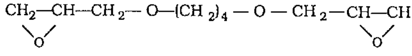
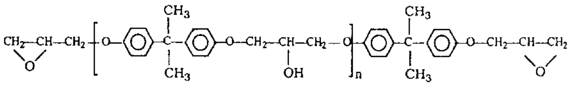
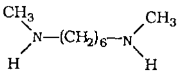
Three types of epoxy-amine model systems were considered for this work. The epoxy/amine systems choosen for the characterization of gelation are the system 1,4-butane diol diglycidyl ether (BDDGE)/4,9-dioxa-1, 1,2-dodecanediamine (DDDD) obtained from Aldrich-Chemie. For the observation of only the vitrification the epoxy resin used in this study was the diglycidyl ether of bisphenol-A (DGEBA) from Dow Chemical (DER 332) and the difunctional diamine N,N'-dimethyl-1,6-hexane diamine (NN'DMHDA) purchased from Aldrich-Chemie.

The third epoxy/amine system DGEBA-DDDD will present at one and the same time gelification and vitrification phenomena under curing. The formula of these reactants have been reported in the Table 1.

---

*Corresponding author

Table 1

Monomer	Formula	Abbreviation
1,4 butane diol diglycidyl ether		BDDGE
4,9 dioxa 1,12 dodecane diamine	$NH_2\text{-}(CH_2)_3\text{-}O\text{-}(CH_2)_4\text{-}O\text{-}(CH_2)_3\text{-}NH_2$	DDDD
diglycidyl ether of bisphenol A		DGEBA
N,N' dimethyl-1,6-hexane diamine		NN'DMHDA

The preparation of the samples was performed according to the same way for the three systems and was described elsewhere (6). The reactants were weighted and mixed in stoichiometric ratio quantities at room temperature before being used for dynamic mechanical analysis and electrical experiments. The isothermal curings have been performed at 60°C for the systems BDDGE-DDDD and DGEBA-DDDD and at 50°C for the system DGEBA-NN'DMHDA.

Dynamic mechanical analysis

Mechanical analysis was carried out with a Rheometrics Dynamic Analyser, model RDA-700. Measurements were made in the dynamic mode between parallel plates at angular frequencies between 1 rad/s and 100 rad/s.

The oscillatory strain was choosen near 1 % to ensure that the measurements were being made in the linear viscoelastic region.

A.C measurements

The microdielectrometry is based on the microdielectrometer Eumetric System III of Micromet instruments. This system generates sinusoïdal signals between 0.1 and 50 000 Hz and transmits them to the electrodes of the sensor.

Among all the available sensors, we have used the low conductivity chip sensor with integrated circuit.Built on a solid insulating substrate of low space requirement 2,5 mm x 0.5 mm x 0.25 mm), the chip sensor measures conductivities between 10^{-16} and 10^{-5} S/cm. The two thirds of its surface are occupied by active elements (interdigitated electrodes) and the remaining third contains miniature amplifiers, connection elements and a thermal diode.

The signal detected is analysed to determine phase and gain. A calibration table transforms these results into permittivity and loss factor.

D.C measurements

The precedent application of an alternative field can lead to a complex dielectric response involving dipolar motions and possible ionic migration. Direct current measurements are then a suitable technique to isolate ionic contribution and to study its evolution during the polymerization.

Our laboratory finalized an experimental device made of :

- an electrometer with incorporated source of voltage Keithley 617
- a microdielectric sensor IDEX-type to access the values of the current crossing the

system. It measures conductivities between 10^{-14} and 10^{-3} S/cm and is only made of comb-electrodes

- an IBM PS/2 computer to acquire, stock and treat the data

The voltage cycle checked out to follow the curing of the reactive mixture is shown Fig.1a. The cycle was defined like this because :

- it only generates weak perturbations within the material
- the values of the voltage (± 1 V) are in the same order of magnitude as in microdielectrometry
- by alternating + 1 V and - 1 V, we intend to attenuate electrode polarization effects
- the frequency of data collection is consistent with the kinetics of reaction for the different temperatures.

The behaviour of the current corresponding to this cycle is qualitatively represented on Fig.1b. We have studied the evolution of the value I of the current during the curing.

For ac or dc measurements, the liquid resins were deposited on the sensor in a thin layer and the curing temperature was controlled with a Micromet Eumetric Programmable oven and software system.

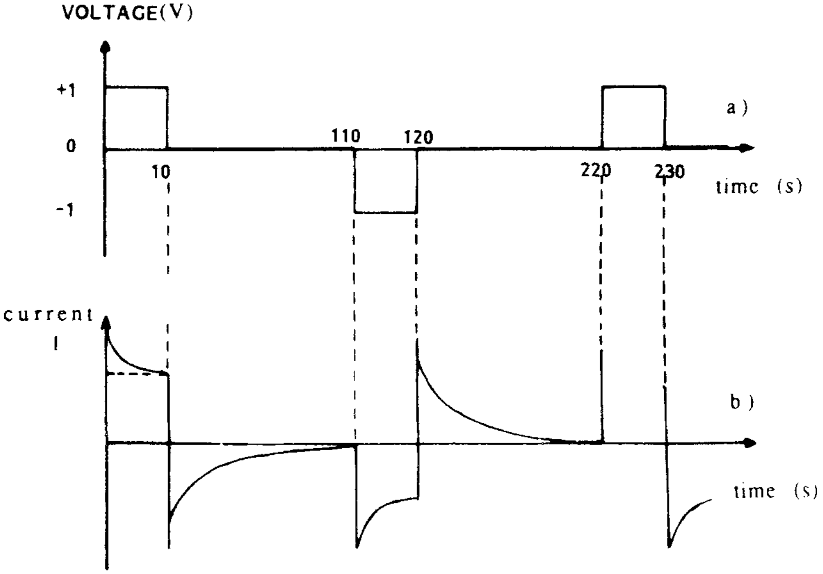


Figure 1: a) Dc measurements a) voltage cycle defined ; b) behaviour of the current within the material corresponding to this cycle

Results and Discussion

The characteristics of the three systems will be indicated as follow : BDGE-DDDD (gelation «G» only), DGEBA-NN'DMHDA (vitrification «V» only) and DGEBA-DDDD (gelation then vitrification «G+V») in stoichiometric proportions.

Concerning the dynamic mechanical analysis , we have reported in the Fig.2, the characteristic curves of tg δ versus isothermal curing time at 60°C for the DGEBA-DDDD system. It has been shown (5-6) that the point for which tg δ curves overlap is frequency independent and corresponds to the gel point of the system. Identical observation is made on the system BDDGE-DDDD and confirm this interpretation as this system only gelifies. On the contrary no crossover point appears in the mechanical analysis of DGEBA-NN'DMHDA for which the frequency dependence of the tg δ curves corresponds to the vitrification of the system, as observed in Fig.2 for this second phenomena in DGEBA-DDDD appearing after the characteristic gel point. As expected the BDDGE-DDDD system presents after the gel point only a decrease of the tg δ curves as the time of curing is going on.

The gel point observed by DMA at a temperature of curing of T = 60°C is t = 76 min for BDDGE-DDDD epoxy model and t = 38 min for the DGEBA-DDDD one.

The electrical measurements were first carried out by microdielectrometry under ac field. The measured dielectric properties include ε' (permittivity) and ε" (loss factor) represent the dipolar reorientation and ion transport.

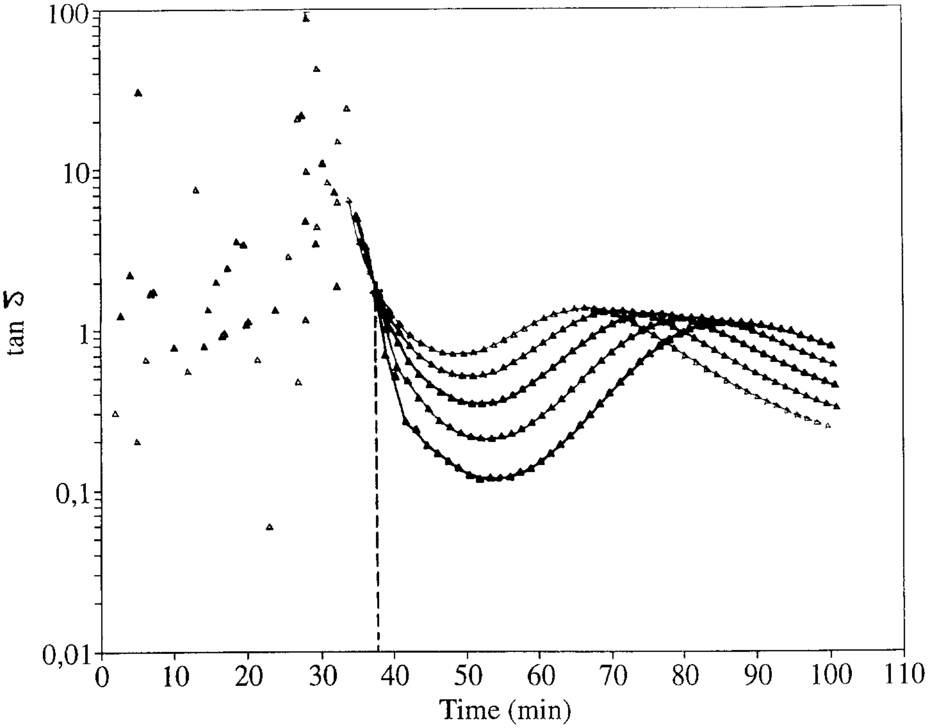


Figure 2: Evolution of tan δ with time of curing at T = 60°C for the DGEBA-DDDD system «G+V»

Ionic conductivity (σ) can be calculated from ε" via equation (1) and can be used to follow the rheological changes that take place when the thermoset undergoes cure (13).

$$\sigma = \varepsilon'' \varepsilon_0 \omega \quad (1)$$

with : σ : ionic conductivity

ω : angular frequency (2πf)

f : frequency (Hz)

ε_0 : absolute permittivity of free space ($8.85.10^{-12}$ F/m)

The ionic conductivity is related in fact to the viscosity, because it determines the velocity of ions in the medium (18).

Such representation has been reported in the Figs.3,4 and 5 respectively for BDDGE-DDDD (G), DGEBA-NN'DMHDA (V) and DGEBA-DDDD (G+V). We observe in Figs.3 and 5 a modification of the ionic mobility resulting in an inflexion point which seems to be dielectric event resulting of the gelation. On the contrary Fig.4 indicates a different shape of the conductivity curve. The decrease of the conductivity is more pronounced and if we excluded the inflexion point observed at the beginning of the curve which is due to temperature effects difficult to control, the curve does not present any inflexion point as no chemical gelation occurs.

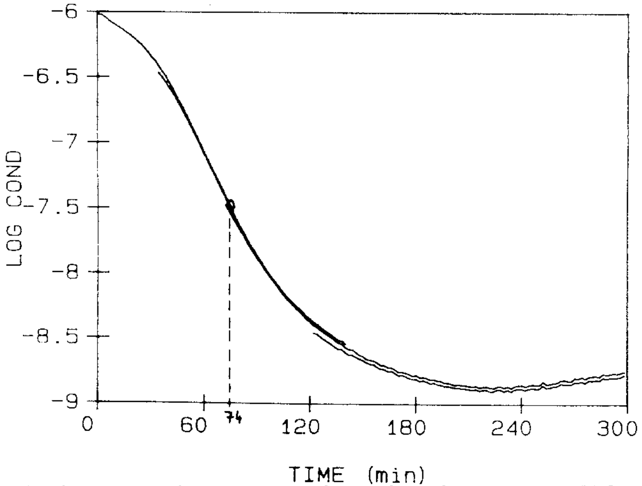


Figure 3: Log ionic conductivity versus time of curing at T = 60°C for the BDDGE-DDDD system «G»

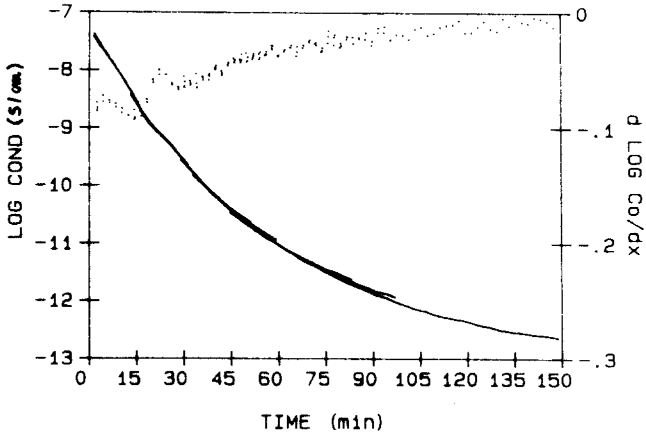


Figure 4: Log ionic conductivity versus time of curing at T = 50°C for the DGEBA-time of curing at T = 60°C for the DGEBA-NN'DMHDA system «V»

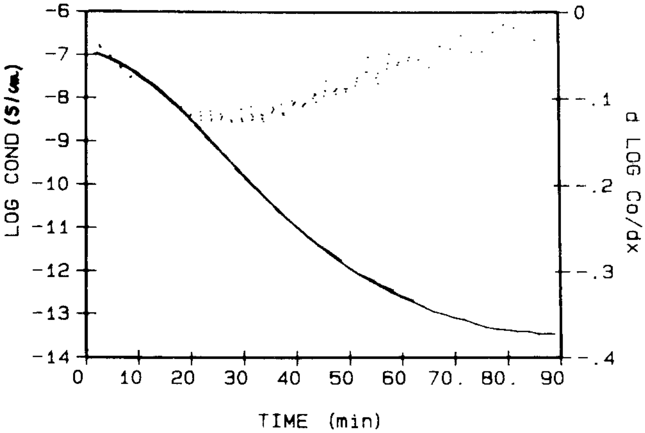


Figure 5: Log ionic conductivity versus time of curing at T = 60°C for the DGEBA-DDDD system «G+V»

The time at which the change in ionic conductivity occurs is in perfect correlation with the time for which is observed the frequency independent point of the mechanical tg δ curves (74 mn for BDDGE-DDDD, 38 mn for DGEBA-DDDD for a curing temperature of 60°C).

When the phenomena of vitrification occur for the systems DGEBA-DDDD and DGEBA-NN'DMHDA, the dipolar relaxations occur later in the time at successively lower frequencies. For the system BDDGE-DDDD (which only gelates), they are not observed.

The dipolar relaxations are clearly evidenced by the dependence of the permittivity ε' (Fig. 6) and the dielectric losses ε" (Fig. 7) with the change of frequencies. So the dipolar relaxation is associated with the vitrification of the curing resin.

To confirm such results, it has appeared interesting to develop the dc measurement technique for the observation of the ionic conduction clearly separated of the dipolar currents when their stabilization is obtained. As it is illustrated on Fig.8 for the BDDGE-DDDD system, the evolution of the value I of the current with curing time is sigmoïdal. The inflexion allocated to the gel point of the system must be carefully exploited because the Idex sensor is unable to detect within the materials currents below pA but this value confirms the ac analysis.

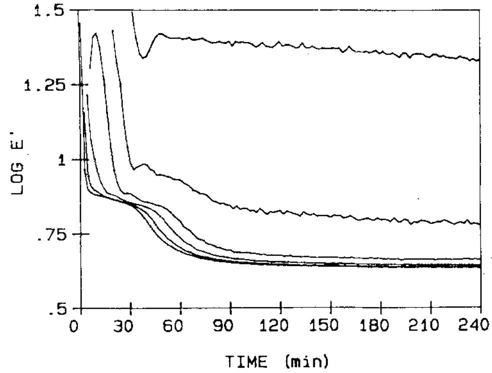


Figure 6: Dependance of ε' versus the time of curing at T = 60°C for the DGEBA-DDDD system «G+V»

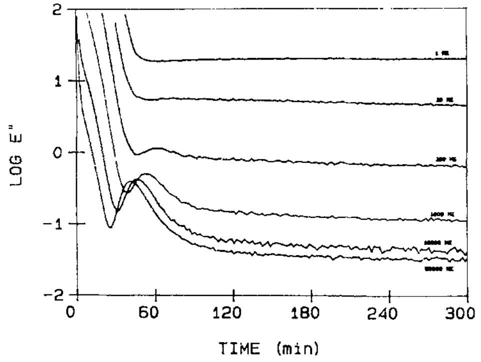


Figure 7: Dependance of ε" versus the time of curing at T = 60°C for the DGEBA-DDDD system «G+V»

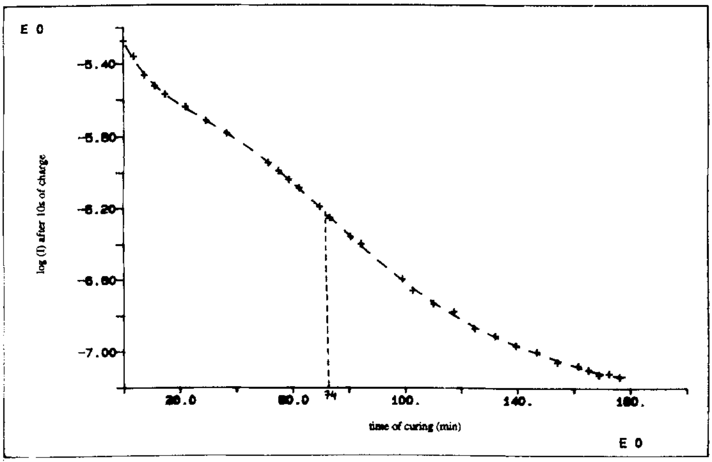


Figure 8: Evolution of the logarithmic value of the current I versus the time of curing at T = 60°C for the DGEBA-DDDD system «G+V»

Conclusion

The isothermal curing of well-defined epoxy/amine model systems has been followed with dynamic mechanical analysis and with electrical techniques of measurements (microdielectrometry and direct current technique). The simultaneous interpretation of the corresponding spectra was very convenient to assign their mechanical and electrical behaviours to the phenomena of gelation and/or vitrification as the systems present specifically one or both of these chemical phenomena.

Electrical techniques have particularly evidenced their own efficiency to detect them during the network formation by the evolution of electrical parameters such as ε', ε'' and σ very sensitive to the modification of the system.

Such results seem promising to measure in situ the resin viscosity during the processing and consequently to monitor and optimize the curing conditions.

This study allows a better insight of the different steps of the curing and the following essential conclusions can currently be drawn :

- the gelation process is evidenced by an inflexion point on the curve representing the evolution of ionic conduction with isothermal curing time and by the point of the mechanical loss tangent which is frequency independant ;
- the vitrification is undoubtedly characterized by the frequency dependent relaxation phenomena observed in the two techniques. In electric measurement appears the relaxation of the dipoles which are present in the system, in relation with the segmental motions inside the growing network (10).

These conclusions are at this time verified on an industrial system DGEBA-3DCM which displays gelation and vitrification (20).

References

1 Enns J B, Gillham J K (1983) J Appl Polym Sci 28: 2567
2 Wisanrakkit G, Gillham J K (1991) J Appl Polym Sci 42: 2453
3 Pascault J P, Williams R J J (1990) J Polym Sci Polym Phys Ed 28: 85
4 Hale A, Macosko C W, Bair H E (1991) Macromolecules 24: 2610
5 Winter H H (1987) Polym Eng Sci 27: 1698
6 Feve M (1989) Makromol Chem Macromol Symp 30:95
7 Harran D, Grenier-Loustalot M.F., Monge P (1988) Europ Polym J 24:225
8 Jovic J M, Lee C H (1989) J Appl Polym Sci 37:889
9 Plazek D J, Chay I C (1991) J Polym Sci Phys Ed 29: 17
10 Lairez D, Adam M, Emery J R, Durand D (1992) Macromolecules 25: 286
11 Matejka L (1991) Polym Bull 26:286
12 Senturia S D, Sheppard N F, Lee H L, Marshall S H (1983) SAMPE Journal 22:7
13 Senturia S D, Sheppard N F (1986) Adv in Polym Sci 80:1
14 Kranbuehl D E, Delos S E, Yi E, Mayer J, Jarvie T (1986) Polym Eng Sci 26:338
15 Mangion M B M, Johari G P (1990) Macromolecules 23:3687
16 Carlini C, Rolla P A, Tombari E (1990) J of Appl Polym Sci 41:805
17 Mangion M B M, Johari G P (1991) J Polym Sci Polym Phys 29:1117
18 Kranbuehl D E, Debos S E, Jue P K (1986) Polymer 27:11
19 Mangion M B M, Wang M, Johari G P (1992) J. Polym. Sci. Polym. Phys. 30:433
20 Mathieu C, Boiteux G, Seytre G, Feve M, Pascault J P, Ulanski J, Dublineau P Proceedings of IEE, Manchester England Sept 1992

Accepted January 18, 1993 C