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Physicochemical changes in epoxy-amine systems studied by ionic conductivity and ionic carriers mobility measurements

Summary — The main objective of this work was to find the correlations between the ionic conductivity, viscosity and physicochemical changes occurring during the isothermal cure of the epoxy-amine systems. The studies of the ionic conductivity evolutions have been performed using dielectric and direct-current techniques. The measurement data were compared with the ion mobility values evaluated from the time-of-flight investigations and with the dynamic viscosity determined by dynamic mechanical analysis. Different epoxy-amine reacting systems have been analyzed: the diglycidyl ether of bisphenol A with diamino-4,4′-dimethyl-3,3′-dimethyldicyclohexylmethane (DGEBA-3DCM) which gelates and vitrifies during the cure and the diglycidyl ether of 1,4-butanediol with 4,9-dioxa-1,12-dodecane diamine (DGEBD-4D) which only gelates during its polycondensation. It was found that even with an appearing of gelation or viscoelastic properties the conduction process could be described as thermally activated. The inconsistencies between ionic conductivity and ion mobility evolutions indicate that the concentration of the mobile charge carriers in the medium changes during the reaction. It was also observed that the vitrification could be responsible for the large changes of free volume in the system influencing the ionic conduction mechanism and therefore the ionic conductivity evolutions. It was also found that the Stokes′s law is fulfilled at the beginning of the cure only.

Key words: epoxy resins′ isothermal cure, ionic conductivity, ionic carriers′ mobility, time-of-flight of ionic carriers, direct-current measurements, dielectrometry.

BADANIA ZMIAN FIZYKOCHEMICZNYCH W UKŁADACH EPOKSYDOWO-AMINOWYCH ZA POMOCĄ POMIARÓW PRZEWODNICTWA JONOWEGO I RUCHLIWOŚCI NOŚNIKÓW JONOWYCH

Streszczenie — Głównym celem tej pracy było znalezienie korelacji pomiędzy przewodnictwem jonowym, lepkością oraz zmianami fizykochemicznymi pojawiającymi się podczas izotermicznego utwardzania układów epoksydowo-aminowych. Badania zmian przewodnictwa jonowego dokonane zostały przy użyciu technik dielektrycznych i stałoprądowych (rys. 2—6). Następnie wyniki pomiarów porównano z wartościami ruchliwości jonów oszacowanymi z badań czasu przelotu jonów metodą time-of-flight (TOF) oraz z wartościami lepkości dynamicznej określonymi metodą dynamicznej analizy mechanicznej (DMA) (rys. 7). Analizowano różne układy reaktywne epoksydowo-aminowe: eter diglicydowy bisfenolu A z diamino-4,4′-dimetylo-3,3′-dimetylodicyklohexylometanem (DGEBA- -3DCM), który żeluje i ulega zeszkleniu podczas procesu utwardzania oraz eter diglicydylowy 1,4-butanodiolu z 4,9-dioksa-1,12-dodekano diaminy (DGEBD-4D), który podczas polikondensacji wyłącznie żeluje (tabela 2). Stwierdzono, że nawet w przypadku pojawienia się żelowania lub właściwości elastycznych proces przewodzenia może być opisany jako aktywowany termicznie. Niezgodności pomiędzy zmianami przewodnictwa jonowego i ruchliwości jonów wskazują, że w procesie utwardzania następują zmiany koncentracji ruchliwych jonów. Wykazano, że prawo Stokesa może być spełnione wyłącznie na początku procesu utwardzania.

Słowa kluczowe: izotermiczne utwardzanie żywic epoksydowych, przewodnictwo jonowe, ruchliwość nośników jonowych, czas przelotu nośników jonowych, pomiary stałoprądowe, dielektrometria.

The chemical reactions occurring during the cure of a resin cause physical changes associated with the transitions of gelation and/or vitrification. From the point of view of the industrial processing requirements, an important problem is the ability to predict and to monitor *in situ* these physicochemical changes. It is well known that mechanical and thermodynamical properties are changing simultaneously and several techniques of the cure monitoring are therefore in use, for example: mechanical techniques [1—3], DSC investigations [3—5], SEC or HPLC chromatography [3, 5], viscosity measure-

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ments [1, 2, 6] or near infrared spectroscopy [3, 7]. The electrical techniques are also engaged because direct current conductivity as well as dielectric parameters of a sample vary during the chemical reactions. Among the *in situ* electrical methods (electric response depends on the nature, the mobility and the concentration of charges) we may recall dielectrometry (AC technique) [6—9], direct-current measurements (DC investigations) [10—13] or impedancometry [7, 14]. The electrical parameters used for the cure monitoring are usually the permittivity, the loss factor, the loss tangent, the ionic conductivity and the relaxation time. However, to achieve the real-time control of the chemical reactions the fundamental correlations between the dielectric response (*e.g.* charge migration and dipole relaxation) and the corresponding physicochemical changes (*e.g.* reaction mechanism, gelation and/or vitrification) have to be clarified. It is well known that the viscosity and the ionic conductivity are macroscopic properties that characterize the chain segment mobility and ion mobility, respectively. The viscosity measures the response of the polymer chain segments to an applied mechanical stress field whereas the ionic conductivity measures the response of ionic carriers to an applied electric field. Both these quantities are varying during epoxy resin cure, however the mechanisms of the ionic conductivity changes during the reactions and these changes are still not well understood.

The main objective of our studies was to find the correlations between the ionic conductivity, viscosity and physicochemical changes in the reacting system (gelation and/or vitrification) during isothermal cure of the epoxy-amine systems. For this purpose, we have performed several experimental series using AC and DC measurements. The results have been then compared with the dynamic viscosity values obtained from the dynamic mechanical analysis (DMA). We have also elaborated a Time-of-Flight (TOF) technique to monitor the evolutions of ionic carrier mobility in the course of the reaction [15, 16]. This method was proposed to investigate and verify the basic assumption that ionic conductivity is directly related to the medium viscosity [15]. The above-mentioned assumption is based on the presumption that the ion concentration is constant and that only the ion mobility decreases in the course of the reaction.

Using TOF and DC techniques we have shown in our earlier studies that in the epoxy resin systems: diglycidyl ether of 1,4-butanediol with 4,9-dioxa-1,12-dodecane diamine (DGEBD-4D) and diglycidyl ether of bisphenol A with 4,4′-methylenebis[3-chloro-2,6-diethylaniline] (DGEBA-MCDEA) the above mentioned assumption was not fulfilled [13]. The differences found between the time dependence of the ionic conductivity and of the ion mobility were explained by the decrease in the concentration of ion charge carriers during the reaction according to our results and other observations [13, 17, 18]. In our previous paper it was shown that except of the beginning of the curing the evolution of the ionic conductivity did not follow the evolution of the viscosity. Also the empirical Walden's rule could be applied only in the limited range of the advancement of the reaction. This was due to the changes of the concentration of mobile ions during the reaction [13].

EXPERIMENTAL

Materials

For the experiments we have selected two epoxy-amine reacting systems: diglycidyl ether of bisphenol A with diamino-4,4′-dimethyl-3,3′-dimethyldicyclohexylmethane (DGEBA-3DCM) which gelates and vitrifies during the reaction and diglycidyl ether of 1,4-butanediol with 4,9-dioxa-1,12-dodecane diamine (DGEBD-4D) which only gelates during the cure. The cure of the systems and the *in situ* measurements have been performed isothermally at constant temperatures for the stoichiometric mixtures of reactants (epoxy/

Table 1. Chemical structures and characteristic of the monomers used

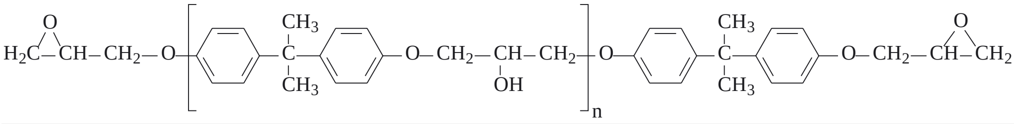
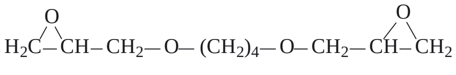
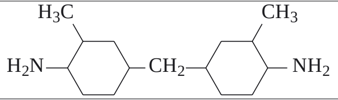
Monomers	Molar mass g/mol	Functionality	Producer
	348	2	Dow Chemicals (trade name DER332)
	202	2	Aldrich
	238	4	BASF (trade name Laromin C260)
$NH_2—(CH_2)_3—O—(CH_2)_4—O—(CH_2)_3—NH_2$	204	4	Aldrich

Table 2. Physical characteristics of the chemical systems; denotations: T_c — cure temperatures, T_{g0} — glass transition temperature at the conversion of 0 %, $T_{g\infty}$ — glass transition temperature at the conversion of 100 %, ${}_{gel}T_g$ — glass transition temperature at the gel point, α_{gel} — advancement of the reaction corresponding to the gel point

DGEBA-3DCM										
Studied phenomena	T_c, °C	T_{g0}, °C	$T_{g\infty}$, °C	${}_{gel}T_g$, °C	Temperature of curing, °C					
					50	60	70	80	90	100
gelation vitrification	50—100	-32	184	55	Gel time point, min (α_{gel} = 0.5800)					
					263	138	75	43	25	15
DGEBD-4D										
Studied phenomena	T_c, °C	T_{g0}, °C	$T_{g\infty}$, °C	${}_{gel}T_g$, °C	Temperature of curing, °C					
					50	60	70	80	—	—
gelation	50—80	-103	-12	—	Gel time point, min (α_{gel} = 0.5745)					
					144	75	40	22.5	—	—

amino = 1). The DGEBA-3DCM and DGEBD-4D mixtures have been prepared at room temperature. The characteristics of the components are listed in Table 1, whereas the basic physical properties of the systems are presented in Table 2.

Methods

The basics and the practical applications of AC [6—9, 19], DC [10—13] and DMA [20] techniques for cure monitoring are very well known and frequently illustrated in the literature. The backgrounds, the references and the experimental conditions of the TOF measurements we have also described elsewhere [15, 16].

Dielectric measurements (AC) have been carried out using an impedance analyzer Hewlett-Packard 4284A. The computer controlled DC and TOF experiments were executed using a Keithley 617 electrometer (Keithley Instruments Inc., USA) with an incorporated voltage source (0—100 V). The epoxy-amine reactive systems were placed in the thermostated oven at or between the preheated electrodes of the measurement unit. The interdigitated configuration of nickel or gold electrodes (IDEX sensor, spacer 0.120 mm, form factor of electrodes

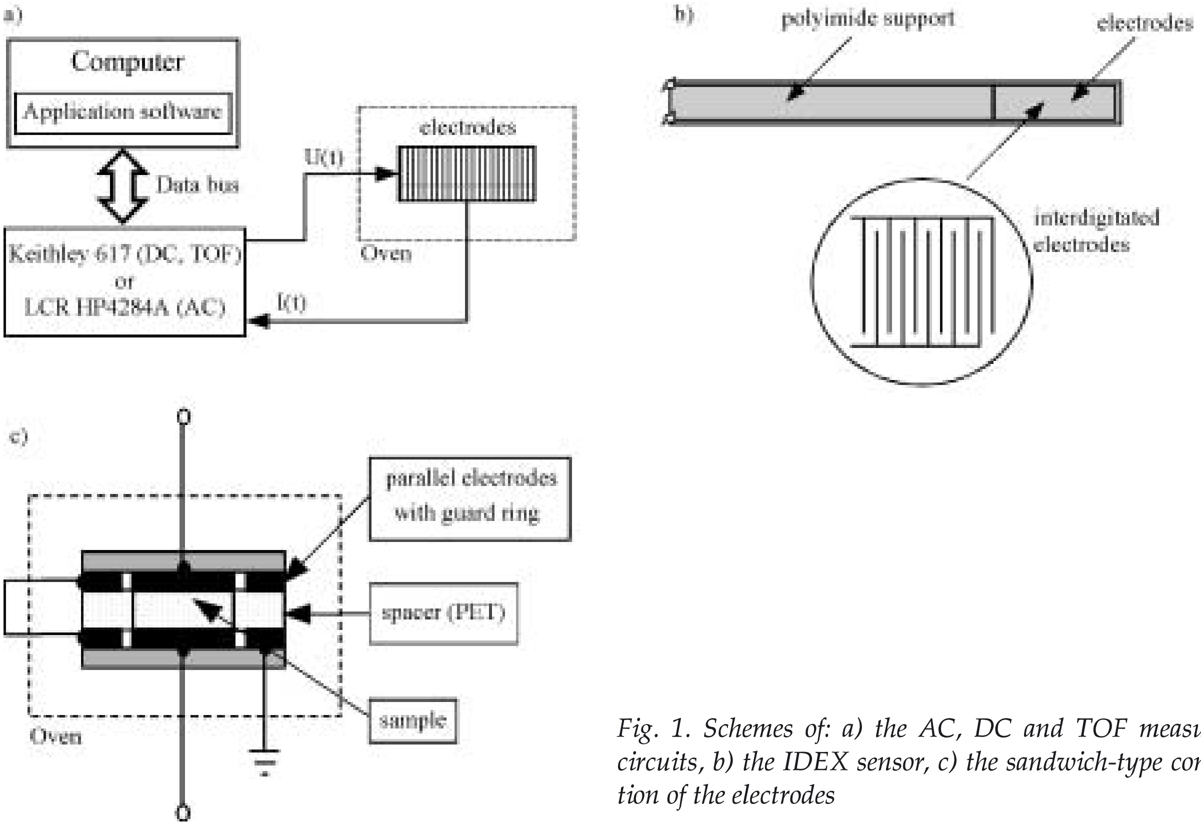


Fig. 1. Schemes of: a) the AC, DC and TOF measurement circuits, b) the IDEX sensor, c) the sandwich-type configuration of the electrodes

surface/distance A/D = 800 mm, Micromet Instruments Inc., USA) was chosen for the AC experiments. For the DC and TOF experiments we have also used the parallel plates configuration of round electrodes (diameter = 16 mm) with guard rings and with spacer made of poly(ethylene terephthalate) (PET) film of the thickness of 0.08 mm. The material of electrodes was Cu. The schematic diagrams of the electric measurements and of the configurations of the electrodes are shown in Fig. 1.

RESULTS AND DISCUSSION

Dielectric and direct current measurements

The AC conductivity (σ) can be calculated from the dielectric loss $\varepsilon''(\omega)$ dependence on the angular frequency (ω), according to the equation:

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

where: ε_0 — *dielectric constant of vacuum* ($0.8542 \cdot 10^{-12}$ *F/m*).

For the DGEBA-3DCM system, the AC conductivity values are frequency independent at the beginning of the cure and consequently the conduction process is mainly ionic (Fig. 2a). However, with an advancement of the reaction, the conductivity starts to be frequency dependent and one can see the maxima due to dipolar polarization related to the vitrification phenomena. For that reason, the measured AC conductivity is the superposition of the ionic component and the dipolar component. For the DGEBD-4D system that shows gelation only (Fig. 2b), the dipolar polarization effects are not observed and therefore the conduction process is mainly ionic. Nevertheless, for higher advancements of the reaction the viscoelastic properties of the reacting medium make the plots of the conductivity frequency dependent too. For the both investigated systems the ionic conductivity values can be therefore determined as these parts of the curves that are frequency independent.

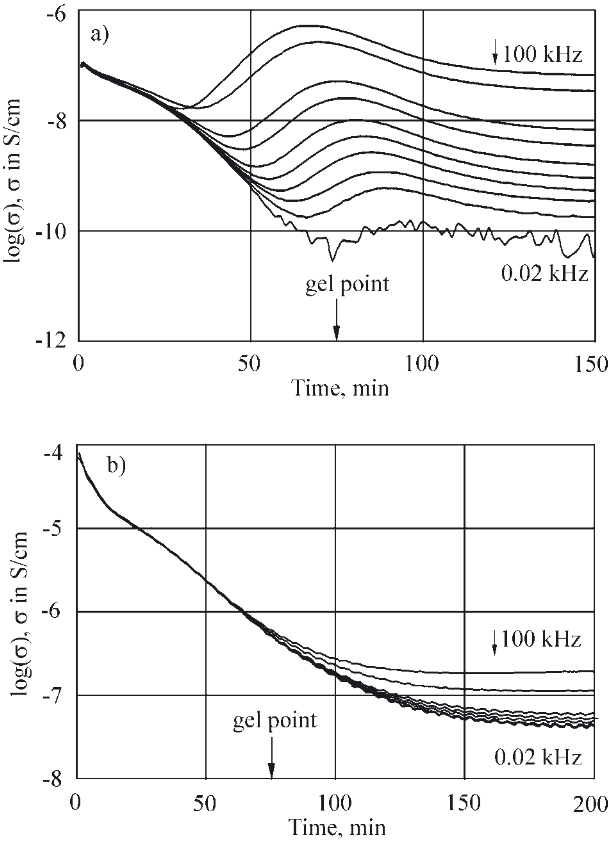


Fig. 2. Evolution of logarithm of the AC conductivity (dielectric measurements, Ni electrodes IDEX sensor, frequency was equal 0.02, 0.1, 0.2, 0.5, 2, 5, 10, 50 or 100 Hz, U = 5 V), obtained for: a) DGEBA-3DCM system isothermally cured at 70 °C, b) DGEBD-4D system isothermally cured at 60 °C

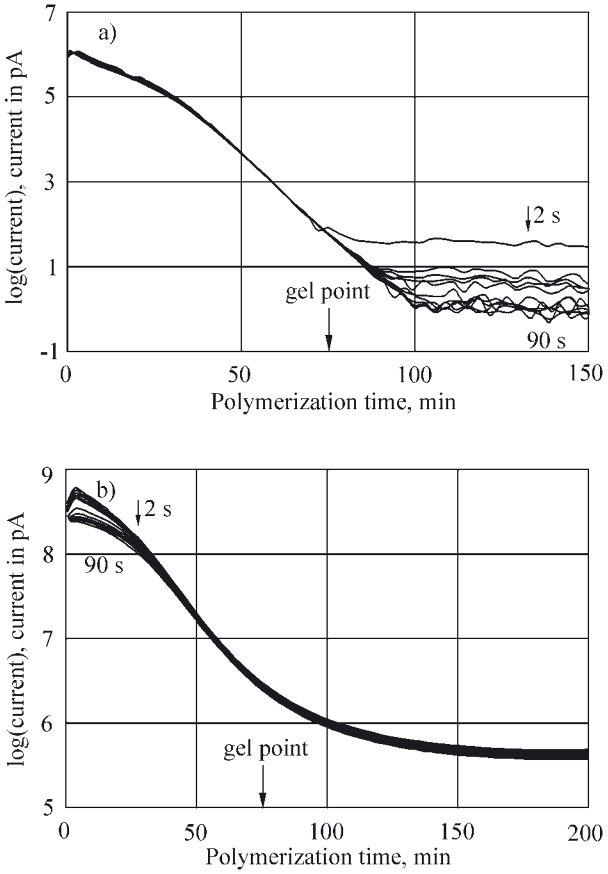


Fig. 3. Evolution of logarithm of the isochronal current values measured after different times of polarisation (2—90 s of charging) during isothermal cure of: a) the DGEBA-3DCM system at 70 °C (DC measurements, Ni electrodes IDEX sensor, polarization time 90 s, U = 5 V), b) DGEBD-4D system at 60 °C (DC measurements, parallel sandwich-type Cu electrodes, d = 0.080 mm, polarization time 90 s, U = 1 V)

The Fig. 3a and 3b show the evolutions of DC current values for different times of the sample polarization in the range 2—90 s that were applied during subsequent voltage cycles in a course of the cure. For the DGEBA-3DCM system where both gelation and vitrification phenomena occur and are not well separated, the isochronal current values recorded after different times of polarization decrease in the same manner with the time of cure at the first stage of the reactions. Then the isochronal current values start to be different due to the vitrification (Fig. 3a). For the DGEBD-4D system which undergoes the gelation only, this effect is not observed (Fig. 3b). However, at the beginning of the cure the small divergences between the current after different times of polarization are observed. This effect can be associated with the polarization of the electrodes due to high level of conduction at the beginning of the reaction.

Comparing the AC and DC results for the DGEBA-3DCM system (gelation and/or vitrification), similar evolutions of AC and DC ionic conductivity at low viscosity of the medium (Fig. 4) are observed. For longer reaction time the differences between the AC and DC data appear due to much lower equivalent frequency of DC measurements. The evolutions of AC conductivity at 20 Hz and of DC conductivity after 10 s of polarization are similar for DGEBD-4D reacting system (Fig. 5). The differences are smaller in the early stage of reaction. For longer reaction times, the differences appear, but the curves run in parallel. The difference in the current values can result from different geometry of electrodes used in AC (interdigitated IDEX sensor) and DC (parallel plates configuration of electrodes) measurements.

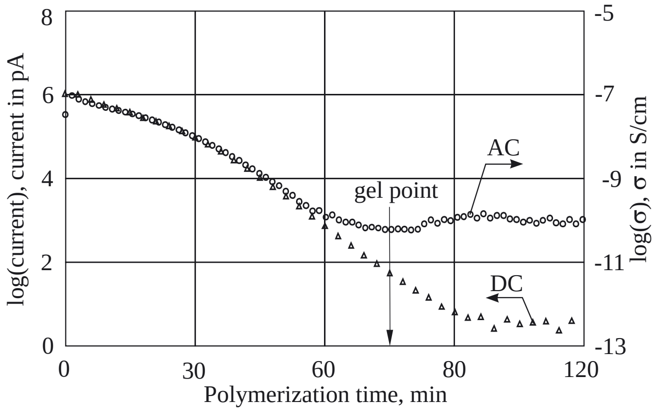


Fig. 4. Comparison of the evolution of logarithm of the isochronal current values after 10 s of charging (DC measurements, Ni electrodes IDEX sensor, polarization time 90 s, U = 5 V) and of the AC conductivity (dielectric measurements, Ni electrodes IDEX sensor, 20 Hz, U = 5 V) for the DGEBA-3DCM system isothermally cured at 70 °C

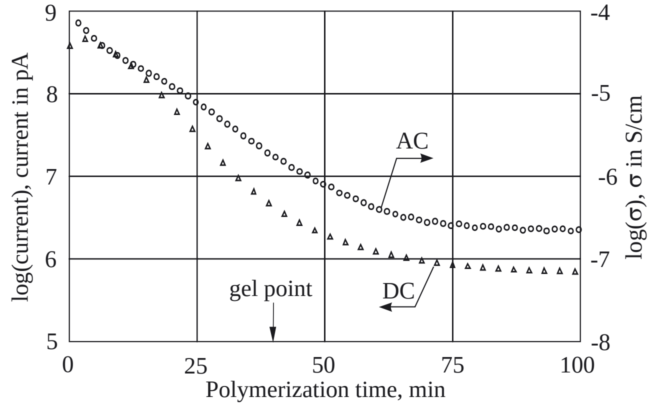


Fig. 5. Comparison of the evolution of logarithm of the isochronal current values after 10 s of charging (DC measurements, parallel sandwich-type Cu electrodes, d = 0.080 mm, polarization time 90 s, U = 1 V) and of the AC conductivity (AC measurements, Ni electrodes IDEX sensor, 20 Hz, U = 1 V) for the DGEBD-4D system isothermally cured at 70 °C

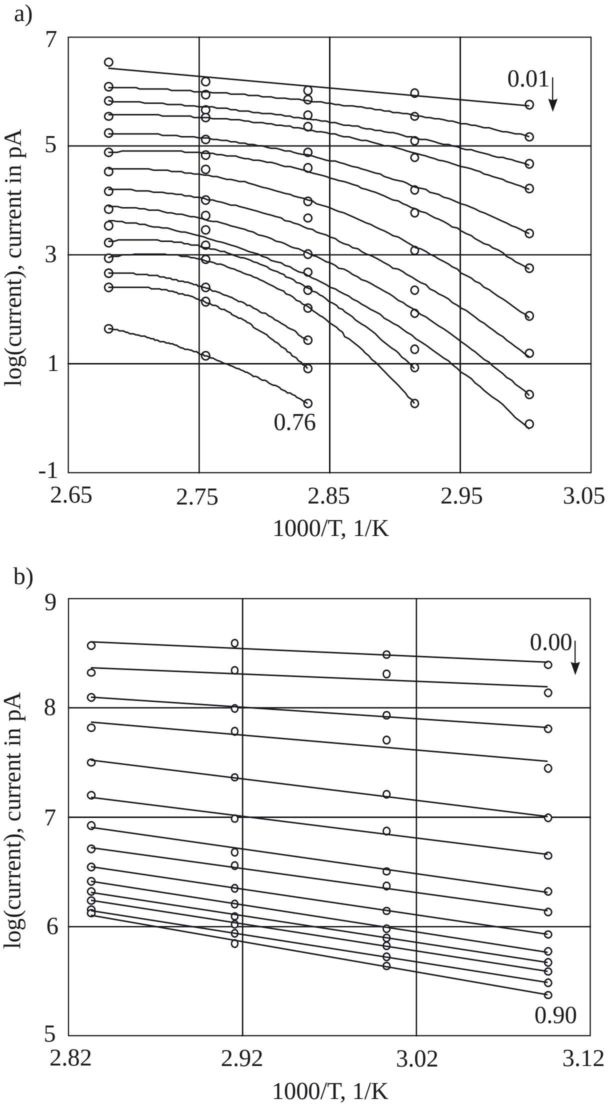


Fig. 6. Arrhenius plots of logarithm of the DC current versus inverse of temperature after different advancements of reaction a for: a) the DGEBA-3DCM system isothermally cured at 60 °C, 70 °C, 80 °C 90 °C and 100 °C (Ni electrodes IDEX sensor, U = 5 V, time of charging 40 s), α = 0.01, 0.05, 0.13, 0.20, 0.31, 0.36, 0.46, 0.52, 0.57, 0.61, 0.63, 0.66, 0.69, 0.71 or 0.76; b) the DGEBD-4D system isothermally cured at 50 °C, 60 °C, 70 °C and 80 °C (Cu sandwich-type electrodes, d = 0.080 mm, U = 1 V, time of charging 10 s), α = 0.0, 0.07, 0.14, 0.21, 0.33, 0.44, 0.55, 0.61, 0.68, 0.73, 0.77, 0.80, 0.84 or 0.90

The Arrhenius plots of DC ionic current for the DGEBA-3DCM system are linear at the beginning of the cure only (Fig. 6a), yielding the activation energy E_a = 0.185 eV. It indicates that the glass transition temperature increases rapidly during the cure exceeding the cure temperature. The large changes of free volume influence the ionic conductivity well before gelation. The conduction process can be therefore related to free volume by a formula proposed by Watanabe *at al.* [21]:

$$\sigma = \frac{q_i^2 n_0 D_0}{k_B T} \exp\left[-\left(\frac{E_n}{k_B T} + \frac{B_D V_i}{V_f} \right) \right] \quad (2)$$

where: q_i — *ionic charge*, n_0 — *ionic carriers number of the reference*, D_0 — *diffusion coefficient of the reference*, k_B — *Boltzmann constant: 1.3807 · 10^{-23} J/K*, T — *temperature in K*, B_D — *numeric factor*, V_i — *critical volume for the particle migration*, V_f — *free volume of the medium*, E_n — *activation energy of the charge carriers formation.*

In contrast, the Arrhenius plots of the ionic DC current for different advancements of the reaction of DGEBD-4D system are linear during all the reaction (Fig. 6b). The activation energy changes only slightly, starting from the value 0.062 eV. One can conclude that the glass transition temperature is considerably below the temperature of cure before gelation and that an increase in the glass transition temperature during the cure has weak influence on the ionic conduction mechanism. Therefore, the conduction process can be simply described as thermally activated with activation energy $E_\sigma = E_\text{n} + E_\mu$:

$$\sigma = \sigma_0 \exp(-E_\sigma / k_B T) \quad (3)$$

where: σ_0 — *conductivity of the reference*, E_σ — *activation energy of the ionic conduction process*, E_μ — *activation energy of the ionic carriers mobility*, E_n — *activation energy of the charge carriers formation.*

Evolution of mobile ions concentration

The concept and the experimental conditions of the TOF measurements were described elsewhere [15, 16]. It is assumed that the ion mobility can be evaluated from the DC measurements using the cell with ion blocking electrodes. Such kind of electrodes allow to accumulate the ions in the vicinity of the electrodes. In order to force the free ions to migrate and accumulate near the electrodes (polarization), the electric field should be initially applied and properly sustained before the polarity of the applied voltage is reversed and the flowing current is recorded. A decrease in the current should be detected as a result of the accumulation of ionic carriers near the opposite electrode and then an average time-of-flight of ions t_i across the sample thickness could be evaluated. Taking into account the voltage U and the sample thickness d, the calculation of the average value of the ion mobility μ_i is possible according to the equation:

$$\mu_i = d^2/(t_i \cdot U) \quad (4)$$

The time-of-flight of ions and ion mobility evolutions for DGEBA-3DCM [16] and DGEBD-4D [15] have been previously presented and discussed. For DGEBA-3DCM system it was not possible to detect the transitions times except of the beginning of the cure because of the vitrification phenomena and the low mobility of the ions in the medium [~10^{-9} cm^2/(V · s) at the beginning of cure] [16]. For the DGEBD-4D system, the transition time increases with the time of cure, as expected. However, in the gel point region the transient times began to be stabilized and when the gel point was approached the determination of time-of-flight from the TOF signals became difficult. The logarithmic plot of the current versus time-of-flight for the DGEBD-4D system show that during the gelation the ionic conductivity (σ) is decreasing faster than the ion mobility. Taking into account the equation:

$$\sigma = \Sigma n_i q_i \mu_i \quad (5)$$

where: q_i — *ionic charge*, n_i — *free carrier concentration*, μ_i — *ion mobility*,
one can conclude that the free carrier concentration is decreasing.

Analysis of the data obtained from DMA (dynamic viscosity) and from the TOF investigations (ion mobility) of DGEBD-4D system leads to the conclusion that the Stokes' law

$$\mu_i = q_i / 6\pi\eta r_i \quad (6)$$

where: r_i — *the ion radius*,
is fulfilled in the limited range of the advancements of reaction before gelation only (Fig. 7). Afterwards, the viscosity changes much faster than the ion mobility. Comparing the DC current and dynamic viscosity values one can notice that an implication of the Stokes' law: σ · η = *const.* is fulfilled at the beginning of the cure only

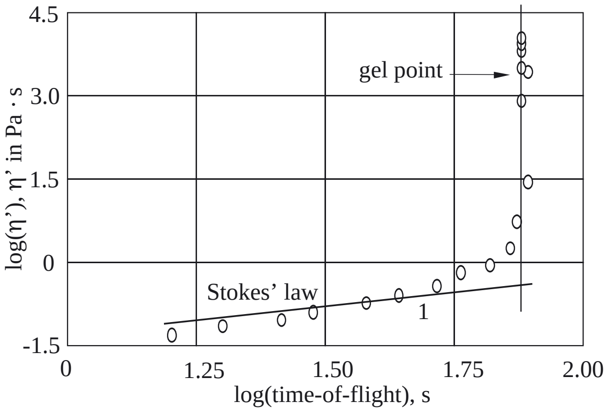


Fig. 7. Correlation of the logarithmic values of the dynamic viscosity η' (DMA measurements, plates 40 mm, 0.16—16 Hz) and of the time-of-flight of ions τ_i (TOF experiment, Au electrodes IDEX sensor, U = 5 V) for the isothermal cure of the DGEBD-4D system at 50 °C; line with a slope of 1 indicates the Stokes law

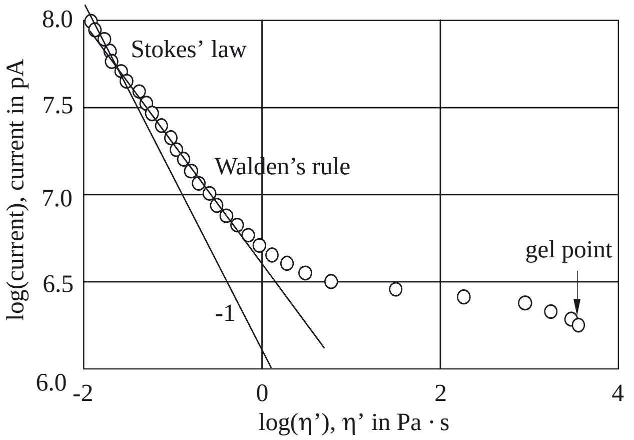


Fig. 8. Relationship between the logarithmic values of the ionic current (DC measurements, Cu sandwich-type electrodes, d = 0.080 mm, 10 s, U = 1 V) and of the dynamic viscosity η' (DMA measurements, plates 40 mm, 0.16—16 Hz) for the DGEBD-4D system isothermally cured at 50 °C; the lower line indicates a slope of -1

(Fig. 8). The further behavior follows the empirical Waldens' rule ($\sigma \cdot \eta^m = const.$, where the exponent m varies during the reaction), but also only in the limited range of the advancements of reaction.

This can be due to decrease in the permittivity during the reaction causing the changes of the dissociation of ion pairs [22]:

$$K_A = \frac{C_{ion\,pair}}{C_{cation}C_{anion}} = \frac{4\pi N_A^3}{3000}\exp\left[\frac{z_1 z_2 q^2}{a_i \varepsilon_s k_B T}\right] \qquad (7)$$

where: $C_{ion\ pairs}$ — *concentration of the ion pairs,* C_{cation} — *concentration of cations,* C_{anion} — *concentration of anions,* K_A — *ion-pair association constant,* N_A — *Avogadro number,* a_i — *ion size parameter,* z_1, z_2 — *charge on the ions,* ε_s — *static permittivity.*

The permittivity changes of the DGEBD-4D system are shown in Fig. 9. It is seen that the permittivity values are changing strongly during the reaction leading to the changes of the dissociation of ion pairs.

CONCLUSIONS

The Arrhenius plots of the ionic current derived from the DC measurements for different advancements of the reaction show that although gelation or viscoelastic properties of the medium are appearing, the conduction process can be simply described as thermally activated. By contrast, the vitrification phenomenon influences the ionic conduction mechanism because of large changes of free volume of the reacting medium.

Therefore the DC and AC methods yield similar results concerning the evolution of ionic conductivity up to an appearance of the relaxation processes due to vitrification. Then the vitrification strongly influences the conductivity making it dependent on frequency in the AC spectroscopy or polarization time dependent in the DC measurements.

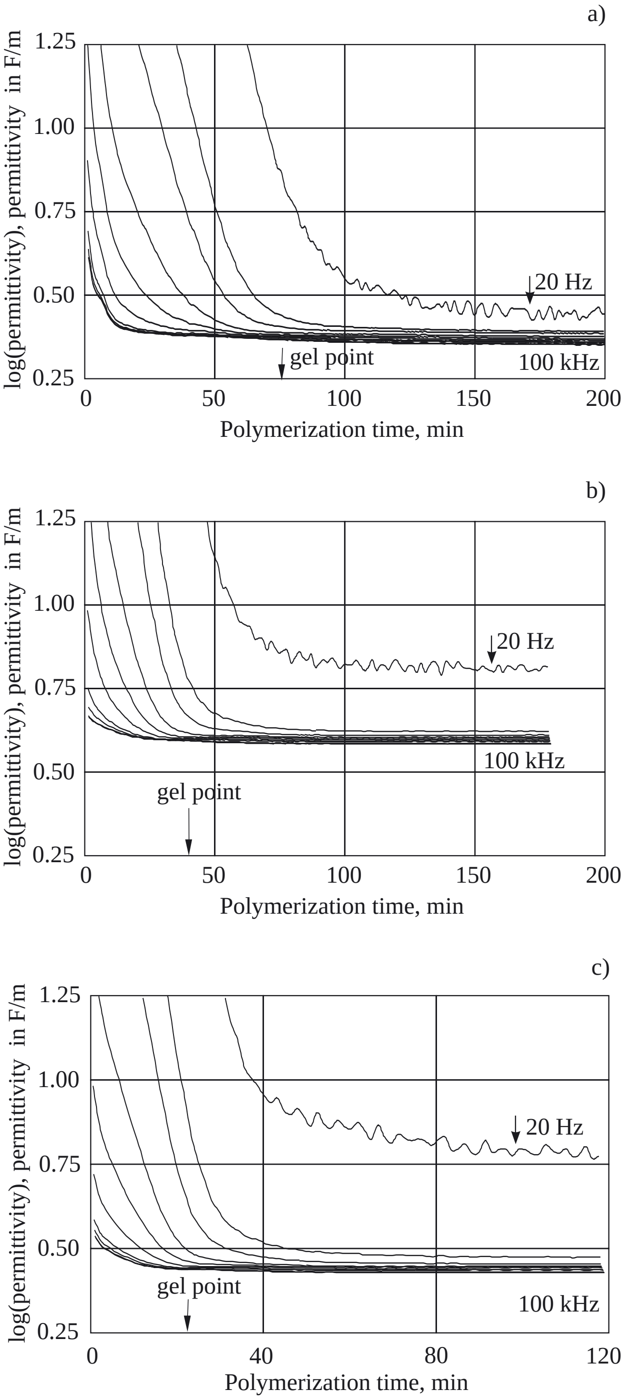


Fig. 9. Evolution of logarithm of permittivity (AC measurements, Ni electrodes Idex sensor, 20Hz—100kHz, U = 1V) during the cure of the DGEBD-4D system at a) 60 °C, b) 70 °C, c) 80 °C

The inconsistencies have been found between ionic conductivity and ion mobility evolutions. This suggests that additional effect has to be taken into account, such as the decrease in the free charge carriers number in the medium during the reaction. The comparison of the ionic conductivity from AC and DC measurements with the dynamic viscosity has shown that these changes follow the Stokes' law at the beginning of the cure only. They can be further described by the empirical Waldens' rule in the pre-gel state. Therefore, although the AC and DC methods can be applied for the *in situ* monitoring of resin cure, they cannot be easy generalized for different systems and for different cure conditions.

REFERENCES

1. Eloundou J. P., Feve M., Gérard J. F., Harran D., Pascault J. P.: *Macromolecules* 1996, **29**, 6907.
2. Eloundou J. P., Feve M., Gérard J. F., Harran D., Pascault J. P.: *Macromolecules* 1996, **29**, 6917.
3. Deng Y., Martin G.: *Polymer* 1996, **37**, 3593.
4. Stéphan F., Fit A., Duteurtre X.: *Polym. Eng. Sci.* 1997, **37**, 436.
5. Girard-Reydet E., Riccardi C. C., Sautereau H., Pascault J. P.: *Macromolecules* 1995, **28**, 7599.
6. Simpson J. G., Bidstrup S. A.: *J. Polym. Sci., Part B: Polym. Phys.* 1995, **33**, 55.
7. Mijovic J., Andjelic S., Fitz B., Zurawsky W., Mondragon I., Bellucci F., Nicolais L.: *J. Polym. Sci., Part B: Polym. Phys.* 1996, **34**, 379.
8. Casalini R., Corezzi S., Livi A., Levita G., Rolla P. A.: *J. Appl. Polym. Sci.*, 1997, **65**, 17.
9. Wasylyshyn D. A., Johari G. P.: *J. Polym. Sci., Part B: Polym. Phys.* 1997, **35**, 437.
10. Stéphan F., Seytre G., Boiteux G., Ulański J.: *J. Non-Cryst. Solids* 1994, **172—174**, 1001.
11. Friedrich K., Vinh-Tung C., Boiteux G., Seytre G., Ulański J.: *J. Appl. Polym. Sci.* 1997, **65**, 2529.
12. Koike T.: *Polym. Eng. Sci.* 1993, **33**, 1301.
13. Friedrich K., Ulanski J., Boiteux G., Seytre G.: *Polimery* 2006, **51**, 264.
14. Mijovic J., Bellucci F.: *TRIP*, Elsevier 1996, **4**, No. 3, 74.
15. Friedrich K., Ulański J., Boiteux G., Seytre G.: *IEEE Transactions on Dielectrics and Electrical Insulation, Dielectrics and Electrical Insulation Society* 2001, **8**, 572.
16. Ulański J., Friedrich K., Boiteux G., Seytre G.: *J. Appl. Polym. Sci.* 1997, **65**, 1143.
17. Gallone G., Levita G., Mijovic J., Andjelic S., Rolla P. A.: *Polymer* 1998, **39**, 2095.
18. Johari G. P., Wasylyshyn D. A.: *J. Polym. Sci., Part B: Polym. Phys.* 2000, **38**, 122.
19. Senturia S. D., Sheppard N. F.: *Adv. Polym. Sci.* 1986, **80**, 1.
20. Feve M.: *Annales des Composites* 1986, **1—2**, 7.
21. Watanabe M., Sanui K., Ogata N., Kobayashi T., Ohtaki Z.: *J. Appl. Phys.* 1985, **57**, 123.
22. Wasylyshyn D. A., Johari G. P.: *J. Polym. Sci., Part B: Polym. Phys.* 1997, **35**, 437.

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