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Isothermal curing of epoxy resins as seen by direct current and rheological measurements

Summary — The investigations of epoxy-amine systems' curing were carried out by direct-current (DC) measurements in order to get better understanding of the evolutions of ionic conductivity and viscosity in the reactive medium. This study extends our earlier DC and ion mobility investigations (Time-of-Flight method) on this subject. The additional rheological examinations (Dynamic Mechanical Analysis) have allowed to determine the correlations between evolution of electric and viscoelastic properties such as dynamic viscosity. The experiments have been carried out for the epoxy-amine reacting system that gelates and vitrifies: diglycidyl ether of bisphenol A with 4,4'-methylenebis(3-chloro-2,6-diethylaniline) (DGEBA-MCDA) and for the reacting system that gelates only: diglycidyl ether of 1,4-butanediol with 4,9-dioxa-1,12-dodecane diamine (DGEBD-4D). An inconsistency between the time dependence of ionic conductivity and viscosity was explained by the fact that the concentration of the mobile ion charge carriers is decreasing with the advancement of reaction. This observation lead to the conclusion of limited application of the electric techniques for the direct *in situ* monitoring of chemical reactions.

Key words: ionic conductivity, ionic carriers' mobility, direct-current measurements, dynamic mechanical analysis, epoxy resins, amines, isothermal curing.

BADANIA IZOTERMICZNEGO UTWARDZANIA ŻYWIC EPOKSYDOWYCH Z WYKORZYSTANIEM POMIARÓW STAŁOPRĄDOWYCH ORAZ REOLOGICZNYCH

Streszczenie — Proces utwardzania żywic epoksydowych aminami zbadano metodą pomiarów stałoprądowych (DC) w celu lepszego zrozumienia ewolucji przewodnictwa jonowego i lepkości w reaktywnym medium (rys. 1, 2). Praca ta poszerza wcześniejsze badania przewodnictwa i ruchliwości jonów metodą pomiaru czasu przelotu (ToF). Dodatkowe badania reologiczne (dynamiczna analiza mechaniczna — DMA, rys. 3, 4) pozwoliły na wyznaczenie korelacji pomiędzy zmianami właściwości elektrycznych i lepkosprężystych. Przedmiotem badań były dwa reaktywne układy epoksydowo-aminowe: żelujący i ulegający zeszkleniu [eter diglicydylowy bisfenolu A (DGEBA) + 4,4'-metylenobis(3-chloro-2,6-dietyloanilina) (MCDEA)] oraz wyłącznie żelujący [eter diglicydylowy 1,4-butanodiolu (DGEBD) + 4,9-diokso-1,12-dodekanodiamina (4D)]. Stwierdzoną niezgodność pomiędzy zależnościami czasowymi przewodnictwa jonowego i lepkości wyjaśniono faktem, że koncentracja ruchliwych jonowych nośników ładunku maleje z postępem reakcji (rys. 5—8). Obserwacja ta prowadzi do wniosku o ograniczonym zastosowaniu technik elektrycznych do bezpośredniego (*in situ*) monitorowania reakcji chemicznych.

Słowa kluczowe: przewodnictwo jonowe, ruchliwość nośników jonowych, pomiary stałoprądowe, dynamiczna analiza mechaniczna, żywice epoksydowe, aminy, utwardzanie izotermiczne.

The chemical reactions occurring during resin curing cause physicochemical changes associated with gelation and/or vitrification transitions. The dielectric, mechanical and physicochemical properties are changing simultaneously. Several non-electric techniques for cure monitoring have been proposed, for example: mechanical analysis [1—6], near infrared spectroscopy [5, 7], DSC [5, 8—12] or viscosity [1, 2, 4, 7, 9] measurements. Among the *in situ* electric techniques we may recall dielectrometry (AC technique) [3—5, 9—16], impedancometry [7, 17] or direct-current measurements (DC investigations) [3, 13, 18]. However, for the realization of the real-time control of chemical reactions in the reactive media by electrical measurements the fundamental correlations between dielectric response (electrical response depends on the nature, the concentration and the mobility of charge carriers as well as the dipole relaxations) and corresponding physicochemical changes (*e.g.* reaction mechanism, gelation and/or vitrification) have to be clarified.

This study extends our earlier investigations on the possibilities of monitoring of the isothermal curing of

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the epoxy-amine systems under isothermal conditions by electrical techniques [18—20]. Our previous ion carrier mobility measurements (Time-of-Flight method — ToF) were performed in an order to verify the basic assumption of the electrical techniques that the ion conductivity is directly related to the medium viscosity [20]. The above mentioned concept is based on the presumption that the ion concentration is constant and that only the ion mobility decreases in course of the reaction. Using ToF and DC techniques we have shown that in the epoxy resin systems, namely 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 is not fulfilled. The differences found between the time dependencies of ion conductivity and of ion mobility in course of curing were explained by the decrease in the concentration of ion charge carriers during the reaction, as one can conclude from our results and other observations [20—22].

In the present work DC measurements and the Dynamic Mechanical Analysis (DMA) are applied for the same epoxy-amine systems (DGEBA-MCDEA — exhibiting gelation and vitrification; DGEBD-4D — showing gelation only) for testing if it is possible to determine any correlation between the evolution of ionic conductivity and dynamic viscosity in these resins during curing.

EXPERIMENTAL

Materials

The measurement series have been performed for the stoichiometric mixtures of the reactants. DGEBD-4D samples have been prepared at room temperature. For DGEBA-MCDEA system (melt temperature of the MCDEA component = 92 °C) the mixing temperature was 100 °C. The viscous liquid epoxy-amine samples were then immediately placed in the thermostated oven on the preheated electrodes of the measurement unit. The chemical characteristics and physical properties of the components have been in details presented in [18]. The rheological behavior and kinetic characteristics of DGEBD-4D system are reported in [1] and those of DGEBA-MCDEA system in [2] and [8]. The degree of conversion for the gel point is 0.5745 for DGEBD-4D system [1] and 0.5895 for DGEBA-MCDEA system [2].

Testing methods

The experimental details of DC measurements were published elsewhere [3, 4, 13, 23], the basics of DMA techniques can be found in [24], whereas the backgrounds and the experimental conditions of ToF measurements in [18—20].

DC Measurements

DC measurements are performed for the cells with non ion-blocking electrodes. DC voltage (U) is applied to the cell for a short time and the flowing current is recorded. Then the electrodes are shortcircuited and the sample is depolarized for a long time. The polarity of the applied voltage is then reversed, and the flowing current is again recorded. This sequence is repeated several times during the sample curing. The isochronal values of the flowing currents (the current values after the same time of charging) are plotted against the advancement of the reaction, and it is assumed that the obtained curves represent evolution of the conductivity.

The measuring circuit for DC measurements consists of Keithley 617 electrometer (Keithley Instruments Inc., USA) with an incorporated voltage source (0—100 V) and PC-compatible computer for a data acquisition, storage and handling and the thermoregulated measurement oven. The parallel plates configuration of copper (Cu) round electrodes (ϕ = 16 mm) with guard rings and with PET films of different thickness as a spacer (0.02—0.2 mm) was used for DGEBD-4D system, and the interdigitated configuration of nickel (Ni) electrodes (IDEX sensor, distance layer 0.120 mm, form factor of electrodes surface/distance A/D = 800 mm, Micromet Instruments Inc., USA) was used for DGEBA-MCDEA system. The non ion-blocking materials for the electrodes have been previously selected on a basis of ToF experiments [20].

DMA Measurements

In DMA measurements the sample is placed between the parallel plates and the sinusoidal oscillations are induced by one of the plates. The forces strained by the sample deformations are measured by the opposite plate sensor and the complex viscosity η^* can be determined.

The viscoelastic measurements have been carried out using the Rheometrics Dynamic Analyser RDA2 (Rheometrics, USA) with the parallel aluminum round plates of 25 or 40 mm for the samples around 1.5 mm thick. The dynamic mechanical spectra have been registered in the frequency range between 0.16 Hz and 16 Hz with the amplitude depending on the physicochemical state of the system with the maximum of 50 % in the liquid state and close to 1 % after the gelation.

The gel points and the gelation times have been determined by the viscosity and dynamic viscosity rheological measurements [1, 2].

RESULTS AND DISCUSSION

For both DGEBA-MCDEA (Fig. 1) and DGEBD-4D (Fig. 2) systems there are no polarization phenomena during DC measurements as one can deduce from weak differences between the current values after different times of charging. The measurements were possible up

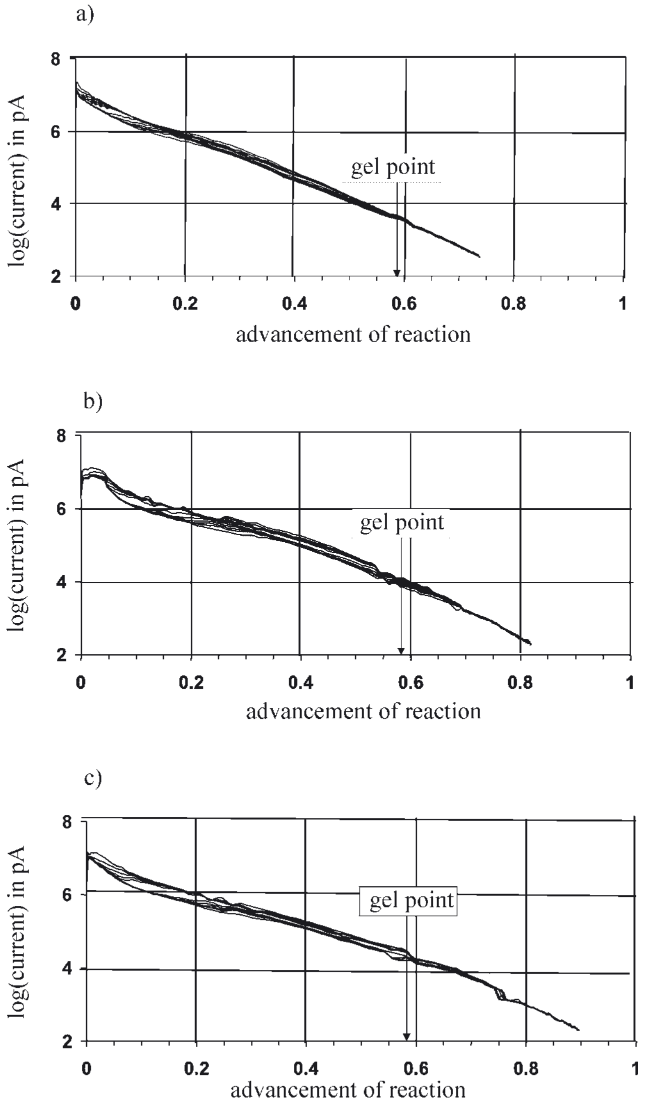

Fig. 1. Evolution of isochronal values of DC current after different times of applied electric field from 2 (the most upper curve) to 90 sec (the lowest curve) for DGEBA-MCDEA system isothermally cured at 140 °C (a), 150 °C (b) and 160 °C (c) (Ni electrodes IDEX sensor, polarization period of 90 sec, U = 5 V)

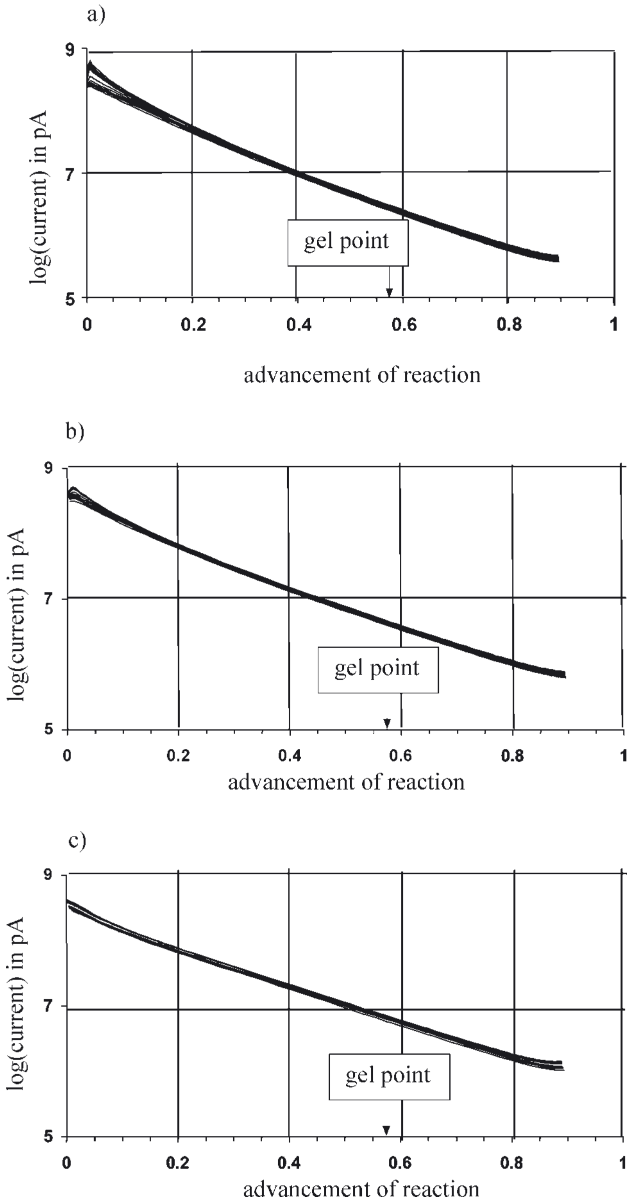

Fig. 2. Evolution of isochronal values of DC current after different times of applied electric field from 2 (the most upper curve) to 90 sec (the lowest curve) for DGEBD-4D system isothermally cured at 60 °C (a), 70 °C (b) and 80 °C (c) (parallel sandwich-type Cu electrodes, d = 0.080 mm, polarization period of 90 sec, U = 1 V)

to the resistance limitations of the sensor and of the measurement circuit. Due to relatively low current level flowing in DGEBA-MCDEA system it was not possible to measure the ion current changes during the entire hardening process at lower temperatures.

DMA measurements have allowed to determine the evolution of dynamic viscosity η of the samples during the curing. Dynamic viscosity values are initially frequency independent as seen in Figure 3 and Figure 4.

The rheological investigations of DGEBA-MCDEA system (Fig. 3) show that at each curing conditions the phenomena of gelation (indicated by arrows) and of vitrification (corresponding to the maxima of η plots) are well separated. The gel points were determined from the tan δ_m (ω) curves (not shown here) as the points where these curves are crossing at one point [at gel point tan δ_m (ω) should be frequency independent; tan δ_m = loss factor, ω = frequency].

The viscoelastic measurements of DGEBD-4D system (Fig. 4) show that dynamic viscosity values are frequency dependent already well before the gel point determined using the viscosity measurements technique [1], *i.e.* the elastic properties of the reacting medium manifest much earlier than the gelation occurs, in contrast to DGEBA-MCDEA system. Such changes of the elastic properties should be reflected also by changes of DC behavior before the gel point.

Comparing the evolutions of DC ionic conductivity (σ) and of the dynamic viscosity (η) (Fig. 5 — DGEBA-

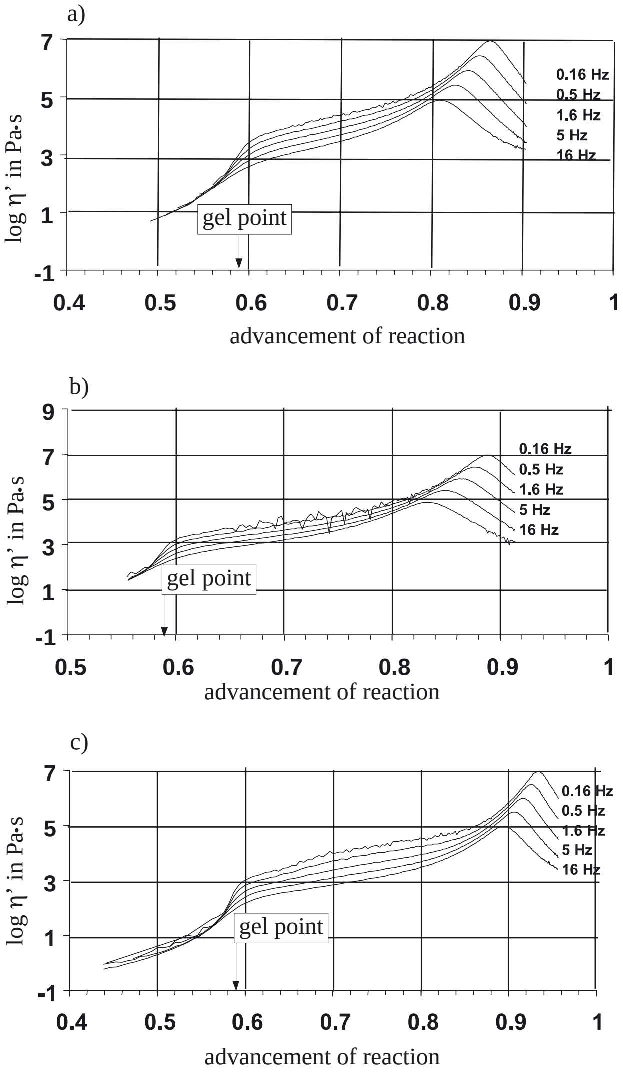

Fig. 3. Evolutions of the real part of the complex viscosity (η in Pa · s) with advancement of the reaction for DGEBA-MCDEA system isothermally cured at 140 °C (a), 150 °C (b) and 160 °C (c) (the plates diameter 25 mm, 0.16—16 Hz)

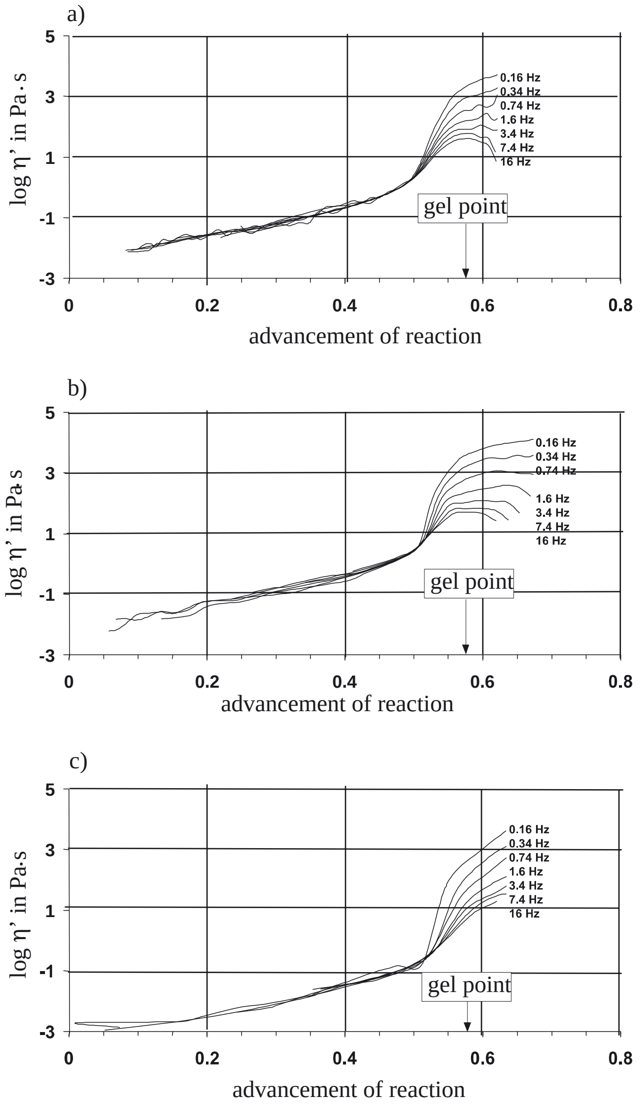

Fig. 4. Evolutions of the real part of the complex viscosity (η' in Pa · s) with advancement of the reaction for DGEBD-4D system isothermally cured at 60 °C (a), 70 °C (b) and 80 °C (c) (the plates diameter 40 mm, 0.16—16 Hz)

-MCDEA; Fig. 6 — DGEBD-4D) one can notice that the implication of the Stokes law, *i.e.* σ · η = *constant* (where σ = ionic conductivity) is fulfilled [agreement of experimental data (points) with dashed line] at the beginning of the curing only at lower temperatures. As the cure is going on, the dependence of the logarithmic values of the ionic conductivity and the logarithmic values of the viscosity follows the empiric Walden's rule [25]: $\sigma \cdot \eta^m$ = *constant*. However also this relation works also only in the limited range of the advancement of reactions before gelation and then the ion conductivity changes are still much more slower than these of the dynamic viscosity (the exponent *m* varies during the reaction).

The ionic conductivity depends on the concentration of ions and their mobility [26]:

$$\sigma = \sum n_i q_i \mu_i \tag{1}$$

where: n_i — *concentration of ion carriers*, q_i — *charge carried by the ion*, μ_i — *ionic mobility*.

According, to the Stokes's law [24, 25]:

$$\mu = q/6\pi\eta r \tag{2}$$

where: *r* — *ion radius*.

The ion mobility μ should be inversely proportional to medium viscosity η and should follows the Arrhenius-type dependence with an activation energy E_μ.

The concentration of ionic carriers is also thermally activated with activation energy E_n [28, 29]. If the ion carriers mobility μ and the concentration of ion carriers *n* are thermally activated with the activation energies E_μ and E_n respectively, the ion conductivity is thermally activated with the activation energy

$$E_a = E_\mu + E_n \tag{3}$$

The Arrhenius plots of the isochronal values of the ion current for different advancements of the reaction show that both in DGEBA-MCDEA and DGEBD-4D sys-

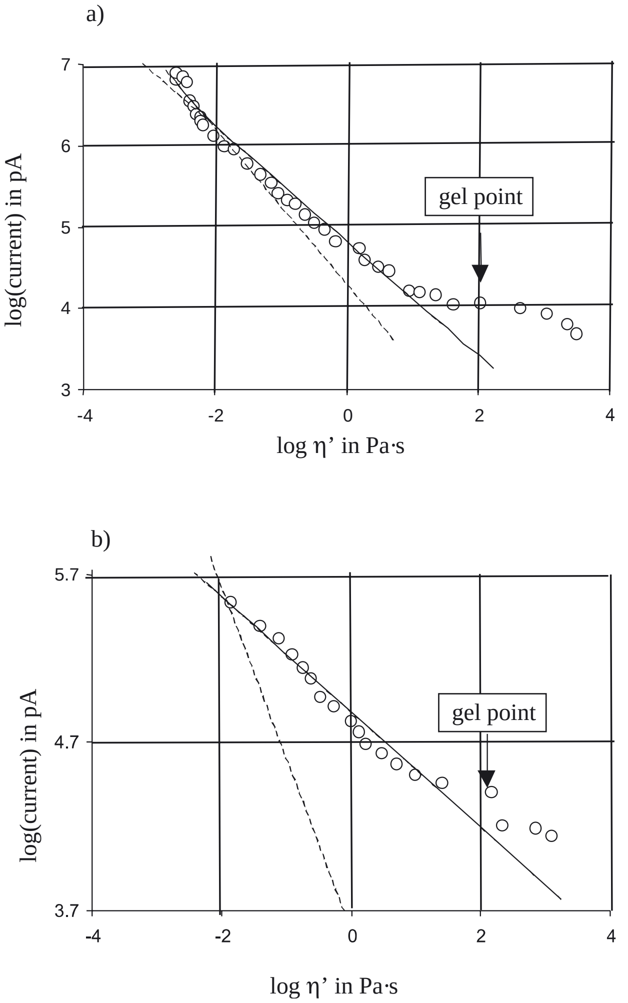

Fig. 5. Dependences of the ionic current (isochronal values taken after 10 sec, Ni electrodes IDEX sensor, U = 5 V) on the real part of the complex viscosity (η′ in Pa · s, plates diameter 25 mm, 0.16—16 Hz) for DGEBA-MCDEA system isothermally cured at 150 °C (a) and 160 °C (b); the broken line indicates a slope of -1

tems the conduction is indeed thermally activated during all the reaction. For DGEBD-4D and DGEBA-MCDEA systems the values of glass transition temperatures before gelation are considerably below the temperature of the curing [20].

The changes of the slopes of the Arrhenius plots indicate the continuous increase in the activation energy of conduction during the reaction up to the gel point, as shown in Figures 7 and 8.

After the gelation these changes are much weaker; this effect of "saturation" is well seen in DGEBD-4D system, as shown in Figure 8.

CONCLUSIONS

DC measurements and DMA technique have been applied for monitoring of physicochemical changes in the epoxy-amine systems under isothermal curing. The comparison of DC (ion current) and DMA (dynamic viscosity) data allowed to establish the correlations between the changes of electric and viscoelastic properties during isothermal curing of epoxy systems where the Stokes's law is fulfilled. Except of the beginning of the curing the evolution of the ionic conductivity does not follow the evolution of the viscosity. Also the empirical

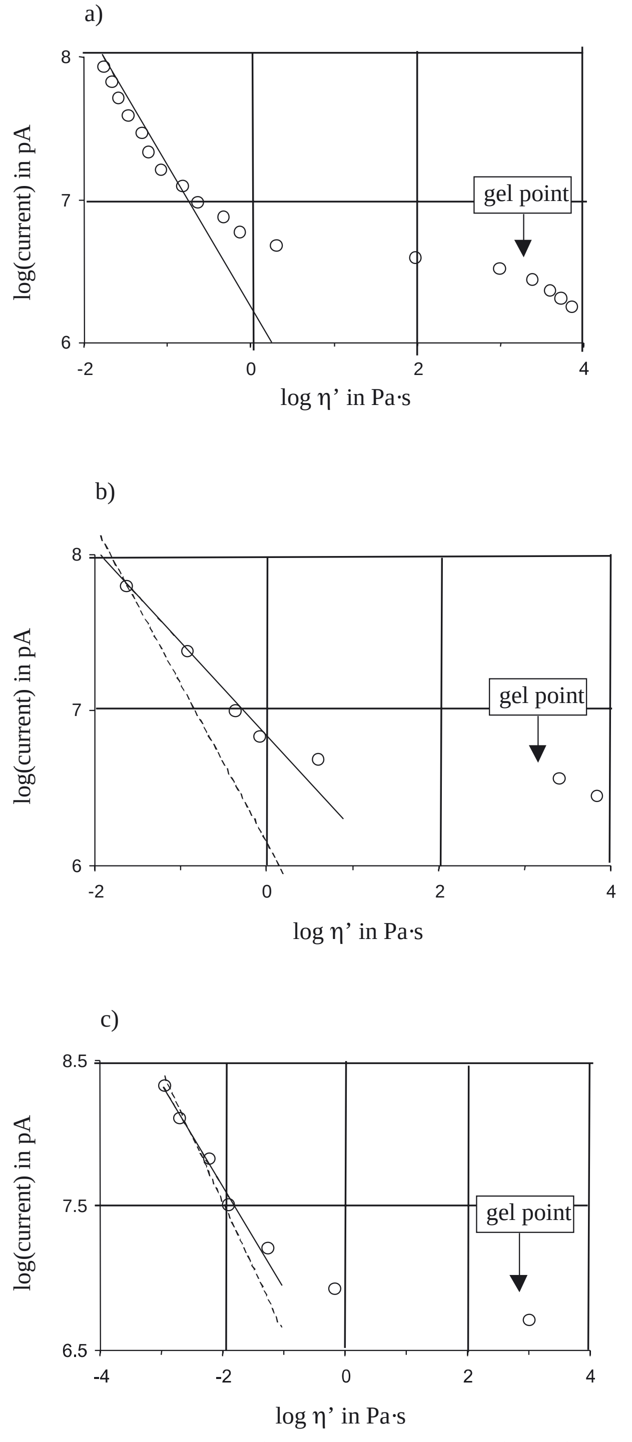

Fig. 6. Dependences of the ionic current (isochronal values taken after 10 sec, Cu sandwich-type electrodes, d = 0.080 mm, U = 1 V) on the real part of the complex viscosity (η′ in Pa · s, plates diameter 40 mm, 0.16—16 Hz) for DGEBD-4D system isothermally cured at 60 °C (a) and 70 °C (b); the broken line indicates a slope of -1

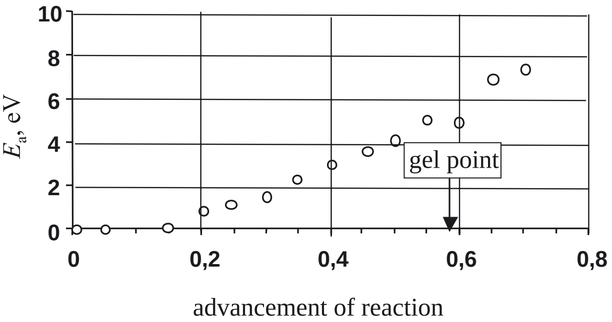

Fig. 7. The plot of the activation energy of the conduction process (E_a) for different advancements of the reactions for DGEBA-MCDEA system (DC measurements, Ni electrodes IDEX sensor, U = 5 V, time of charging 10 sec)

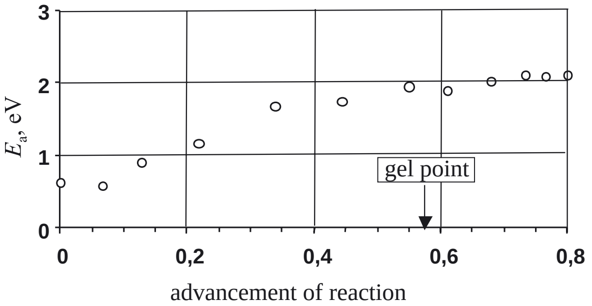

Fig. 8. The plot of the activation energy of the conduction process (E_a) for different advancements of the reactions for DGEBD-4D system (DC measurements, Cu sandwich-type electrodes, d = 0.080 mm, U = 1 V, time of charging 10 sec)

Walden's rule can be applied only in the limited range of the advancement of the reaction. This is probably due to changes of the concentration of the mobile ions during the reaction. These observations demonstrate limited application of the electrical techniques for the *in situ* reaction monitoring.

It was found, that the activation energy of ionic conductivity increases with an advancement of the reaction up to the gel point, and then some "saturation" of this tendency is observed.

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