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Electrical impedance spectroscopy of epoxy systems: The case of 1,4-butanediol diglycidyl ether/*cis*-1,2-cyclohexanedicarboxylic anhydride and triethylamine as initiator

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Abstract

A series of epoxy cured samples, with different molar composition of 1,4-butanediol diglycidyl ether (EP), *cis*-1,2-cyclohexanedicarboxylic anhydride (CH) and triethylamine (TEA) as initiator, was studied by Electrical Impedance Spectroscopy (EIS) in the frequency range 10^{-2}–10^{5} Hz. The resistivity of the system was evaluated by using the complex impedance analysis method. Resistivity values in the range between 10^{7} and 10^{13} Ω cm were obtained and related to the composition (molar fraction $\mathbf{x}_{\mathrm{EP}}$ or $\mathbf{x}_{\mathrm{CH}}$) of the epoxy system. The gel formation characteristics of the samples were obtained as theoretically described by Flory.

Keywords: Electrical impedance spectroscopy; Epoxy systems; Molar fraction variation

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1. Introduction

Epoxy resins are widely used in electric and electronic [1–3] devices because of their chemical, mechanical and electric properties. They present low solubility and permeability of inorganic and organic solvents, practically are chemically inert and during the curing process present good adhesion on metallic surfaces. The combination of mechanical compatibility with metals, the corrosion protection and their dielectric properties make them very important for every kind of electric, electronic and mechanic technological design. For this reason the research of the properties of epoxy systems including new formulations, new ways of curing and evaluation of dielectric properties constitutes a very important part of the technological development.

In the last 20 years, various publications [4–10] describe the electrical impedance spectroscopy as a very advantageous technique which permits a relatively easy evaluation of the electric properties through the separation of the different effects which contribute to the

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overall polarization mechanism of the material. A great number of these works report studies over the evolution of the dielectric properties during the curing [4–27] process looking for a relation between them and the degree of cure. Part of these works aims in monitoring of the rheological and dielectric properties for industrial processing applications. In our earlier studies with epoxy systems [28–31] we focused on the composition varying molar ratio between epoxy and anhydride. This methodology permitted to establish knowledge about the kinetics of the curing process and the physical properties of the final products. In spite of the significant number and important publications based on electrical impedance spectroscopy of polymers and specifically on epoxy systems, no publication is registered with variation of the molar composition in this area. So, the aim of this paper is to present an electrical impedance spectroscopy study of cured epoxy systems over a wide composition range which allows to analyze the role of the components in relation to their own dielectric properties. On the other hand the solidification during the curing process starts with initial elevation of the reaction mixture viscosity followed by gelation and finally the vitrification of the sample. The gelation characteristic of molecular systems with polyfunctionality was predicted by Flory and constitutes one of the important aspects of the evaluation of the curing process [28,32,33]. The samples with different compositions correspond to different degrees of aggregation reflecting the physical state before gelation, the state with gelation and finally the vitreous state of the system. Therefore, this work permits to obtain the correlation between the dielectric properties and the physical state of the studied epoxy system and to analyze the obtained behaviour in terms of Flory's theory.

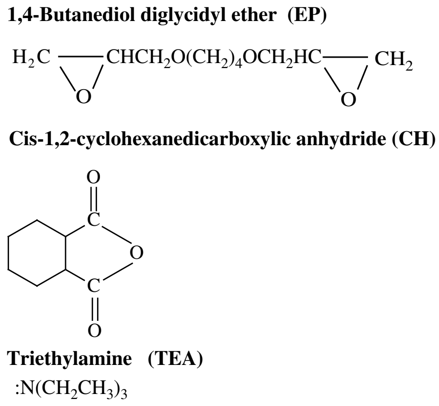

Fig. 1. The chemical structures of the reactants.

2. Experimental

2.1. Materials

The samples studied in this work are the products after curing of different mixtures of 1,4-butanediol diglycidyl ether (EP) with *cis*-1,2-cyclohexanedicarboxylic anhydride (CH) and triethylamine (TEA) as initiator, all of them provided by Aldrich Chemical Co. with analytical grade. Fig. 1 shows the chemical structures of the reactants. Table 1 summarizes the molar compositions of the mixtures before the curing in terms of $\mathbf{x}_{\mathrm{EP}}$, $\mathbf{x}_{\mathrm{CH}}$ and $\mathbf{x}_{\mathrm{TEA}}$ respectively, where $\mathbf{x}$ is the molar fraction of the components. The samples have a constant TEA molar fraction, $\mathbf{x}_{\mathrm{TEA}} = 0.0017$, that functions as an initiator for the reaction. Two kinds of excess components were studied: an anhydride excess, $\mathbf{x}_{\mathrm{EP}} = 0.00$–$0.29$ (samples 1 to 12), and an epoxy excess $\mathbf{x}_{\mathrm{EP}} = 0.51$–$1.00$ (samples 14 to 21). The sample 13 ($\mathbf{x}_{\mathrm{EP}} = 0.34$) corresponds to the stoichiometric composition and is a reference system for both excess series. The sample one corresponds to 100% CH + TEA, and sample 21 corresponds to 100% EP + TEA.

2.2. Sample preparation

The three components given in Fig. 1 react according to scheme of Fig. 2. All samples were prepared by mixing the three components with continuous stirring for about 15 min at room temperature (20 °C) according to Table 1. A clear mixture was obtained. Immediately after mixing, the mixture adequately conditioned was cured in pre-heated oven at 120 °C during 2 h [28,29]. The obtained materials were stored in a desiccator at room temperature until the measurements were performed.

2.3. Apparatus and procedures

Fig. 3 shows schematically the cell developed in our laboratory for the EIS measurements. The cell consists of a capacitor, constituted externally by stainless steel and internally by brass electrodes, 4.6 cm diameter, isolated by teflon. The cured samples were placed between the electrodes and by means of adequate cables, the cell was connected to the frequency response analyzer. The samples were prepared over cooper discs with the electrodes dimensions. For the samples where no gelation was observed ($\mathbf{x}_{\mathrm{EP}} > 0.60$) the discs were separated by four small (2 mm × 2 mm) pieces of analytical grade filter paper.

The electrical impedance spectroscopy experiments were carried out in a Potentiostat with a frequency response analyzer, AUTOLAB PGSTAT 30/FRA2, in the frequency range between 10^{-2} and 10^{5} Hz, controlled by a personal computer equipped with adequate software for data acquisition and treatment. A 1 V dc potential and a 10 mV ac signal were applied to the

Table 1
Molar compositions of the mixtures before the curing in terms of x_{EP}

	Anhydride excess samples											
Sample number	1	2	3	4	5	6	7	8	9	10	11	12
x_{EP}	0.00	0.02	0.04	0.06	0.07	0.08	0.11	0.13	0.15	0.20	0.25	0.29
	Stoichiometric sample											
Sample number	13											
x_{EP}	0.34											
	Epoxy excess samples											
Sample number	14	15	16	17	18	19	20	21				
x_{EP}	0.51	0.55	0.57	0.59	0.63	0.75	0.91	1.00				

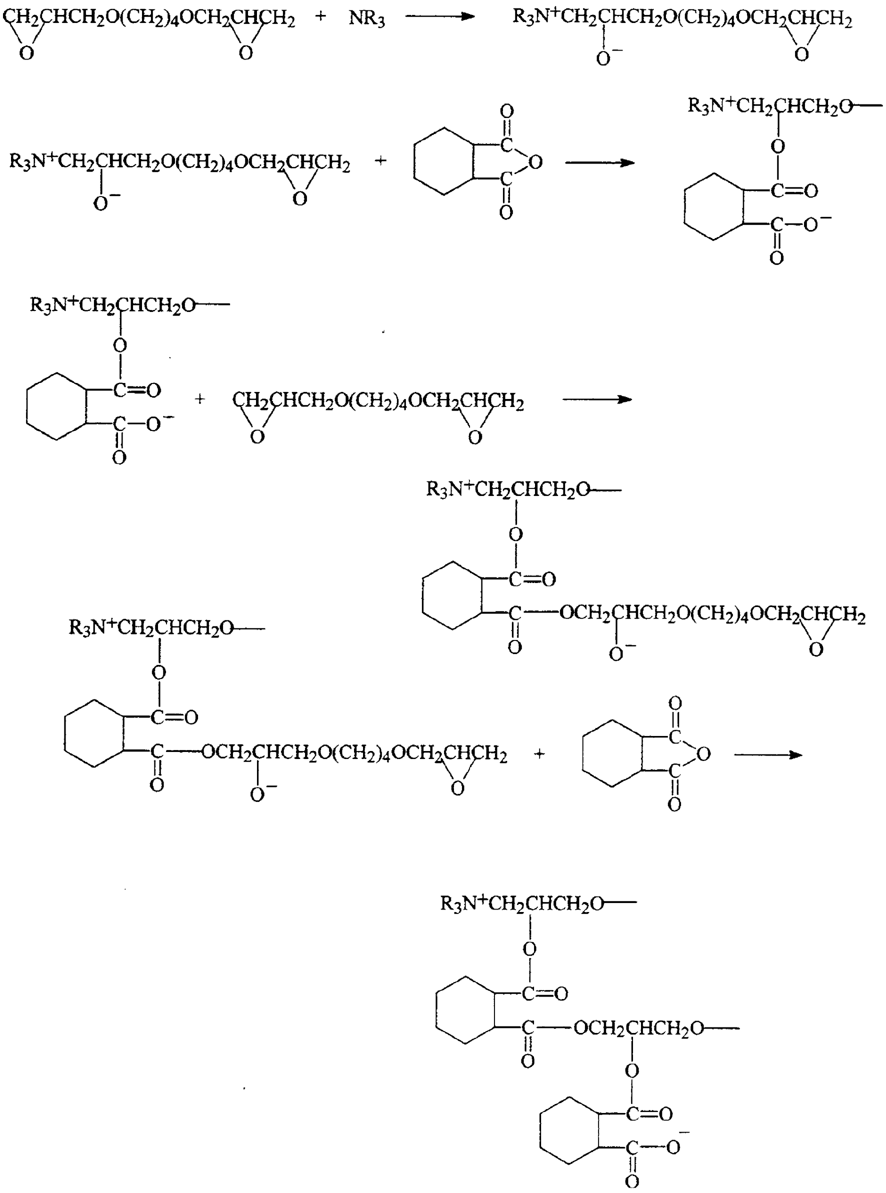

Fig. 2. Chemical reactions in EP/CH/TEA system [34].

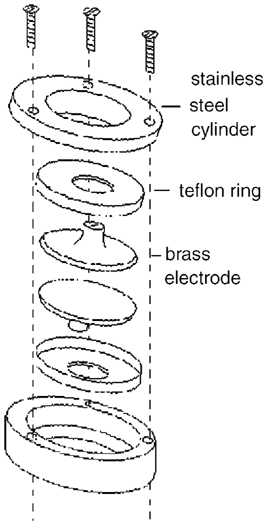

Fig. 3. The electric impedance cell.

system. Twenty experimental points have been recorded in every frequency decade. All experiments have been repeated three times in order to verify variation of the system during the measurements and to test repeatability. The cell constant K for every sample was obtained by using the relation, $K = S/L$ where S is the electrode area and L the sample thickness.

3. Results and discussion

According to electrical impedance spectroscopy technique the dielectric system, between the capacitor plates, is submitted to a $V(t)$ ac sinusoidal potential wave. The response of the system, which depends on their dielectric characteristics, is detected as a sinusoidal electric current $I(t)$ with the same frequency of the excitation potential wave but with different phase caused by the dielectric relaxation processes. The impedance Z of the system is defined as the ratio between excitation potential $V(t)$ and response current $I(t)$. In different publications [4,5,7–10,15–19,25] Mijovic and collaborators discussed the response of polymers in the form of complex impedance and permittivity. When an electric field is applied to capacitor plates separated by a dielectric material like an epoxy resin or other polymeric specimen, the electric charges of atoms, molecules and ions suffer local displacement relative to their original equilibrium positions and the material is polarized. The maximum polarization is obtained when the applied electric field is capable to affect all the material electric charges producing a well defined orientation of these charges in the material. Generally the polarization effects in homogeneous dielectric material can be classified in four categories [3–8,14,15,20,25] namely: electronic polarization—the result of electronic orbital displacement in relation to the center of the atoms; atomic polarization—caused by atoms displacement through the application of the electric field; dipolar polarization—the result of the orientation of permanent dipoles present in molecules, molecular segments or supramolecular structures; ionic polarization—the result of charge migration to the electrodes through the action of the electric field. The migration mechanism is denominated extrinsic [5] when the electric charges are originated in ionic impurities of the epoxy system and intrinsic when the charges are associated to the chemical characteristics of the epoxy components and they present protonic conductivity and resonance effects. The relaxation times of the two first polarizations mechanisms are extremely small. They correspond [25] to ultra-violet, visible and infrared frequencies and generally can be detected in frequencies greater than 10^{12} Hz. However dipolar and migrating polarizations can be detected in frequencies smaller than 10^9 Hz. This reality requires a very wide frequency range of ac potential in order to detect any kind of polarization. It is to expect that the dielectrical response of epoxies and polymers includes mainly two components, the dipolar polarization and the migration of free charges. The experiments of the present study were performed in the low frequency range between 10^{-2} and 10^5 Hz.

It is well known that the results of EIS can be presented in the form of Nyquist diagrams.

Fig. 4(a) and (b) presents Nyquist diagrams, the first one for three samples with compositions characterized by anhydride excess and the other one with three samples with epoxy excess. As we mentioned before we have studied systematically the total of twenty one samples with different compositions. All samples present Nyquist diagrams with a semicircle.

No sample has presented Maxwell–Wagner–Sillars [2,10,25] polarization which is caused by charge accumulation in the electrodes and is detected as a vertical line in the Nyquist diagrams. The diagrams showed in Fig. 4 can be described by the equivalent circuit proposed in Fig. 5. The choice of this circuit was the result of a reasonable fitting of the experimental values using the PAR's 3.95 "Equivalent Circuit" software, and the maintenance of the number of circuit elements at a minimum. This procedure allows the association of these elements to the phenomena probably occurring at the epoxy system.

The complex impedance of the equivalent circuit is given by Eq. (1):

$$Z = R_0 - \mathrm{j}\left(\frac{R}{RC\omega - \mathrm{j}}\right) \tag{1}$$

where $\omega = 2\pi f$ and $\mathrm{j} = \sqrt{-1}$. Transforming this equation to $Z = Z' - \mathrm{j}Z''$, we obtain:

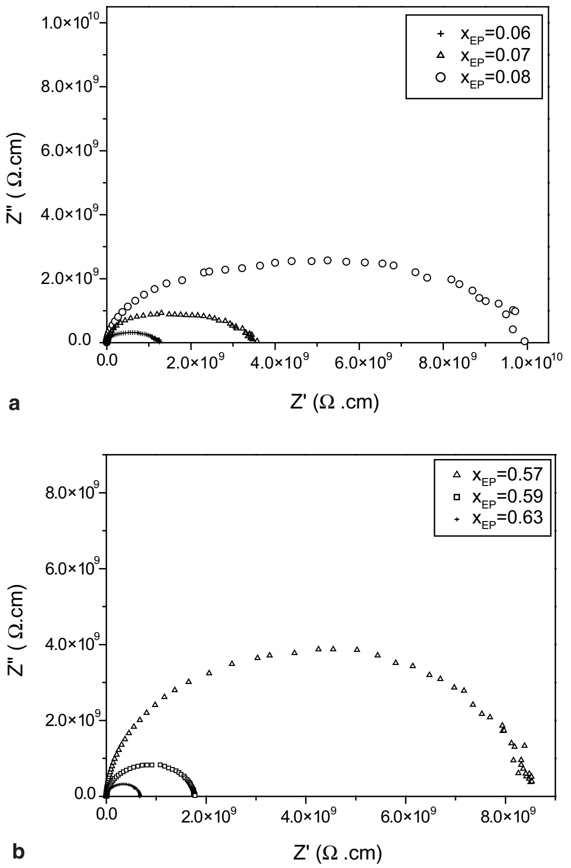

Fig. 4. Nyquist diagrams (Z' versus Z'') for anhydride and epoxy excesses (a) and (b), respectively.

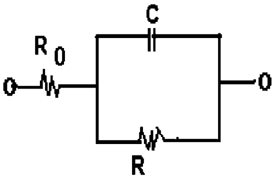

Fig. 5. Electric equivalent circuit.

$$Z' = R_0 + \left(\frac{R}{1 + R^2C^2\omega^2}\right) \tag{2}$$

and

$$Z'' = \frac{R^2C\omega}{1 + R^2C^2\omega^2} \tag{3}$$

In this circuit, R_0 is the resistance in high frequencies and can be related to dipolar relaxations, R is the resistance in low frequencies and it is assigned to migrating charges, and C is the system capacitance. According to Eqs. (2) and (3), the resistance R_0 prevails the impedance response in high frequency range, and the sum of the resistances $R + R_0$ predominates in low frequencies. Then, the resistance R can be evaluated for every epoxy sample through the arc diameter of the Nyquist diagrams (Fig. 4(a) and (b)) as well as it can be directly obtained by the Bode diagram, where the $\log|Z|$ is plotted versus the $\log f$, in the low frequency range, as showed in Fig. 6(a) and (b), or even the diagram Z'' versus $\log f$ in the Z'' maximum value, using Eq. (4), as showed in Fig. 7(a) and (b).

$$Z''_{\max} = R/2 \tag{4}$$

The resistance R can be given [5] in terms of the resistivity by means of:

$$\rho = 1/\sigma = RK \tag{5}$$

where K is the cell constant and σ is the conductivity associated to migrating charges. The resistivity values obtained according to the three different methods, described above, are very similar. For example, in the sample with epoxy molar fraction $\mathbf{x}_{\mathrm{EP}} = 0.63$, the ρ obtained

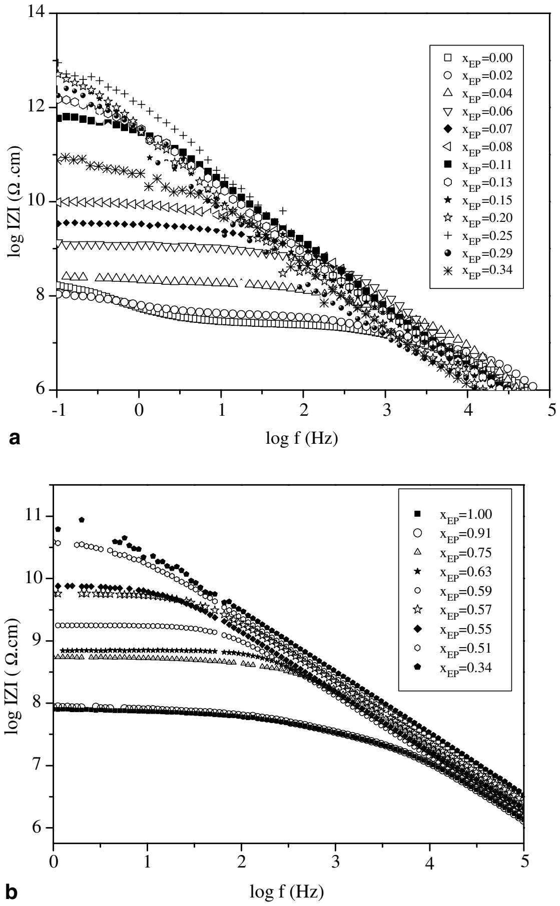

Fig. 6. Bode diagrams ($\log|Z|$ versus $\log f$) for anhydride and epoxy excesses (a) and (b), respectively.

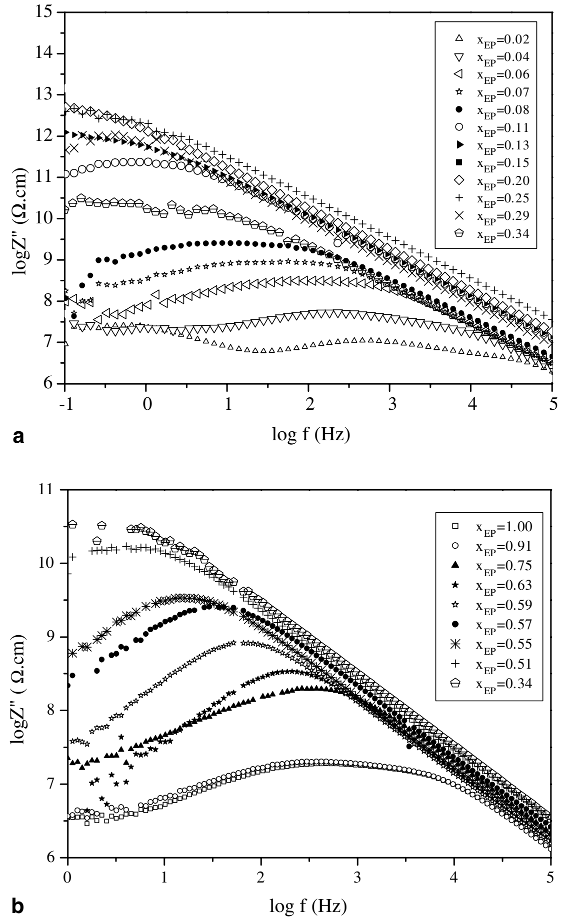

Fig. 7. Diagrams Z'' versus log$f$ for anhydride and epoxy excesses (a) and (b), respectively.

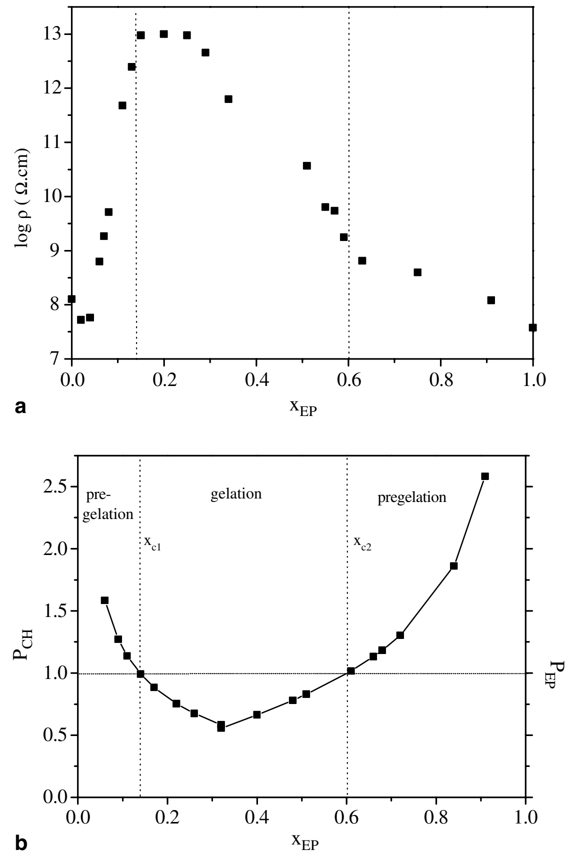

Fig. 8. (a) The relation between resistivity (logρ) and epoxy molar fraction $\mathbf{x}_{EP}$ and (b) the theoretically expected behaviour of P_{EP} and P_{CH} as function of $\mathbf{x}_{EP}$.

values are: $\rho = 7.10 \times 10^8$ Ω cm for the Nyquist diagram, $\rho = 6.80 \times 10^8$ Ω cm for the Bode diagram and $\rho = 6.74 \times 10^8$ Ω cm for the Z'' versus log$f$ diagram. This way, the resistivity was determined in a frequency range where it is to expect that the polarization is attributed more to the migrating charges and less to the permanent dipoles polarization. Fig. 8(a), which presents the relation between resistivity and epoxy molar fraction, shows that the resistivity starts with very low values in the anhydride excess range, increases with increasing $\mathbf{x}_{EP}$ and consequently decreases until very low values in the epoxy excess range.

In order to elucidate the dielectric behaviour of the system a discussion of the gelation according to the Flory's concepts can be helpful. According to the Flory's theory [28,32,33] the conditions for the formation of an infinite network can be derived from the critical branching coefficient β_c which is related to the functionality of the reactants (Eq. (6)), in this case the epoxy and the anhydride.

$$\beta_c = (f - 1)^{-1} \qquad (6)$$

where f is the functionality of the reactant. In general, the branching coefficient β is related to the fractions of anhydride groups and epoxy groups present in the reactional mixture which are given by P_{EP} and P_{CH}. Castiglia et al. [28] considering functionality two for the anhydride and four for the epoxy showed that gelation conditions of the epoxy resin are given theoretically by the Eqs. (7) and (8) for anhydride and epoxy excesses, respectively.

$$P_{CH} = (0.16/\mathbf{x}_{EP}0.16)^{1/2}$$
$$\text{for } \mathbf{x}_{EP} \text{ between 0.0 and 0.33} \qquad (7)$$

$$P_{EP} = (0.66\mathbf{x}_{EP}/(1 - \mathbf{x}_{EP}))^{1/2}$$
$$\text{for } \mathbf{x}_{EP} \text{ between 0.33 and 1.00} \qquad (8)$$

The theoretically expected behaviour of P_{EP} and P_{CH} as function of $\mathbf{x}_{EP}$ is demonstrated in Fig. 8(b). The two critical composition conditions are given by $\mathbf{x}_{EP1} = 0.14$

and $\mathbf{x}_{EP2} = 0.60$, respectively. In other words, theoretically, no gelation occurs in the $\mathbf{x}_{EP}$ regions from 0.00 to 0.14 and from 0.60 to 1.00 because it would correspond to non-physical values of the fraction of reacted anhydride and epoxy groups greater than 1. The same authors using Temperature Scanning Brillouin Spectroscopy (TSBS) for the same epoxy system obtained experimentally the pregelation regions $\mathbf{x}_{EP}$: 0.00–0.14 (CH excess) and $\mathbf{x}_{EP}$: 0.56–1.00 (EP excess), that are in agreement with the theoretical values $\mathbf{x}_{EP1}$ and $\mathbf{x}_{EP2}$ [28]. Fig. 8(a) shows that the experimentally obtained value of $\log \rho$ increases exponentially with $\mathbf{x}_{EP}$ in the anhydride excess and consequently reaches a constant value. This change occurs in the $\mathbf{x}_{EP} = 0.15$ which is very near to the theoretically obtained $\mathbf{x}_{EP1} = 0.14$. In the epoxy excess range the values of $\log \rho$ change linearly with decreasing $\mathbf{x}_{EP}$ until $\mathbf{x}_{EP} = 0.59$, which again is very near to the theoretical $\mathbf{x}_{EP2} = 0.60$ and then increase to reach the maximum in the gelation range. Taking into account the experimental findings of the thermal analysis—DSC, the Temperature Scanning Brillouin Spectroscopy (TSBS) and that from the Electric Impedance Spectroscopy (EIS) we affirm that the techniques TSBS and EIS, contrary to the DSC technique, are sensitive to the gelation as well as to pregelation range. The regions characterized by the theoretical $\mathbf{x}_{EP}$ values of 0.00–0.14 and 0.60–1.00 or the experimental ones of 0.00–0.15 and 0.59–1.00 are related to the process of increasing molecular dimension and can be considered pregelation regions where the system has not reached yet the dimension of an incipient polymer network.

The resistivity variation during the curing process has been discussed by various authors [7–9,15,20,25,26]. They find that the resistivity increases with increasing viscosity until the system reaches the gel point. After this point the viscosity tends to infinity and the resistivity remains constant. Consequently the decrease of conductivity cannot be attributed only to the increase of viscosity. Insofar, the polymerization proceeds and the formation of a three-dimensional net is obtained, the mobility of the electric charge carriers is affected but the conductivity is not reduced to zero. Until the gel point the conductivity can be related to the macroscopic viscosity of the material [20] and reflects the mobility of the long range migrating charges. After the gel point the conductivity is related to the short range mobility. In the present study the variation of the resistivity is not obtained during the curing process as a non-equilibrium, non-steady state situation, but it is the result of measurements of different cured samples with different extents of aggregation and formation of three-dimensional network. A possible interpretation of the behaviour obtained in Fig. 8(a) is related to the composition of the samples.

In the non-stoichiometric reactional mixtures there is an excess of free active molecules, epoxy or anhydride, which contributes with localized micro-viscosity through clusters inside the polymer matrix, where extrinsic and intrinsic migrating charges respond to the applied electric field. The different resistivity values in cured samples after the gel point is related to the composition. Approximating to the stoichiometric composition, the density of crosslinking increases, the conductivity decreases but still migrating charges contribute effectively for a measurable resistivity. It is well discussed that when an external electrical field is applied in a dielectric material the internal local electric field is not known. It can be considered that similarly to the ionic compounds [35], the internal local field reaches very elevated values which can promote the local charge migration without direct relation to the materials viscosity.

4. Conclusion

The EIS technique was used to study cured samples of 1,4-butanediol diglycidyl ether (EP) with *cis*-1,2-cyclohexanedicarboxylic anhydride (CH) with different molar compositions using constant concentration of triethylamine (TEA) as initiator. The complex impedance was used for the analysis of the obtained dielectric response. The sample resistivity was obtained in the low frequency regime where the migrating charges polarization dominates the response. The ionic resistivity was evaluated using Nyquist, Bode or $Z'' \times \log f$ diagrams. A variation of the resistivity behaviour was detected in $\mathbf{x}_{EP}$ values between the pregelation and gelation ranges for both, epoxy and anhydride, excess regions. Similarly to TSBS technique which is sensitive to the variation of viscoelastic properties, the EIS is sensitive to the dielectric properties variation which occurs in the change from the pregelation to the gelation range. This change cannot be obtained by DSC classical techniques. In the samples with pregelation conditions the macroscopic viscosity determines the conductivity behaviour and can be attributed to the long range, intrinsic and extrinsic free charges transportation. In the gelation region the conductivity can be related to the short range mobility of charges due to the microscopic local viscosity and the effect of the local internal electric field.

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