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Anomalous trends in conductivity during epoxy–amine reactions

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Measurements were carried out of conductivity due to migrating charges as a function of extent of reaction for a series of epoxy–amine formulations. All systems were characterised by the reaction mechanism common to this generic group of materials and by an increase in the steady shear viscosity during reaction. The measured conductivity, however, followed one of three distinct patterns as a function of extent of reaction. Intuitively unexpected, and hence particularly interesting, was the observed increase in conductivity during reaction in several formulations. This communication marks the first time that such response has been reported in the literature. An explanation of the observed trends was offered in terms of an interplay between the contributions of extrinsic and intrinsic migrating charges to the overall (measured) conductivity. Without such information, all correlations between the measured conductivity and the major processing parameters (viscosity, extent of reaction) remain strictly batch-specific and empirical. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: conductivity; dielectric; reactive system)

INTRODUCTION

The use of conductivity by migrating charges to monitor the advancement of reactions in polymer-forming systems has been reported in a number of research articles (e.g. refs [1–10]) and reviews[11,12]. According to the vast majority of published reports, the source of conductivity in reactive mixtures are the ever-present but seldom identified (or quantified) 'ionic impurities'. Since the mobility of these ionic impurities must be impaired by the increase in viscosity during reaction, it is commonly assumed that a correlation should exist between the decreasing conductivity, on the one hand, and the increasing viscosity and/or extent of reaction, on the other.

Unfortunately, the hypotheses that the conductivity always decreases and that ionic impurities (viewed as remnants from synthesis) are the lone charge carriers in reactive polymer-forming formulations whose mobility can be used as a direct measure of the advancement of cure—are both incorrect! The experimentally measured 'ionic conductivity' (occasionally also referred to as 'ionic viscosity') is an empirical parameter that is batch-specific and devoid of any fundamental significance. The major reason for that stems from the fact that ionic impurities represent but one contribution to the overall or apparent conductivity. The measured conductivity encompasses the contributions from both *extrinsic and intrinsic* mechanisms, each of which must be elucidated and quantified when attempting to develop a fundamental correlation between conductivity and the advancement of reactions. As a result of the interplay between extrinsic and intrinsic contributions to the overall conductivity during reaction, in some reactive systems, an increase in viscosity can be accompanied by an increase (!) in the measured conductivity. Naturally, this observation is incompatible with the concept of a continuously decreasing conductivity as a result of decreasing mobility of ionic impurities, and an explanation for the observed trend must be found. The origin of this interesting and important finding, which has not been reported in the literature hitherto, is described in this communication.

The principal objective of this study is to clarify some common misconceptions associated with the origin of measured conductivity in reactive systems.

EXPERIMENTAL

Materials

A series of epoxy–amine formulations were prepared and investigated. The compounds investigated include the following epoxies: phenyl glycidyl ether (PGE, Aldrich), cresyl glycidyl ether (CGE, Aldrich), diglycidylether of bisphenol A (DGEBA, Epon 825—Shell Chemical Comp.), triglycidylether of para aminophenol (TGEPA, Araldite 0510—Ciba-Geigy Corp.), and tetraglycidyl diamino diphenyl methane (TGDDM, MY 721—Ciba-Geigy Corp.), and amines: dipropylamine (DPA), N-methyl aniline (NMA), and aniline (AN), all from Aldrich. Their chemical structures are shown in *Table 1*.

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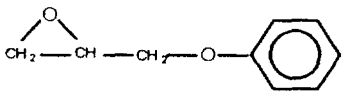
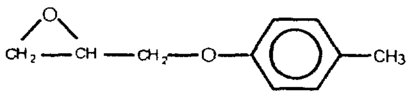
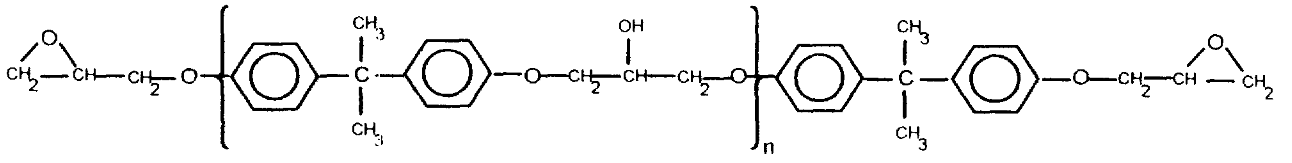
Table 1 Chemical structures of epoxy and amine compounds



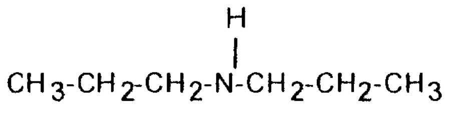
Phenyl Glycidyl Ether (PGE)



Cresyl Glycidyl Ether (CGE)

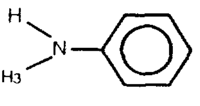


Diglycidyl Ether of Bisphenol A (DGEBA)

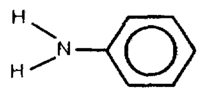


$CH_3\text{-}CH_2\text{-}CH_2\text{-}N(H)\text{-}CH_2\text{-}CH_2\text{-}CH_3$

Dipropylamine (DPA)



N-methyl aniline (NMA)



Aniline (AN)

Stoichiometric ratio of epoxy and amine groups was used in every formulation.

Techniques

Dielectric measurements were conducted simultaneously at the University of Pisa and the Polytechnic University. The results were fully reproducible and interchangeable. At Pisa, we utilised a GenRad Digibridge model 1693 interfaced to a computer via an IEEE 488 interface bus. The conductivity was determined by measuring at different reaction times the admittance of a 20 pF parallel plate capacitor fully immersed in the reaction mixture. Each measurement was performed at 23 different frequencies between 100 Hz and 200 kHz. The sample was immersed in a thermal bath whose temperature was controlled to within ±0.5°C. The empty cell capacitance was determined by calibration with cyclohexane. At the Polytechnic, we employed two instruments: (1) Solartron 1260 Impedance Gain/Phase Analyzer (10 μHz to 32 MHz); and (2) Hewlett-Packard 4284A Precision LCR Meter (20 Hz to 1 MHz). Each instrument was modified by the addition of a temperature controlled chamber and interfaced to a computer via IEEE 488.2 interface bus. Two and three-electrode cell configurations were utilised as described elsewhere. The impedance/gain phase analyzer was further modified by the addition of a high-impedance adapter (HIA), assembled in our laboratory, which becomes necessary when the measured impedance exceeds the limit of the analyzer (100 MΩ). Schematics of our entire setup and further experimental details are available elsewhere[13–15].

Steady shear viscosity was measured at Pisa using a Physica Messtechnik viscometer model MC20. Measurements were conducted at a shear rate of 65 s^{-1}. Temperature was controlled within ± 0.2°C and data was collected at time intervals of 72 s. A Brookfield Viscometer Model was utilised at the Polytechnic as described elsewhere[16]. FTIR spectroscopy was also performed as described in our recent communication[17].

RESULTS AND DISCUSSION

The procedure for obtaining the overall conductivity from the impedance spectra has been outlined in detail in our previous communications[8,13,15] and will not be restated here. Suffice it to say that the sample resistance (R) is calculated from the maximum imaginary impedance (Z''_{max}) according to $R = 2Z''_{max}$. The overall conductivity (σ), a material property, is evaluated from $\sigma = 1/\rho = L/SR$, where ρ is the overall resistivity and S/L the cell constant. An alternative method consists in plotting the quantity $\epsilon_0\epsilon''\omega$ as a function of frequency. The overall conductivity is equal to the frequency-independent value of $\epsilon_0\epsilon''\omega = Y'(\omega)\epsilon_0/C_0$, where ϵ_0 is the dielectric permittivity of vacuum, ϵ'' is the imaginary part of the dielectric permittivity, $Y'(\omega)$ is the real admittance, and C_0 is the capacitance of the empty cell. Extent of reaction and/or viscosity can then be related to conductivity by one of various empirical equations reported in the literature (e.g. refs [8,13,18]).

We begin our discussion by emphasising that two general characteristics were found in all epoxy–amine formulations investigated, non-polymer-forming and polymer-forming (linear or network) alike. First, a two-step reaction mechanism, whereby primary amine and epoxy groups react to form hydroxyl and secondary (earlier stage) and/or tertiary amines (later stage), was common to all systems. The etherification reaction occurs under special conditions only, as described elsewhere[19]. The mechanism and kinetics of epoxy–amine reaction have been discussed at length elsewhere (e.g. refs [20,21]) and will not be invoked here. The second common characteristic of all epoxy–amine systems investigated was an increase in the steady shear viscosity during reaction. A composite plot of steady shear viscosity *versus* reaction time for three different epoxy– amine formulations is shown in *Figure 1*.

We then set out to investigate how the measured conductivity varies in the course of reaction and whether a common pattern exists for all epoxy–amine formulations. Three distinct trends in conductivity during reaction were identified, and throughout the text, we refer to these trends as types I, II and III.

Imaginary impedance in the frequency domain with reaction time as a parameter during CGE–NMA reaction at 100°C is shown in *Figure 2*. We note that the imaginary impedance peak (Z''_{max}) shifts to lower frequency and higher impedance during reaction. This trend signifies that the resistance and/or resistivity of the reactive mixture increases during reaction, while its conductivity decreases. The decrease in the overall conductivity during CGE–NMA reaction at 100°C is seen in the composite plot of *Figure 3*. At the same time, the steady shear viscosity of this reactive mixture at 100°C increases, as shown in *Figure 1*. A simultaneous decrease in conductivity and an increase in viscosity was also observed in other reactive systems, including DGEBA/MDA, TGEPA/MDA, TGDDM/MDA

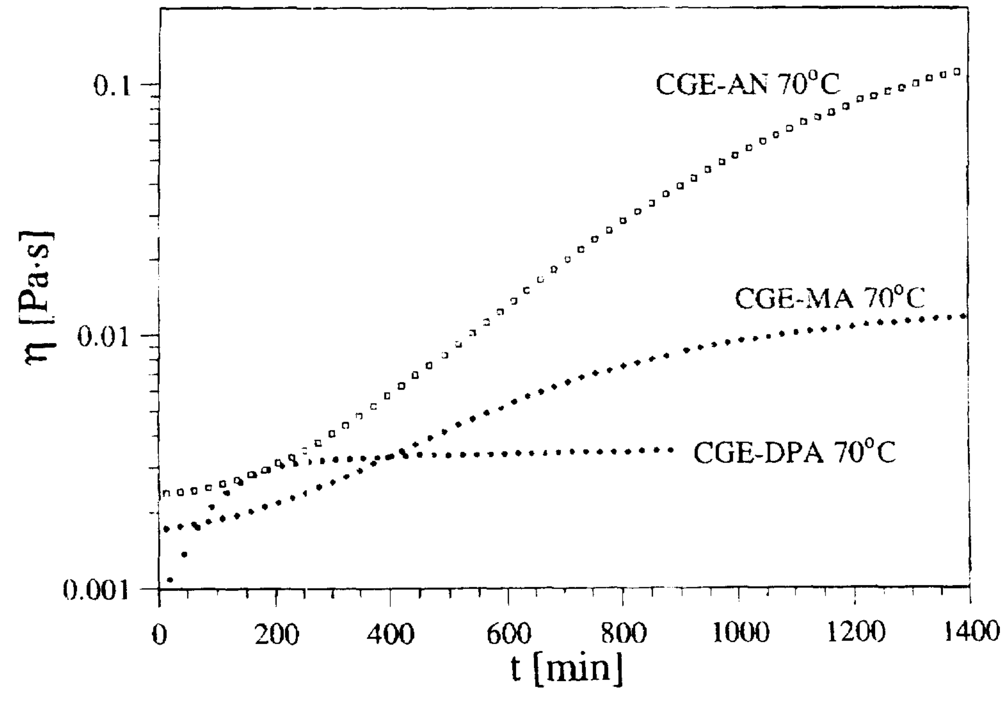


Figure 1 Steady shear viscosity as a function of reaction time at 70°C for the following systems: (a) CGE–AN, (b) CGE–NMA, and (c) CGE–DPA

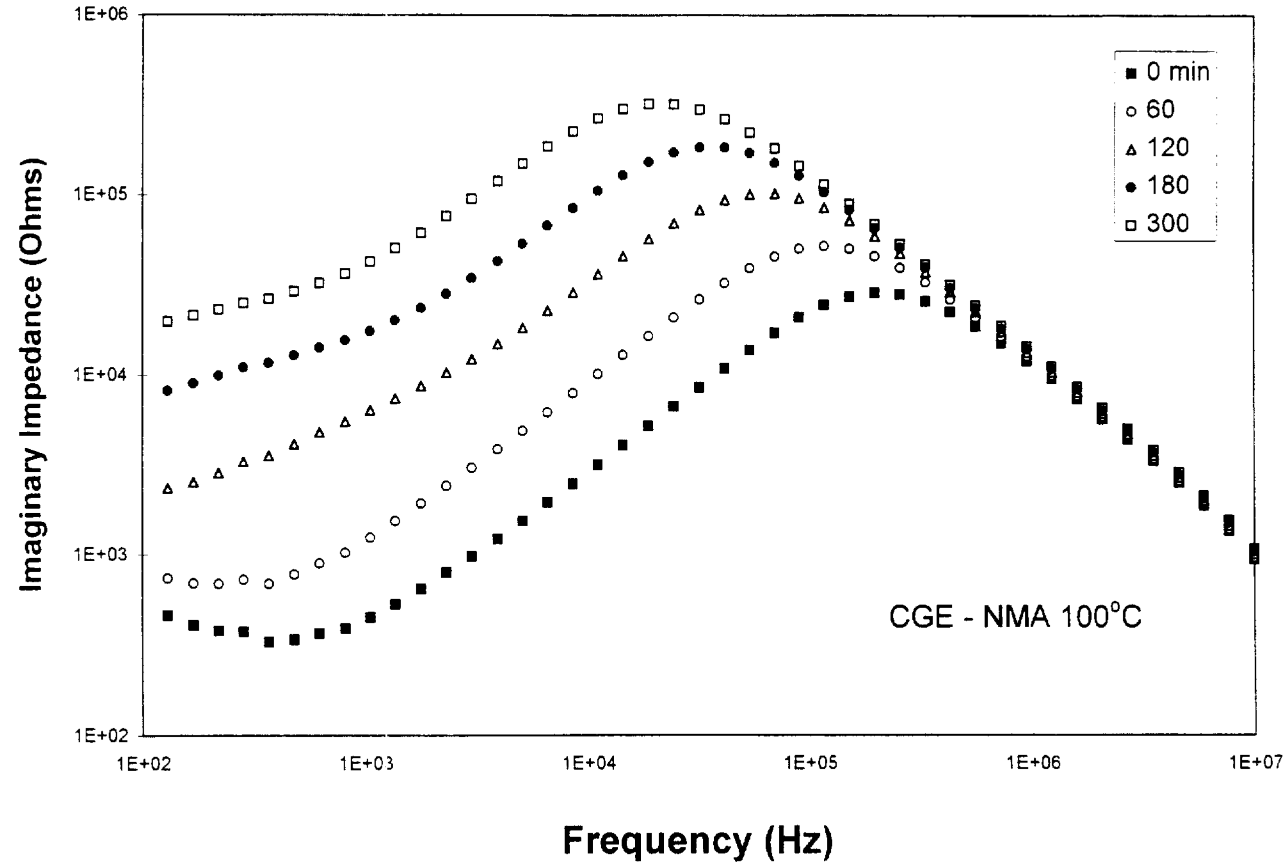


Figure 2 Imaginary impedance in the frequency domain during CGE–NMA reaction at 100°C

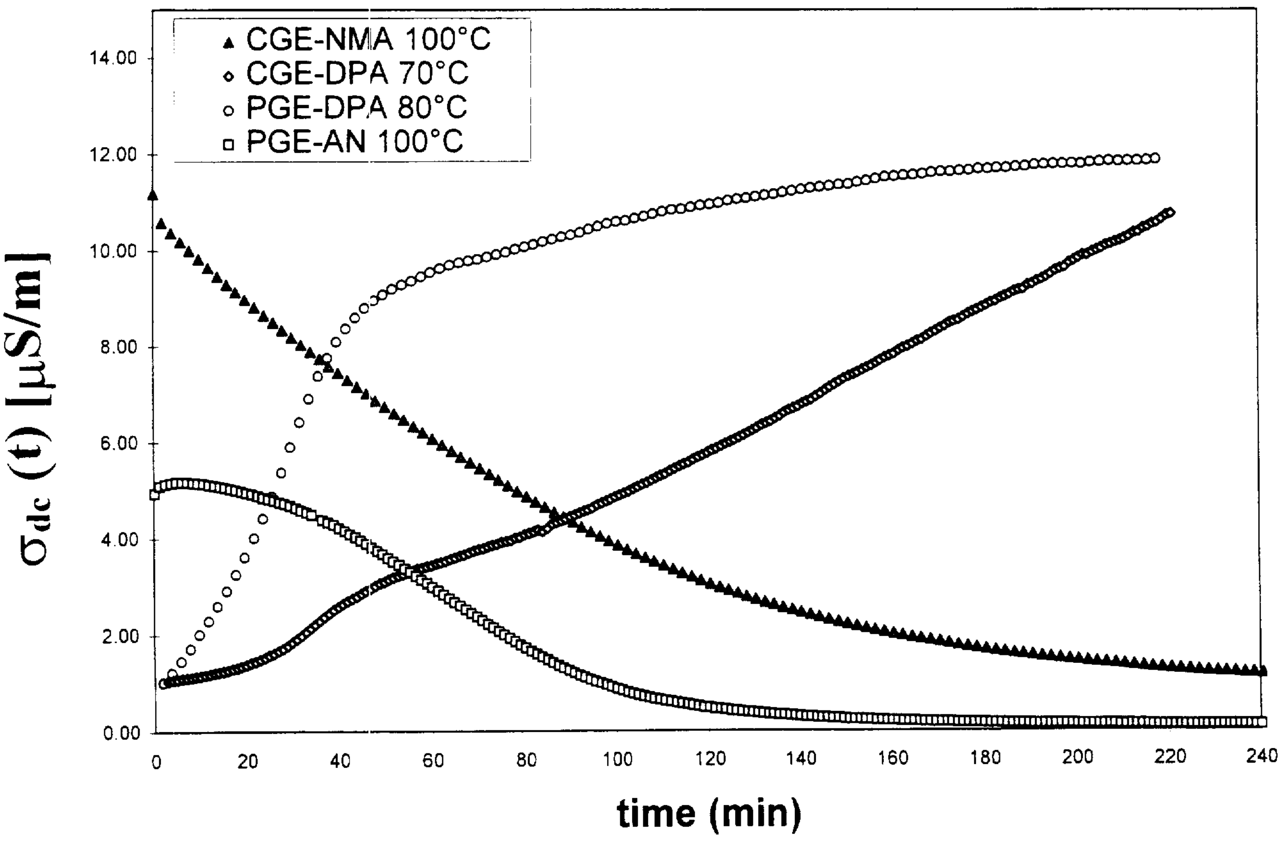


Figure 3 Composite plot of conductivity as a function of reaction time for the following systems: (a) PGE–DPA at 80°C, (b) CGE–DPA at 70°C, (c) CGE–NMA at 100°C, and (d) PGE–AN at 100°C

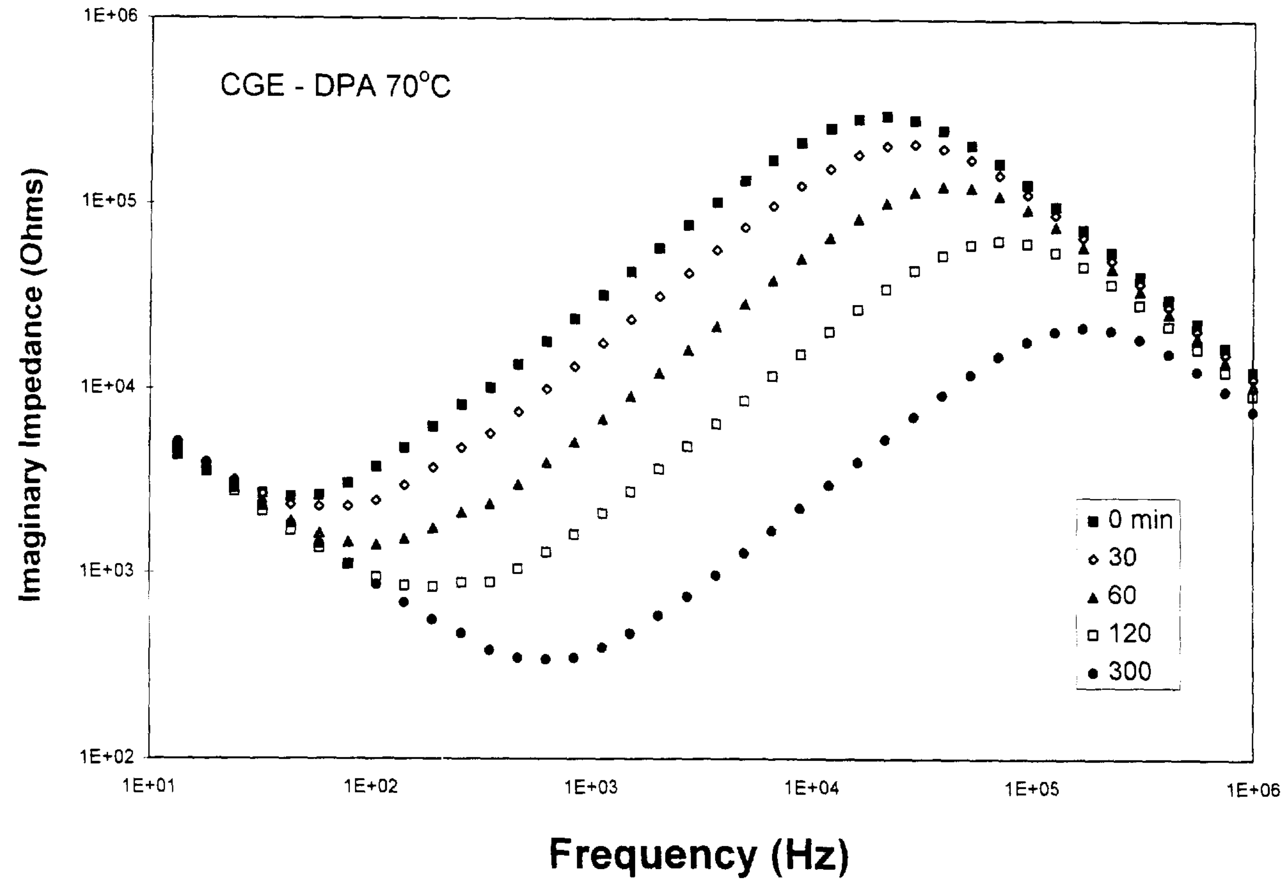


Figure 4 Imaginary impedance in the frequency domain during CGE–DPA reaction at 70°C

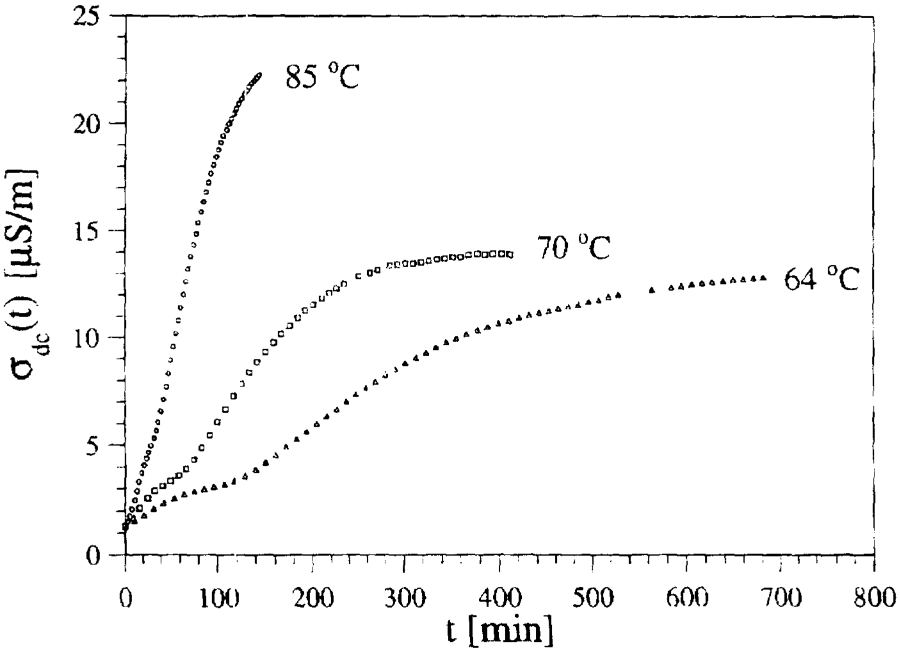


Figure 5 Conductivity as a function of reaction time with temperature as a parameter for CGE–DPA system

etc., and is rationalised for all those cases by invoking a gradual decrease in the ability of ions to diffuse through an increasingly viscous medium. We term this response type I and associated it with the rigid aromatic molecular architecture of the formulation components.

We next investigated the CGE–DPA reaction. The increase in steady shear viscosity during reaction is shown in *Figure 1*. But the results of dielectric measurements were astonishing! In *Figure 4* we show imaginary impedance in the frequency domain with reaction time as a parameter for CGE–DPA reaction at 70°C. A careful examination of this figure reveals that the imaginary impedance peak shifts to higher frequency and lower impedance during reaction, in complete contrast to the CGE–NMA system described in

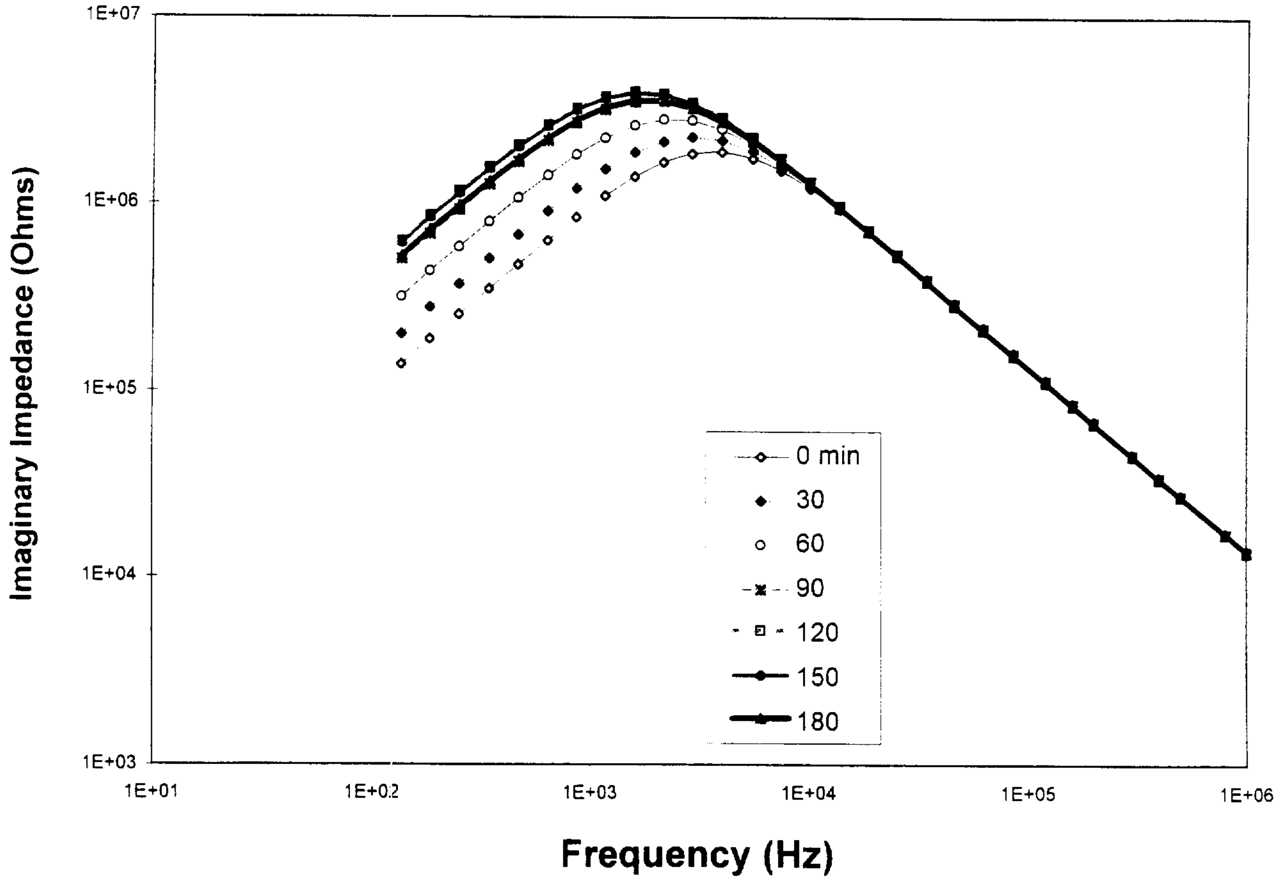


Figure 6 Imaginary impedance in the frequency domain during DGEBA–DPA reaction at 60°C

Figure 2. This further means that the overall conductivity increases during reaction, as clearly seen from the conductivity plots at three different temperatures, shown in *Figure 5*. It is obvious that a simultaneous increase in both conductivity and viscosity during reaction cannot be rationalised by the same mechanism as type I. We therefore term this response type II and associate it with a more flexible (aliphatic) molecular architecture of the amine component.

A third distinct response was observed during DGEBA–DPA reaction. The steady shear viscosity was again found to increase during reaction, but the dielectric response was peculiar. Imaginary impedance in the frequency domain with reaction time as a parameter for DGEBA–DPA reaction at 60°C, is shown in *Figure 6*. The imaginary impedance peak first shifts to lower frequency and higher impedance, but then it reverses its trend. Consequently, the overall conductivity first decreases, levels off, and then gradually increases, giving rise to the pattern which represents a combination of type I and II responses. This response is referred to as type III.

We therefore submit that despite the common reaction mechanism in epoxy–amine formulations and the universally observed increase in steady shear viscosity during reaction, the measured overall conductivity may increase and/or decrease during reaction. This observation is novel and contains an important message. The universally cited but seldom analyzed concept of a decrease in conductivity during reaction caused by a decrease in the mobility of 'ionic impurities' is at best an oversimplification of the situation and can be plainly wrong in some instances, as evidenced by its failure to account for the type II and III response.

Then what is the underlying mechanism that causes the observed trends in conductivity? First, one must realise that the measured (overall or apparent) conductivity is composed of contributions from extrinsic and intrinsic migrating charges. It is for that reason that the measured conductivity is more appropriately described as 'conductivity due to migrating charges' rather than 'ionic conductivity'. The extrinsic charge contributors include ionic impurities (remnants from synthesis steps). As a rule, extrinsic conductivity decreases during reaction. Intrinsic conductivity represents an inherent chemical characteristic of the material and depends on the availability of proton transfers along hydrogen bonds. The contribution of intrinsic charge migrations to the overall conductivity follows a more complex pattern and can decrease and/or increase in the course of reaction. The key point here is that the measured conductivity at any stage of reaction is determined by the interplay between the contributions from extrinsic and intrinsic migrating charges, and that the trend displayed by the measured conductivity will depend on whether the extrinsic or intrinsic mechanism dominates the dielectric response. One important aspect of this concept is exemplified by considering the initial and final values of the measured conductivity in CGE–DPA formulations at three different temperatures (*Figure 5*). The final value of the measured conductivity increases with increasing temperature but cannot be attributed to an activated process because of the unknown relative contributions from extrinsic and intrinsic charges. A temperature independent conductivity in the initial mixture is a result of the commensurate effect of temperature on intrinsic conductivity (which increases with decreasing temperature—as the hydrogen-bonding intensity does) and extrinsic conductivity (which decreases with decreasing temperature).

Is it then possible to separate and quantify the contributions of extrinsic and intrinsic migrating charges to the measured conductivity in reactive systems? Although the extrinsic conductivity decreases during reaction, it cannot be extracted from the measured overall conductivity unless the contribution of intrinsic conductivity can be accurately accounted for. Intrinsic conductivity, on the other hand, is a strong function of the chemical state of the matter and can dominate the measured conductivity in some epoxy–amine model compounds, oligomers and prepolymers, as shown earlier. The major source of intrinsic conductivity in epoxy–amine formulations is the transfer of protons via hydrogen bonds. Since the intensity of hydrogen bonding varies with temperature and the extent of reaction, so does the relative contribution of intrinsic migrating charges to the overall conductivity. For example, in both model and network-forming epoxy–amine systems there exists a critical extent of reaction where the combined concentrations of epoxy, amine and hydroxyl groups satisfy the requirement for the formation of a hydrogen-bonded complex which increases intrinsic conductivity. The presence of such complex has been corroborated by ample evidence from High Performance Liquid Chromatography (HPLC) and Fourier Transform Infrared Spectroscopy (FTIR), but a further discussion of its nature remains beyond the scope of this note and the interested reader is referred to the pertinent publications[17,21,22]. The key point to remember is that the formation of this hydrogen-bonded complex and a concomitant increase in intrinsic conductivity are countered by a decrease in extrinsic conductivity and the direction in which the measured conductivity shifts will depend strongly on the molecular architecture of the formulation components. Based upon the results of this work, we can generally state that the more flexible (aliphatic) the components, the stronger the relative contribution of intrinsic migrating charges. However, a systematic study of the effect of molecular architecture on conductivity was beyond the scope of this work and would be interesting. In the system containing aliphatic amines we also observed an increase in the dielectric constant, which, in turn, could increase the dissociation of impurities. This effect was absent in the presence of aromatic amines. In formulations such as PGE–DPA and CGE–DPA, where intrinsic migrating charges dominate the response, the overall conductivity increases during reaction and we observe a type II behaviour.

In epoxy–amine formulations that yield linear polymers, the terminal epoxy and amine groups are further apart than in the model or network-forming systems, and the likelihood of the participation of these groups in complexes is reduced. The principal contribution to the intrinsic conductivity in linear polymers comes form the hydrogen bonds between hydroxyl groups that are produced during polymerisation. The suggestion that the high conductance in a system containing protons is due to a type of a Grotthuss conduction has been frequently made in the literature[23,24]. An increase in the concentration of hydroxyl groups and hydrogen-bonding during reaction results in an increasing contribution of intrinsic migrating charges to the overall conductivity. This is exemplified in *Figure 7* for DGEBA–DPA reaction at 60°C, where we see a continuous increase in the extent of reaction (measured by FTIR) with time, while the overall conductivity first gradually decreases (when extrinsic migrating charges dominate the dielectric

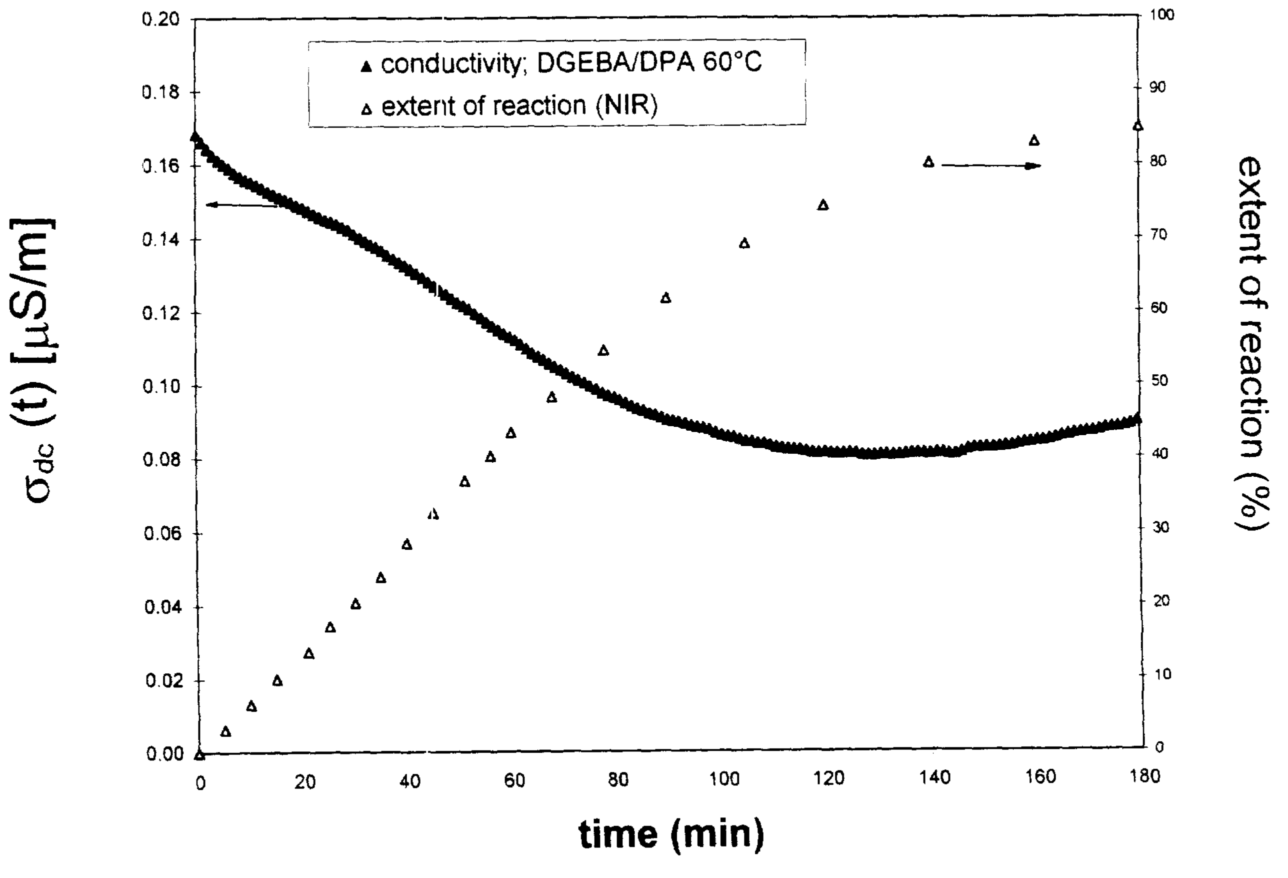


Figure 7 Conductivity (left ordinate) and extent of reaction (right ordinate) as a function of reaction time at 60°C for DGEBA–DPA system

response) and then increases. The increase in conductivity in the later stage of reaction is caused by the emergence of a dominant contribution to the measured conductivity from the hydrogen-bonding between hydroxyl groups.

In network-forming (multifunctional) epoxy–amine formulations the overall conductivity also encompasses contributions from extrinsic and intrinsic migrating charges, each of which is affected differently by the progress of reaction. The dominant influence of extrinsic migrating charges on the overall conductivity throughout cure is a result of the pronounced change in viscosity, but the contribution of intrinsic charges cannot and should not be neglected. When extrinsic migrating charges dominate the response, the overall conductivity decreases and we detect type I response, but this does not imply that the overall conductivity is caused solely by 'ionic impurities' (i.e. extrinsic charges), as almost universally (and erroneously) claimed in the literature. Theoretically, one could arrive at such a value but not before instituting an appropriate methodology for the subtraction of the contribution of intrinsic conductivity from the measured value. In the absence of such information it is not possible to develop fundamental relationships between the measured conductivity and the main processing parameters, namely viscosity and extent of reaction, and hence all such correlations reported in the literature are strictly batch- specific and empirical.

CONCLUSIONS

We have conducted an investigation of conductivity by migrating charges during reaction in various epoxy–amine formulations, polymer-forming and non polymer-forming alike. All formulations were characterised by a common reaction mechanism and an increase in steady shear viscosity, but the measured conductivity displayed three distinctly different trends during reaction. Depending on the molecular architecture (e.g. flexibility, functionality) of the formulation components, it was found that the overall conductivity during reaction could decrease (type I response), increase (type II response) or decrease and then increase (type III response).

The overall conductivity encompasses contributions from extrinsic migrating charges, such as ionic impurities, and intrinsic migrating charges that involve proton transfers along hydrogen bonds. While the extrinsic charge contributions decrease during reaction as a result of an increase in viscosity, the intrinsic conductivity follows a more complex pattern and the trend displayed by the measured (overall) conductivity will depend on which mechanism (extrinsic or intrinsic) dominates the dielectric response. As a direct consequence of this interplay between extrinsic and intrinsic contributions to the overall conductivity, the measured value can increase and/or decrease during reaction. An increase in conductivity during reaction, observed here for a number of epoxy–amine systems, is obviously incompatible with the widely accepted but seldom investigated concept of decreasing conductivity owing to a decrease in the mobility of ionic impurities in increasingly viscous systems. This signifies that the development of fundamental correlations between the measured conductivity and the major processing parameters, such as viscosity and extent of reaction, hinges upon the development of a methodology for separate evaluation of the contribution of extrinsic and intrinsic migrating charges. We are not aware of any such study and it is therefore accurate to say that all correlations in the literature between the measured (overall) conductivity and viscosity (or extent of reaction) are strictly batch-specific and empirical.

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