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## Curing kinetics of phase separating thermosets studied by DSC, TMDSC and dielectric relaxation spectroscopy

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### Abstract

Differential scanning calorimetry (DSC), temperature-modulated DSC (TMDSC) and dielectric relaxation spectroscopy have been performed during isothermal curing of an epoxy network (diglycidylether of bisphenol A cross-linked with diaminodiphenyl methane) and of thermoplast modified epoxy resins (“semi-interpenetrating polymer networks”) consisting of the epoxy network component and different amounts (10 and 20 wt%) of a linear high  $T_g$ -polymer (polyethersulfone). During reaction the homogeneous mixtures phase separate into an epoxy-rich and a linear polymer-rich phase. The time dependent changes in the complex dielectric permittivity are described by a simple two phase model based on two Havriliak–Negami functions combined with Vogel–Fulcher equations for the description of the curing time dependence of the relaxation times. The time increase of the relaxation times in the two phases during isothermal curing is incorporated by time-dependent Vogel-temperatures. The latter are related to the time evolution of the glass transition temperatures  $T_g$  in the two phases measured independently by calorimetry. With TMDSC it was possible to resolve  $T_g$  for both phases since the curing time evolution of the heat capacity could be separated from the heat of reaction. In the conventional DSC the  $T_g$  of the linear polymer rich phase was masked by the heat of reaction. In addition, with TMDSC the vitrification during isothermal curing could be monitored. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Interpenetrating polymer networks; Temperature-modulated differential scanning calorimetry; Differential scanning calorimetry; Dielectric relaxation spectroscopy; Curing

### 1. Introduction

A large number of investigations have been performed in the last decades to get a better understanding of the cure behavior of one phase thermosetting systems. Recently [1] we reported on an extension of time dependent dielectric relaxation spectroscopy (DRS) during isothermal curing of an epoxy resin modified with a linear polymer. It was found that

phase separation takes place during network formation from an initially homogeneous solution into a linear polymer-rich and an epoxy-rich phase [2,3]. The epoxy-rich phase forms the matrix containing a dispersed linear polymer-rich second phase (spherical domains or aggregates). Despite of the two phase morphology the system was considered as a “semi-interpenetrating polymer network” (semi-IPN). The epoxy network component consisted of diglycidylether of bisphenol A (DGEBA) and diaminodiphenyl methane (DDM) and the thermoplastic linear polymer component was polysulfone (PSn).

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In this study we extend the DRS investigations on the epoxy/PSn thermosets to polyethersulfone (PES) as an alternative thermoplastic linear polymer component. In addition to DRS, we applied differential scanning calorimetry (DSC) and temperature-modulated DSC (TMDSC) for measurements of the evolution of the glass transition temperatures  $T_g$  of both phases with curing time [4,5].

The aim of this publication is to present a simple two phase model to describe the development of the real and imaginary part of the complex dielectric permittivity during curing of a phase separating thermoset using concepts which are well established in polymer science. It is an extension of a model for one phase systems which have been proposed by Johari and coworkers for DRS [6,7] and which was recently extended to TMDSC [8]. In addition, we incorporate the evolution of the glass transition temperatures ( $T_g$ ) of both phases with curing time ( $t_{\text{cure}}$ ) as measured by DSC and TMDSC. By combining the experimental results of DRS, DSC and TMDSC we demonstrate that this type of model can be applied successfully to polymeric systems which phase separate and vitrify during a chemical reaction.

## 2. Experimental

DGEBA was supplied by Shell Chemical (Epikote 828) and DDM by Aldrich. The linear polymer PES (molecular weight:  $M_w=42\,000$  g/mol,  $M_w/M_n=2.05$ ) is a commercial Ultrason E3010 sample supplied by BASF. For the thermoplast modified epoxy resins (“semi-IPNs”) mixtures of PES in DGEBA were prepared in such a composition that the weight fraction of PES was 10% or 20% in the final samples. The DGEBA (for the pure networks) or the DGEBA/PES mixtures (for the semi-IPNs) and DDM were heated separately to 393 K, poured together into a preheated glass container and stirred at 393 K for 30 s to get a homogeneous mixture. DGEBA and DDM were used in stoichiometric amounts (2 mol% DGEBA and 1 mol% DDM). Then the dielectric measurements were carried out as described before in [1] and the calorimetric measurements as described in [4,5]. Details of the reaction mechanism and the phase morphology were discussed before in [1–3] and references therein. In the transmission electron micro-

graphs [2] of the epoxy resin modified by 10 wt% PES and cured at 373 K PES-rich spheres ranging from 0.2 to 1  $\mu\text{m}$  diameter were found to be dispersed in the epoxy-rich matrix.

The dielectric permittivity was measured by an impedance analyzer (Hewlett-Packard HP 4192A) in the frequency range between 3 kHz and 3 MHz. The DSC data were measured with a DSC 7 (Perkin-Elmer), the TMDSC data with a DSC 7 with DDSC mode.

In a TMDSC measurement the usual temperature program is superimposed with a periodical temperature perturbation [9]. The heat flow rate into the sample can be separated into an underlying component  $\Phi_u$  and the first harmonic of the periodic component  $\Phi_p$ :

$$\Phi_u = m\Delta h_r \frac{d\xi}{dt}, \quad (1)$$

$$\Phi_p = \Phi_a \cos(\omega_0 t - \varphi), \quad (2)$$

where  $m$  is the sample mass,  $\Delta h_r$  the specific heat of reaction,  $\xi$  the degree of reaction (conversion),  $\Phi_a$  the amplitude of the first harmonic of the heat flow rate,  $\omega_0$  the angular frequency and  $\varphi$  the corresponding phase shift. If the underlying heating rate  $\beta_0 \neq 0$  then Eq. (1) can be rewritten as:

$$\Phi_u = m\Delta h_r \frac{d\xi}{dT} \frac{dT}{dt} = mc_\beta \beta_0, \quad (3)$$

where  $c_\beta$  is the total specific heat capacity which can be evaluated from the underlying heat flow rate. The real part  $c'$  and the imaginary part  $c''$  of the complex specific heat capacity  $c^*(\omega_0) = c'(\omega_0) - ic''(\omega_0)$  are related to the quantities in Eqs. (1) and (2) by:

$$c'(\omega_0) = |c^*| \cos \varphi, \quad c''(\omega_0) = |c^*| \sin \varphi, \quad (4)$$

with  $|c^*| = \sqrt{(c')^2 + (c'')^2} = (\Phi_a/m\omega_0 T_a)$ .  $T_a$  is the amplitude of the first harmonic of the periodic temperature perturbation.

## 3. Results and discussion

### 3.1. Calorimetric experiments

The samples were cured at 373 K for different times. Thereafter they were quenched to 213 K and

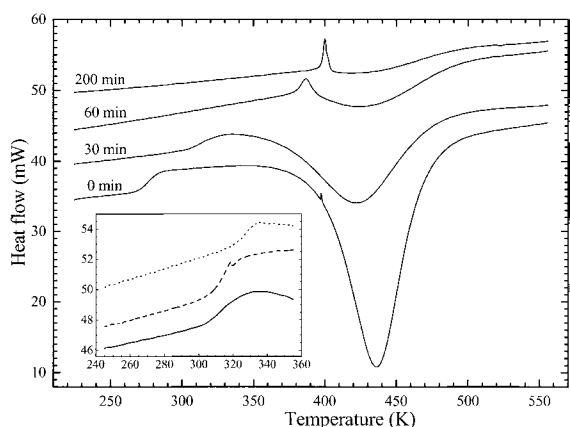


Fig. 1. Temperature dependence of the heat flow of a DGEBA/DDM network containing 20 wt% PES after different curing times at 373 K (heating rate: 10 K/min) measured by conventional DSC. The curing times are 0 min (sample weight: 27.9 mg), 30 min (sample weight: 27.1 mg), 60 min (sample weight: 37.7 mg) and 200 min (sample weight: 17.4 mg). For clarity the curves are vertically shifted. The inset compares curves after a curing time of 30 min: pure network (dotted line, sample weight: 17.8 mg), semi-IPN with 10 wt% PES (dashed line, sample weight: 26.4 mg), semi-IPN with 20 wt% PES (dashed line, sample weight: 27.1 mg).

reheated with 10 K/min to determine the evolution of the glass transitions and the residual heats of reaction for different intervals of isothermal curing. For a semi-IPN with 20 wt% PES these curves are shown in Fig. 1. The measurements were performed by conventional DSC. All curves have a step in the heat flow rate related to the glass transition followed by a broad exothermal  $c'$  corresponding to the residual heat of reaction. The glass transition temperature  $T_g$  is shifted to higher temperatures with increasing curing time and the residual heat is decreased. With increasing curing time the step at  $T_g$  becomes successively masked by the heat of reaction. The corresponding curves for the pure networks and the semi-IPNs with 10 wt% PES are similar but the glass transitions (see inset of Fig. 1) and the exotherms become broader with increasing PES content. This can be explained by the effects of intermixing of PES and DGEBA/DDM [5]. Since the glass transition temperatures  $T_g$  extracted from conventional DSC for the semi-IPNs (see e.g. Fig. 1) are almost identical to those of the pure network it can be concluded that the steps in Fig. 1 correspond to the glass transition of the epoxy (DGEBA/DDM)-rich phase. It should be noted that in the curves for 60

and 200 min curing time a physical aging peak is superimposed to the glass transition indicating that the sample is transformed to the glassy state by the reaction.

The exotherms in the heat flow curves due to the residual heat of reaction are expected to mask the glass transition steps of the PES-rich phases of the semi-IPNs which should occur at higher temperatures than those of the DGEBA/DDM-rich phases because of the high glass transition temperature of pure PES at 495 K. To test this assumption TMDSC measurements have been performed under similar conditions as the conventional DSC experiments shown in Fig. 1. In the  $c'$  vs. temperature curve (inset of Fig. 2) recorded after isothermal curing of 102 min two glass transition steps can be distinguished. The lower glass transition temperature is almost identical to the one extracted from conventional DSC (see Fig. 1) and can be related to the DGEBA/DDM-rich phase whereas the higher  $T_g$  is related to the PES-rich phase. The structural changes related to the glass transitions of the two phases can be clearly separated by TMDSC from the heat of reaction represented by  $c_\beta$ .

In Fig. 2 the heating curves of  $c'$  after different curing times are summarized. In the curve after 52 min

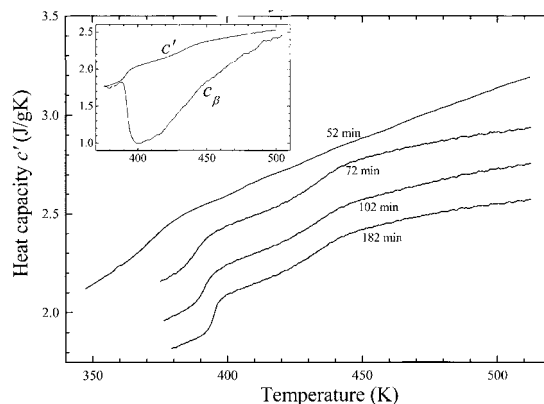


Fig. 2. Specific heat capacity  $c'$  during ramp heating after the indicated curing times at 373 K of a DGEBA/DDM network with 10 wt% PES ( $\beta_0=2$  K/min,  $T_a=0.5$  K,  $f_0=41.7$  mHz, for  $t_{\text{cure}}=52$  min,  $\beta_0=5$  K/min,  $T_a=0.5$  K and  $f_0=83.3$  mHz was used). The curves are shifted successively upwards by 0.2 J/(gK) relative to the curve for  $t_{\text{cure}}=182$  min. The sample weights are: 18.91 mg (52 min), 10.03 mg (72 min), 10.82 mg (102 min) and 10.60 mg (182 min). The inset shows the  $c'$  curve for the sample after 102 min together with  $c_\beta$ .

only one glass transition step can be clearly resolved. However, a second very broad transition with a small intensity seems to be evident at higher temperatures. After 72 min of curing two glass transition temperatures can clearly be extracted. Therefore, we can conclude that phase separation becomes pronounced enough in the time range between 50 and 70 min to be detected by TMDSC. The intensity ( $\Delta c'$ ) of the glass transition at about 445 K is approximately  $\frac{2}{3}$  of that of the glass transition at the lower temperature. This small difference in the intensities is an indication that the PES-rich phase is not pure but contains also an appreciable amount (more than 50 wt%) of the epoxy network component. This corresponds to the considerable lower  $T_g=445$  K of the PES-rich phase compared with the  $T_g$  of the pure PES of 495 K (see above).

The results for  $c'$ ,  $c''$  and the underlying heat flow for isothermal curing at 373 K of the DGEBA/DDM system measured by TMDSC are shown in Fig. 3(a) and (b). The almost linear increase in  $c'$  (Fig. 3(a)) with time during the initial interval of curing reflects the increase of the specific heat capacity due to an increase in configurational and/or vibrational contributions in the liquid state originated by the network growth [8]. The stepwise decrease in  $c'$  between 40 and 60 min corresponds to an isothermal vitrification

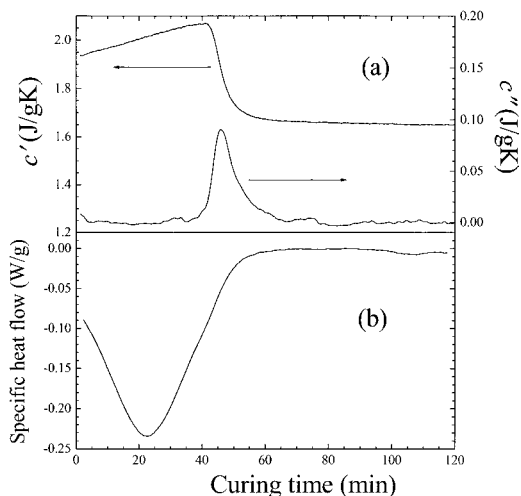


Fig. 3. Real ( $c'$ ) and imaginary part ( $c''$ ) of the complex specific heat capacity (a), and underlying (total) heat flow (b) for the isothermal cure at 373 K of a DGEBA/DDM mixture measured by TMDSC ( $T_a=0.5$  K,  $f_0=41.7$  mHz,  $m=8.8$  mg).

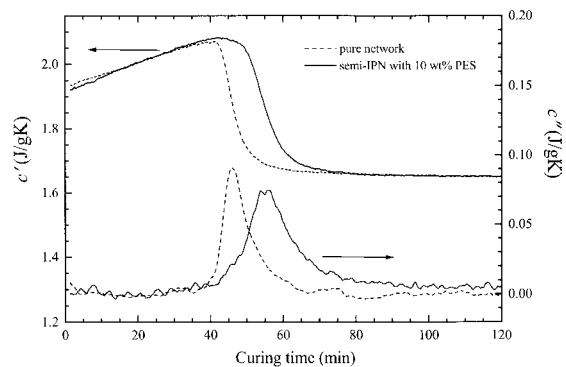


Fig. 4. Real part  $c'$  and imaginary part  $c''$  of the complex specific heat capacity for the isothermal cure at 373 K of a DGEBA/DDM network with 0 and with 10 wt% PES measured by TMDSC ( $T_a=0.5$  K,  $f_0=41.7$  mHz,  $m=8.8$  mg (0 wt% PES),  $m=6.6$  mg (10 wt% PES)).

when the main glass-to-rubber relaxation for a given frequency freezes in. As a measure for the “vitrification time” the inflection point at about 45 min is used. This “vitrification time” is also plotted in Fig. 5 and represents a situation where the characteristic relaxation time of the molecular rearrangements related to the glass transition becomes comparable to the inverse of the angular frequency of the temperature modulation. In the glassy polymer network the specific heat capacity  $c'$  becomes nearly constant. The step in  $c'$  is accompanied by the maximum in  $c''$  (Fig. 3(a)).

In Fig. 4 the components of the complex specific heat capacity as a function of curing time ( $T_{\text{cure}}=373$  K) for DGEBA/DDM are compared with the semi-IPN with 10 wt% PES. In contrast to the pure network, the vitrification transition of the semi-IPN is considerably broader. In the time range between 40 and 50 min an additional small decrease in  $c'$  and a corresponding small shoulder in  $c''$  can be identified. These features may be interpreted as the beginning of the demixing process and correspond to the broad glass transition above 400 K in Fig. 2 for  $t_{\text{cure}}$  of 52 min. Therefore, we conclude that the broad step in  $c'$  and the broad maximum in  $c''$  in the time interval between 40 and 70 min represent a situation where the phase separation occurs, but the two phases are still very similar in composition. This is in agreement with the finding in Fig. 2 where the second phase is clearly represented only for curing times above 72 min. As discussed already above, for the pure network the

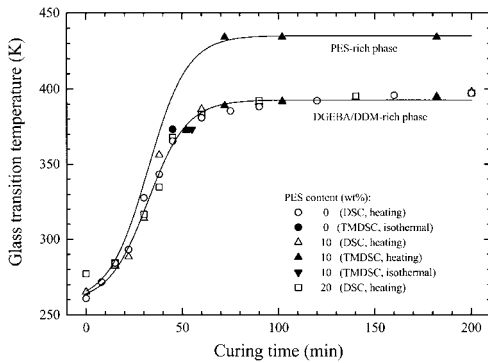


Fig. 5. Curing time dependence (curing temperature: 373 K) of the glass transition temperatures for the pure network and for the DGEBA/DDM-rich (lower curve) and PES-rich phases (upper curve) of the semi-IPNs containing 10 or 20 wt% PES. The glass transition temperatures have been measured by conventional DSC (determined from heating curves like those shown in Fig. 1) and by TMDSC (determined from the heating curves shown in Fig. 2 and from the isothermal measurements shown in Figs. 3 and 4). The solid lines are the supposed evolutions of the glass transition temperatures of both phases of the semi-IPN with 10 wt% PES calculated by the empirical Eq. (5).

irreversible vitrification as represented by only one narrow step in  $c'$  and a narrow maximum in  $c''$  corresponding to the “vitrification time” of about 45 min (also plotted in Fig. 5).

The curing time dependence of the glass transition temperatures are given in Fig. 5 for the pure network and for the semi-IPNs with 10 or 20 wt% PES. For the pure network and the DGEBA/DDM-rich phases of the semi-IPNs (lower curve) there are no significant differences between the glass transition temperature as a function of curing time. The “vitrification times” at about 55 min for the semi-IPN with 10 wt% PES and at about 45 min for the pure network extracted from the isothermal experiments (Figs. 3 and 4) fit to these data. From the TMDSC experiments it was possible to extract also the development of the glass transition temperature in the PES-rich phase (upper curve). Also shown in Fig. 5 (solid lines) is the supposed development of the glass transition temperatures of both phases of the semi-IPN with 10 wt% PES calculated by an empirical function:

$$T_g(t_{\text{cure}}) = \frac{T_{g,-\infty} - T_{g,\infty}}{1 + \exp[(t_{\text{cure}} - t_0)/\Delta t]} + T_{g,\infty}, \quad (5)$$

where  $T_{g,-\infty}$  is a value near the  $T_g$  of the unreacted sample,  $T_{g,\infty} = T_g(t_{\text{cure}} = \infty)$ ,  $t_0$  defines a characteristic time by  $T_g(t_0) = (T_{g,\infty} + T_{g,-\infty})/2$  and  $\Delta t$  is a measure of the width. The parameters used for the DGEBA/DDM-rich phase are:  $T_{g,-\infty} = 258.5$  K,  $T_{g,\infty} = 392.6$  K,  $t_0 = 32.2$  min and  $\Delta t = 10.2$  min; those for the PES-rich phase are:  $T_{g,-\infty} = 258.5$  K,  $T_{g,\infty} = 435.0$  K,  $t_0 = 32.2$  min and  $\Delta t = 10.2$  min. For calculating these curves it is assumed that the system is homogeneous at the beginning and that phase separation proceeds continuously.

### 3.2. A two phase model combining calorimetric and dielectric measurements

In our model for describing the DRS results during curing the complex dielectric permittivity  $\varepsilon^* = \varepsilon' - i\varepsilon''$  is composed of three parts: an equation describing the dc-conductivity contribution  $\varepsilon''_{\text{dc}}(\omega, t_{\text{cure}})$  [10] and two relaxation functions  $\varepsilon^*_{\text{dip},k}(\omega, \tau)$  for the dipole reorientation in the two phases. The index  $k$  denotes either the epoxy (DGEBA/DDM)-rich or the linear polymer (PES)-rich phase. For the dipole reorientation a curing time dependence of the characteristic relaxation times of the two phases  $\tau_k = \tau_k(t_{\text{cure}})$  has to be incorporated. The curing time dependence of the complex dielectric permittivity  $\varepsilon^*(\omega, t_{\text{cure}})$  is then given by:

$$\varepsilon^*(\omega, t_{\text{cure}}) = \varepsilon''_{\text{dc}}(\omega, t_{\text{cure}}) + \varepsilon^*_{\text{dip,PES}}(\omega, t_{\text{cure}}) + \varepsilon^*_{\text{dip,epoxy}}(\omega, t_{\text{cure}}), \quad (6)$$

where  $\varepsilon^*_{\text{dip,PES}}(\omega, t_{\text{cure}})$  and  $\varepsilon^*_{\text{dip,epoxy}}(\omega, t_{\text{cure}})$  are the time dependent relaxation functions of the PES-rich and the epoxy-rich phase, respectively.

The starting point to model the dipole relaxations in the two phases is the knowledge of the curing time dependence of the glass transition temperature in the epoxy-rich and the PES-rich phase as shown in Fig. 5. It can be seen that at the beginning of the reaction there is only one glass transition temperature corresponding to the homogeneous mixture. During reaction two more and more separated glass transition temperatures develop because of phase separation. Each of the glass transitions corresponds to one of the two developing phases.  $\varepsilon^*_{\text{dip},k}(\omega, t_{\text{cure}})$  can be described by Havriliak–Negami functions by incorporating the curing time dependence of the characteristic relaxation

times  $\tau_{\text{HN}, k}$ :

$$\begin{aligned} \varepsilon_{\text{dip}, k}^*(\omega, t_{\text{cure}}) \\ = n_k \left[ \varepsilon_{\infty, k} + \frac{\Delta\varepsilon_k}{[1 + (i\omega\tau_{\text{HN}, k}(t_{\text{cure}}))^{\alpha_k}]^{\beta_k}} \right] \end{aligned} \quad (7)$$

$\alpha_k$  and  $\beta_k$  are shape parameters. The  $\Delta\varepsilon_k = \varepsilon_{0, k} - \varepsilon_{\infty, k}$  are the relaxation strengths with  $\varepsilon_{0, k}$  and  $\varepsilon_{\infty, k}$  the low ( $\omega \ll \tau_{\text{HN}, k}^{-1}$ ) and high frequency ( $\omega \gg \tau_{\text{HN}, k}^{-1}$ ) limiting values of  $\varepsilon'_k(\omega)$  respectively.  $n_k$  represents the averaged fraction of relaxing units for each of the phases.

The time dependence of the relaxation time  $\tau_{\text{HN}, k}(t_{\text{cure}})$  can be calculated for each phase from the curing time dependence of the glass transition temperatures using Vogel–Fulcher laws

$$\begin{aligned} \tau_{\text{HN}, k}(t_{\text{cure}}) = \tau_{0, k}(t_{\text{cure}}) \\ \times \exp\{B_k(t_{\text{cure}})/[T_{\text{cure}} - T_{0, k}(t_{\text{cure}})]\}, \end{aligned} \quad (8)$$

where  $T_{0, k}$  is the Vogel-temperature,  $\tau_{0, k}$  and  $B_k$  are parameters.  $T_{\text{cure}}$  is the curing temperature. The curing time dependence of the Vogel-temperatures can be related to the time evolution of the glass transition temperatures  $T_{g, k}(t_{\text{cure}})$  by

$$T_{0, k}(t_{\text{cure}}) = T_{g, k}(t_{\text{cure}}) - C_k(t_{\text{cure}}), \quad (9)$$

where the  $C_k$  are parameters. The  $T_{g, k}(t_{\text{cure}})$  are fitted by the empirical function (5) as shown in Fig. 5 [10]. The calculated  $\tau_{\text{HN}, k}(t_{\text{cure}})$ -curves for both phases are represented in Fig. 6 together with DRS data. At the beginning of the reaction there is only one  $\tau_{\text{HN}}$ -value corresponding to the homogeneous mixture. During reaction two more and more separated  $\tau_{\text{HN}, k}$ -values develop because of phase separation.

The curing time dependence of  $\tau_{\text{HN}, k}$  of the two phases can now be used to calculate  $\varepsilon'$  and  $\varepsilon''$  by incorporating  $\tau_{\text{HN}, k}(t_{\text{cure}})$  into the Havriliak–Negami functions for both phases (Eq. (7)). The results of the fitting procedure are shown in Fig. 7. In Fig. 7(a)  $\varepsilon''$  data are shown for a frequency of 100 kHz whereas in Fig. 7(b) the conductivity  $\sigma = 8.854 \text{ pF}/m\omega\varepsilon''$  is plotted for different measurement frequencies. For more details about the model, the fitting procedure and the parameters used see [10]. The agreement with the measured values is rather good. The data as well as the simulation show a double maximum in  $\varepsilon''$  or in  $\sigma$  which corresponds to the two phase structure. For

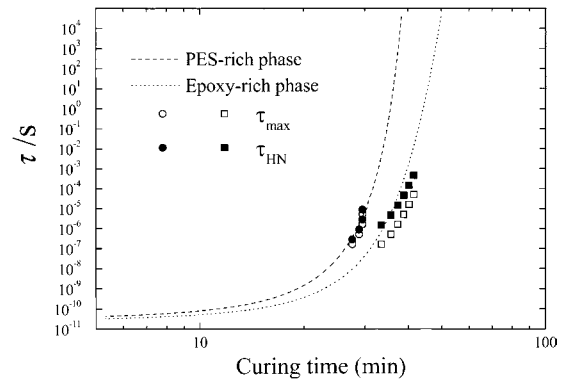


Fig. 6. Curing time dependence of the characteristic relaxation times  $\tau_{\text{max}}$  determined from the  $\varepsilon''(t_{\text{cure}})$ -maxima [1] for different frequencies ( $\omega\tau_{\text{max}}=1$ ) (open symbols) of the thermoplast modified epoxy resin with 10 wt% PES for the DGEBA/DDM-rich and the PES-rich phase. The curing temperature is 373 K. The  $\tau_{\text{HN}}$ -values (filled symbols) are calculated from the  $\tau_{\text{max}}$ -values using the relations given in [11]. The relaxation times for the epoxy-rich phase are indicated by squares whereas those of the linear polymer-rich phase are indicated by circles. Also shown is the evolution of the  $\tau_{\text{HN}}$ -values for the DGEBA/DDM-rich (dotted line) and the PES-rich phase (dashed line) calculated by Vogel–Fulcher Eq. (8) using the curing time dependence of the  $T_g$ 's from Fig. 5.

316 kHz the two phase structure can be observed already at approximately 30 min. This is about 15 min earlier than with the TMDSC measurements (Fig. 4) and can be attributed to the smaller length scale observed by the dielectric relaxation spectroscopy. Therefore, DRS can detect the phase separation process in an earlier stage when the length scale of the phases is still small. For curing times above 50 min the  $\varepsilon''$ -data deviate considerably from the simulated curves. The reason for this deviation is the non-equilibrium state of the system [10]. It is remarkable that the time of about 50 min corresponds to the onset of a physical aging peak in Fig. 1 and the “vitrification time” for a frequency of 41.7 mHz in Fig. 4. Both experiments represent the freezing in of slow relaxation processes responsible for the “reaction induced vitrification” of the material to a non-equilibrium situation. This aspect will be incorporated into the model in a future study [12].

The model proposed for describing the curing time dependence of the dielectric permittivity is rather simple compared with the complicated systems. It is assumed that the relaxations in the two phases can be superposed linearly. Possible contributions

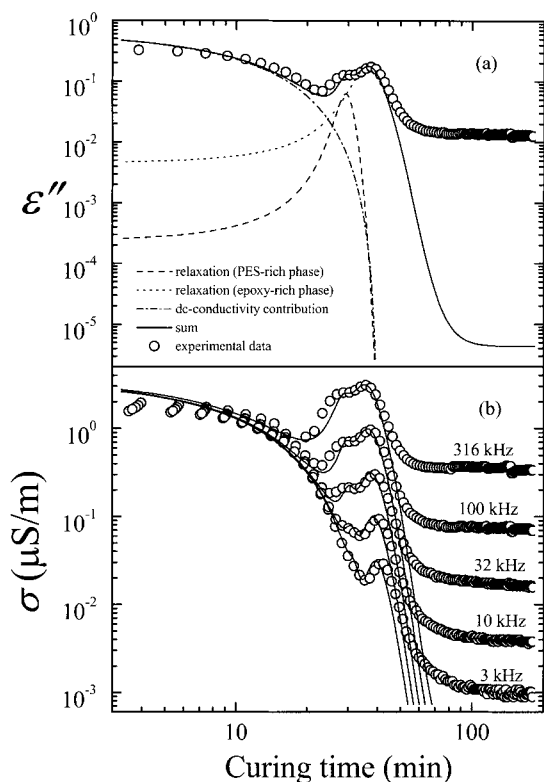


Fig. 7. (a) Curing time dependence of the imaginary part ( $\epsilon''$ ) of the complex dielectric permittivity of a thermoplast modified epoxy resin (semi-IPN) with 10 wt% PES (curing temperature: 373 K) measured with a frequency of 100 kHz (circles). The lines show the dc-conductivity contribution (dash-dotted), the dielectric relaxations of the two phases (dashed, dotted) and the sum of these three parts (solid) calculated as described in the text. (b) Curing time dependence of the conductivity  $\sigma = 8.854pF/m\omega\epsilon''$  of a thermoplast modified epoxy resin with 10 wt% PES for different frequencies. The curing temperature is 373 K. The lines show the fits to the measured curves by the model proposed in the text. The frequencies are indicated in the figure.

from surface regions between the phases are neglected. In addition, it is assumed that the shape of the relaxations (constant Havriliak–Negami parameters) and that the temperature dependence of the relaxation times (constant Vogel–Fulcher parameters) remain constant during the isothermal reaction of low molecular weight substances to a high molecular polymer network. Moreover, it must be considered that the fraction of relaxing units  $n_k$  (Eq. (7)) should increase for the PES-rich phase and decrease for the epoxy-rich phase during the curing reaction. Nevertheless, a constant averaged  $n_k$  is taken for each of both

phases. However, the data evaluation procedure has shown that the error resulting from these assumptions seems to be only in the order of magnitude of the experimental uncertainties.

Finally it should be pointed out that the model proposed here for two phases can also be used for description of the curing behavior of one phase or multiple phase systems. Furthermore, the assumptions of the model are quite general and it is therefore not restricted to curing reactions in polymer networks. Therefore, it can be applied to predict the dielectric behavior of systems with increasing viscosity (before reaching the non-equilibrium glassy state) and phase separation during reaction in general.

#### 4. Conclusions

From the combination of temperature-modulated DSC, conventional DSC and dielectric relaxation spectroscopy it was possible to study the influence of a reaction induced transformation of a low molecular weight liquid to a glassy polymeric network (“reaction induced vitrification”) on the molecular relaxation processes. By fitting a simple model for the curing time dependence of the complex dielectric permittivity a significant deviation of the dielectric data was found for longer curing times where the molecular motions of the main glass–rubber relaxation become considerably slower than the probe frequency. This vitrification is very similar to a quench experiment of a chemically stable material below its glass transition by fast cooling. In both cases the molecular motions are frozen in a non-equilibrium state. The relaxation toward equilibrium becomes extremely slow and can be described by physical aging processes. The appearance of an aging peak in the DSC traces after “reaction induced vitrification” is in accordance with this finding. This effect has to be incorporated into the model to predict the relaxation behavior for long curing times satisfactorily (“non-equilibrium model”).

It could also be shown that the dielectric behavior of a system which phase separates during chemical reaction can be satisfactorily described for short and intermediate curing times by the “equilibrium model” which involves a term for the dc-conductivity contribution and for each phase a term describing the

relaxation of the permanent electrical dipoles as a function of curing time.

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