ACTIVATION ENERGY DETERMINATIONS FROM DIELECTRIC THERMAL ANALYSIS OF REACTING POLYMERIC SYSTEMS

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Methods were developed for calculating reaction activation energies from dielectric property measurements during isothermal and nonisothermal cure of thermosetting polymers. These methods were derived by assuming that features of the dielectric response occurred at unique extent of reaction values. Activation energy results were obtained through dielectric analysis for two thermosetting resin systems: a model epoxy system — tetraglycidyl-4,4'-diaminodiphenylmethane cured with 25 parts per hundred of 4,4'-diaminiphenylsulfone hardener; and a model dicyanate blend resin, 55% (by weight) of bisphenol A dicyanate and 45% of tetra *o*-methyl bisphenol F dicyanate. Results were in excellent agreement with activation energies determined from differential scanning calorimetry measurements.

Introduction

Previously developed dielectric thermal analysis techniques based on non-reacting polymeric systems [1] were extended in this study by developing methods for determining the reaction activation energy from both isothermal and nonisothermal cure experiments. The developed methods were adapted from standard differential scanning calorimetry techniques. The adaptations were made by assuming that an inflection in ε', the storage component of the

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complex dielectric constant ε^*, and the corresponding maximum in ε'', the loss component of ε^*, occur at a unique extent of reaction value during cure.

Background

Isothermal reaction

A method for extracting activation energy information from dielectric data during isothermal cure was first suggested by Lane, Seferis and Bachmann [2], by extending the method described by Prime for isothermal DSC experiments [3]. A relationship was derived from a generalized polymerization rate equation:

$$\frac{d\alpha}{dt} = k f(\alpha) \tag{1}$$

where α is the degree of cure or degree of conversion, $f(\alpha)$ is an appropriate functional expression based on α, and k is the rate constant. For isothermal conditions, this equation was then rearranged and integrated up to the time at which ε'' reaches a maximum value, t_P:

$$\int_0^{\alpha_{pl}} d\alpha / f(\alpha) = k \int_0^{t_p} dt \tag{2}$$

The left side of this equation has a specific value for each value of α_p, i.e. $\alpha_p = \alpha_{pl}$, which can be represented as $C(\alpha_{pl})$. Integrating Eq. (2) then gives:

$$C(\alpha_{pl}) = kt_p \tag{3}$$

After substituting an Arrhenius expression for the rate constant, k, and taking logarithms, the final expression in terms of activation energy, E_a, and the ε'' peak time, t_P, was obtained from Eq. (3) as :

$$\ln (1 / t_p) = \ln (k' / C (\alpha_{pl})) - E_a / RT \tag{4}$$

where k' is the pre-exponential term of the Arrhenius equation.

In DSC experiments, this equation is used to calculate the activation energy of thermosetting polymers during cure that exhibit autocatalytic kinetic behaviour, which is manifested in isothermal DSC scans by a local maximum. Since ε'' also reaches a peak value during polymerization, Eq. (4) may be applied to dielectric data in the appropriate frequency range regardless of the functional form, $f(\alpha)$, of the reaction kinetics. When the ε'' peak is obscured
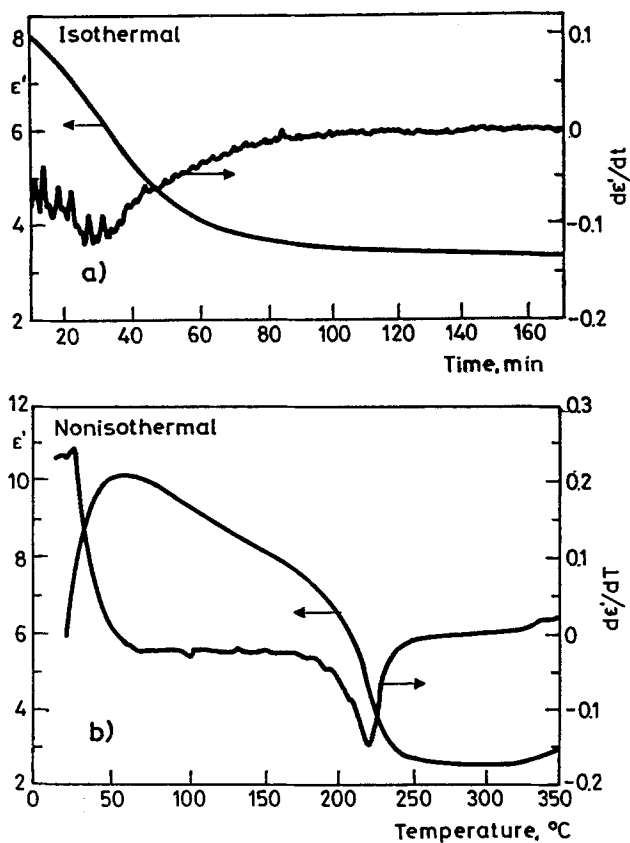
Fig. 1 Permittivity ε' and corresponding derivative plots showing inflection point of ε' from (*a*) isothermal at 220°C and (*b*) dynamic scans of the REX 373 dicyanate system measured at 100 KHz frequency and 1 deg/min heating rate

by ionic conduction effects, the time at which the simultaneous inflection in ε' occurs may be used as a method for determining t_p. As shown in Fig. 1a, the inflection in ε' occurs at the maximum point in $d\varepsilon'/dt$.

Nonisothermal reaction

Extension of the above analysis also permits the reaction activation energy to be calculated from dielectric property measurements during cure at different heating rates. For nonisothermal DSC experiments, Prime modified Eq. (1) by incorporating a constant heating rate, Φ, and an Arrhenius expression for the rate constant [3]:

$$\Phi \frac{\mathrm{d}\alpha}{\mathrm{d}t} = [k\,'\exp(-E_a/RT)]f(\alpha) \tag{5}$$

When integrated from the initial temperature, T_0, to the temperature at which the reaction exotherm reaches a maximum, T_p, this equation becomes:

$$\int_0^{\alpha_{PN}} \mathrm{d}a/f(\alpha) = \frac{k\,'}{\Phi}\int_{T_0}^{T_p} \exp(-E_a/RT)\,\mathrm{d}T \tag{6}$$

As in the isothermal method development, the left side of this equation has a unique value, $C(\alpha_{PN})$, for each α_p, i.e. $\alpha_p = \alpha_{PN}$. After evaluating the integral on the right side by approximation, Prime obtained the relationship between nonisothermal DSC data and activation energy:

$$\ln\Phi \approx -1.052E_a/RT + C(\alpha_{PN}) \tag{7}$$

which can be re-arranged to give:

$$E_a \approx -\frac{R\ \mathrm{d}(\ln\Phi)}{1.052\mathrm{d}(1/T_p)} \tag{8}$$

Again, this equation may be applied to dielectric data by assuming that the ε' inflection and ε'' maximum occur at a unique point during cure. Therefore, the reaction activation energy may be calculated from an Arrhenius-type plot of heating rate *vs.* the corresponding ε'' peak temperature in Eq. (8). Similarly to the isothermal case, when ionic conductivity effects obscure the ε'' peak, the inflection point of the ε' curve defined by the derivative $\mathrm{d}\varepsilon'/\mathrm{d}t$ (or $\mathrm{d}\varepsilon'/\mathrm{d}T$) can be used as shown in Fig. 1b.

Together, Eqs 4 and 8 provide a powerful means for evaluating the apparent reaction activation energy from isothermal and nonisothermal dielectric cure data. The success in applying these methods to experimental dielectric data was demonstrated by calculating the reaction activation energy and comparing with DSC data for the two model thermosetting resins.

Experimental

This resin system was a high performance tetrafunctional epoxy, tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM, MW = 442), cured with a tetrafunctional amine hardener, 4,4'-diaminodiphenylsulfone (DDS, MW = 248). The resin composition contained 25 parts per hundred epoxy (phr) DDS, an epoxy-rich mixture of 43% amine stoichiometry.

TGDDM and DDS were obtained commercially as Ciba-Geigy MY 720 and Ciba-Geigy HT 976 and used as received. The resin mixture was prepared to insure homogeneous mixing without pre-reaction [4]. TGDDM was first heated to 135°C in an oil bath and stirred for an additional 5 minutes, removed from the oil bath, degassed at 95°C under 30 mm Hg vacuum for 30 minutes, and stored at −10°C to prevent pre-reaction. Precautions were taken to minimize resin exposure to moisture.

A commercially available dicyanate system (AROCY REX 373) was used. It is a low molecular co-prepolymer combining 55% (by weight) of a low molecular weight oligomer of bisphenol A dicyanate (AROCY B-30), with 45% of a low molecular weight oligomer of tetra o-methyl bisphenol F dicyanate (AROCY M-30) [9]. The materials were obtained from Hi-Tek Polymers. As this resin can be crosslinked via cyclotrimerization of their molecules, no curing agent was needed for this system.

The majority of experiments were performed using a previously designed disposable two terminal parallel plate dielectric cell [2]. A general Radio 1688 Precision Digibridge, controlled by a Hewlett Packard 9000 computer, measured the capacitance and dissipation of the resin during cure. Selected experiments and reproducibility studies were also performed with a Tetrahedron ADR dielectric system and a TA Instruments DEA 2970 interfaced to a TA Instrumets 2000 Controller.
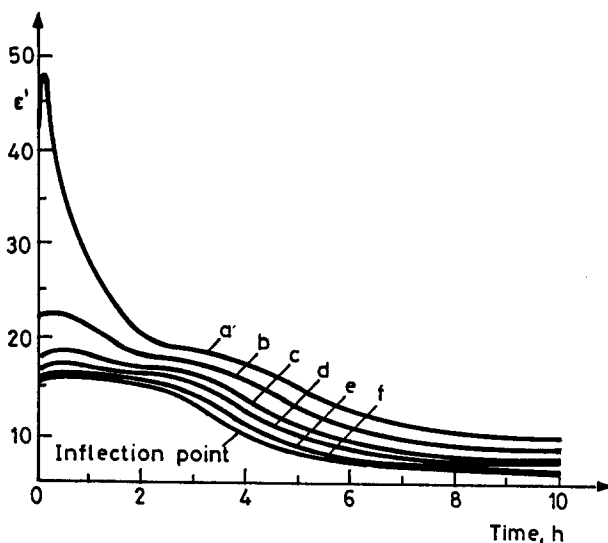

Fig. 2 Permittivity ε' as a function of time for the TGDDM/DDS during isothermal cure at 140°C at different frequencies a) 240 Hz, b) 1 KHz, c) 2 KHz, d) 4 KHz, e) 10 KHz, f) 20 KHz
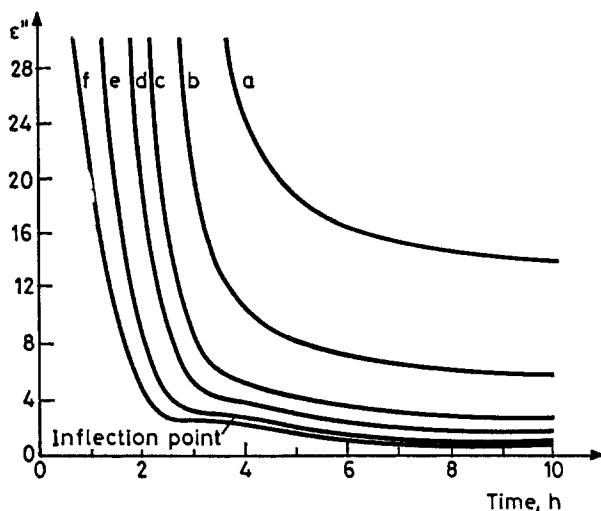
Fig. 3 Loss component ε'' as a function of time for the TGDDM/DDS during isothermal cure at 140°C at different frequencies: *a*) 240 Hz, *b*) 1 KHz, *c*) 2 KHz, *d*) 4 KHz, *e*) 10 KHz, *f*) 20 KHz

The dielectric properties of the TGDDM/DDS system were measured during isothermal cure at 140, 150, 160, 170, 180, 190, 200, 210, and 220°C in an Exocal HT 250 silicon oil bath. Temperature was controlled to within 1 deg/min. The filled two terminal cells were immersed in the bath for 30 seconds to equilibrate at the desired isothermal temperature. Then, the dielectric properties were measured at 240 Hz, 1 KHz, 2 KHz, 4 KHz, 10 KHz, and 20 KHz. Representative dielectric data for TGDDM/DDS cure at 140°C are presented in Figs 2 and 3. As can be seen from the figures, it is difficult to observe the maxima expected from relaxation phenomena since both electric polarization/ionic conductivity and relaxation 'overlap' were observed for this system [6, 7].

Nonisothermal cure measurements were made using a smaller version of the two terminal dielectric cell in the heating chamber of a TA instruments 983 Dynamic Mechanical Analyzer (DMA) controlled by a TA Instruments 2000 Thermal Analyzer. The dielectric cell was placed in the DMA sample area with the radiant heat shield installed. The DMA sample thermocouple was placed flush against the cell to minimize thermal lag between the resin and programmed chamber temperature. The dielectric properties of the TGDDM/DDS system were monitored during cure at constant heating rate of 1, 5, and 10 deg/min at the same frequencies as in the isothermal experiments. Figures 4 and 5 contain examples of dielectric data for the nonisothermal

curing of TGDDM/DDS at 1 deg/min. Dynamic experiments for both the epoxy and dicyanate systems were examined with single sided, double sided,
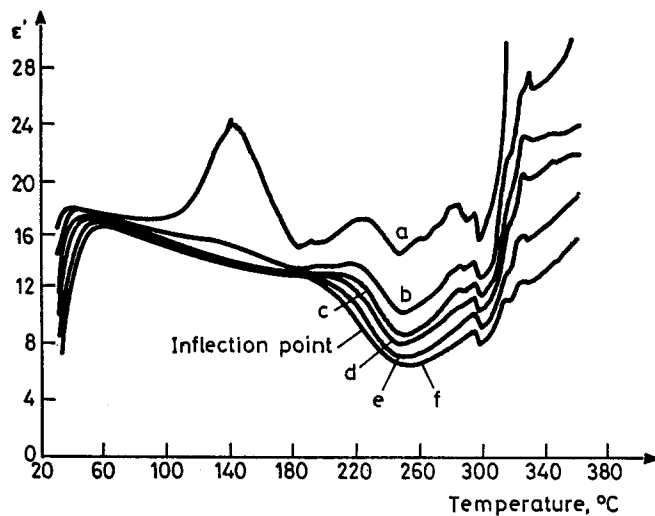

Fig. 4 Permittivity ε' as a function of temperature for the TGDDM/DDS during nonisothermal cure generated at 1 deg/min for different frequencies: *a*) 240 Hz, *b*) 1KHz, *c*) 2KHz, *d*) 4 KHz, *e*) 10 KHz, *f*) 20 KHz
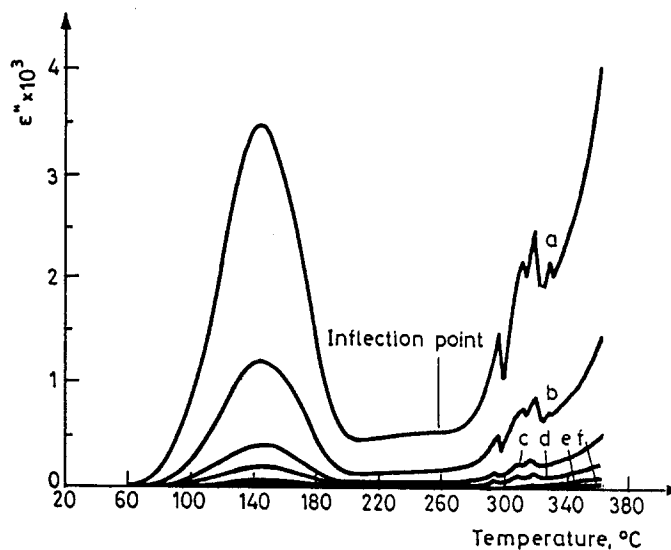

Fig. 5 Loss component ε'' as a function of temperature for the TGDDM/DDS during isothermal cure generated at 1 deg/min for different frequencies: *a*) 240 Hz, *b*) 1 KHz, *c*) 2 KHz, *d*) 4 KHz, *e*) 10 KHz, *f*) 20 KHz

and remote sensors available with the TA Instruments DEA 2970 system. For the dicyanate system, all dielectric experiments were performed with the DEA 2970 Analyzer with single and double sided sensors and they gave identical results. The isothermal temperatures were selected at 180, 190, 200, 220 and 230°C. Nonisothermal experiments were carried out at 1, 3, 5 and 10 deg/min. The frequency range for both conditions was from 1 Hz to 100 KHZ. Only higher frequency data were used for the activation energy calculation to avoid and to obtain more accurate data. The dielectric data for the REX 373 dicyanate system were quite similar to that of TGDDM/DDS epoxy system as can be seen in Figs 2 through 5.

DSC experiments were performed to verify the dielectric activation energy calculations, using a TA Instruments 910 Differential Scanning Calorimeter controlled by the TA Instruments 2000 Thermal Analyzer system. Isothermal DSC experiments were performed at each of the isothermal cure temperatures under constant nitrogen purge, according to a method described by Prime [3]. The 'residual' heat remaining from incomplete reaction was measured by reheating the cured samples from room temperature to 300°C at 10 deg/min.

Nonisothermal DSC experiments were performed from 30° to 350°C at 1, 3, 5, and 10 deg/min. Reaction was assumed to be 100% complete by the onset of degradation, between 290° and 350°C. Consequently, residual heat scans were not performed after the nonisothermal cure experiments.

Moreover, in order to verify our assumption, the extents of reaction for TGDDM/DDS system were calculated from the DSC data using the relationship [4]:

$$\alpha_t = \Delta H_t / \Delta H_{rxn} \tag{9}$$

ΔH_t is the total amount of heat generated by reaction up to time t. ΔH_{rxn} represents the sum of the heat generated during the scan, ΔH_t, and during the residual heat scan, ΔH_{res}:

$$\Delta H_{rxn} = \Delta H_t + \Delta H_{res} \tag{10}$$

The DSC reports heat flow in units of power per gram of sample. Partial integration of the heat flow data as a function of time provided values of ΔH_t, and therefore α_t, throughout the reaction. The value of ΔH_{rxn} used in the calculations was determined from the total heat generated during a nonisothermal DSC scan at 10 deg/min.

The apparent activation energy for the reaction of the two systems were calculated from the isothermal DSC data using the maximum peak time

method described by Eq. 4 and were also determined from the nonisothermal DSC peak exotherm temperatures using Eq. 8. These values were compared to the values calculated from the dielectric data using the developed methodology.

Results and discussion

The reaction activation energy was calculated from the isothermal cure dielectric properties using the peak time method described by Eq. 4. The peak in ε'' was obscured by ionic conductivity at nearly all frequencies, especially at high cure temperature [7]. Consequently, the inflection point in ε' was used to determine t_p as shown in Fig. 2 for the epoxy system.

Table 1 Comparison of TGDDM/DDS (25 phr) DSC extents of reaction at the 20 KHz ε' inflection during isothermal cure

Temperature /°C	t_p (20 KHz) /sec	α_p
140	11898	0.48
150	8532	0.42
160	5938	0.51
170	4302	0.46
180	3303	0.48
190	2214	0.51
200	1418	0.60
210	1278	0.61
220	898	0.71
	Average	0.53 ± 0.09

Table 2 Comparison of time to peak on DSC curve and time to inflection point on DEA permittivity curve for REX 373 dicyanate

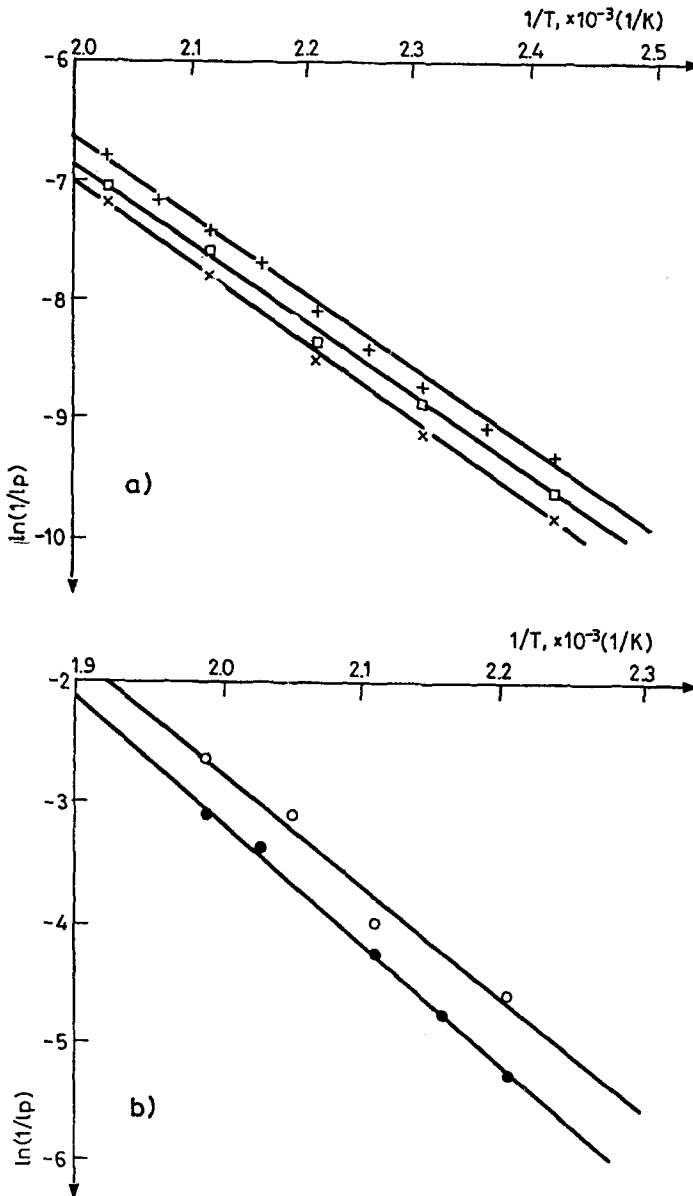| Temperature /°C	t_p (100 KHz) /min.	t_p, (DSC) /min.
180	197	100
190	117	–
200	70	54
215	–	22
220	29	–
230	22	14
250	–	2

Fig. 6 Arrhenius plot (based on Eq. 4 in text) of inverse time to ε' inflection for isothermal cures for: (a) TGDDM/DDS epoxy system at different frequencies: 240 Hz (+), 1 KHz (□), and 20 KHz (x), (b) REX 373 dicyanate system: (●) by dielectric experiment at 100 KHz and (o) by DSC

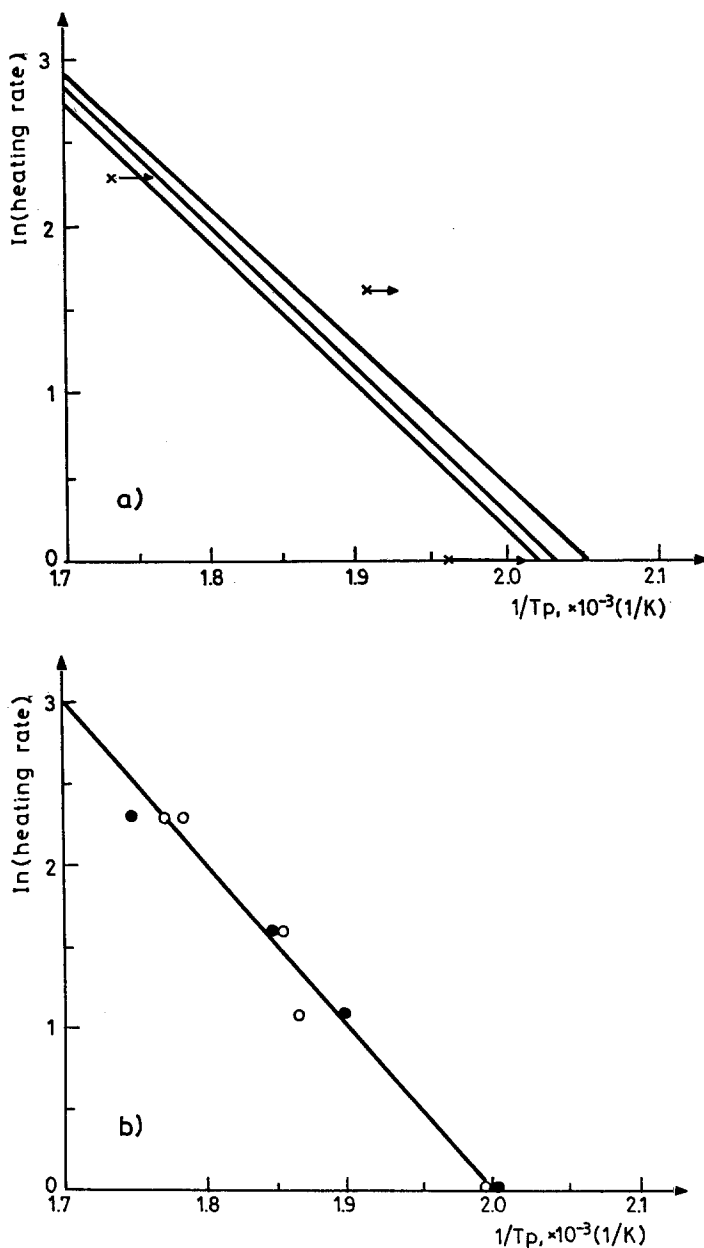**Fig. 7** Arrhenius plot (based on Eq. 8 in text) as a function of inverse temperature to ε' inflection for (a) TGDDM/DDS epoxy system at different frequencies, (b) REX 373 dicyanate system: (●) by dielectric at 100 KHz and (o) by DSC

The assumption that the inflection in ε' and the peak in ε'' occur at a unique point in the cure was supported by DSC measurements which compared favorably to 20 KHz ε' values of t_p at each cure temperature. These values are summarized in Table 1 for the epoxy system. Variations in α_p are within the limits of experimental error. The uniqueness assumption in the derivation of Eq. (4) is further suggested by the dicyanate data summarized in Table 2 for isothermal measurements by DEA and DSC. As can be seen, the ε' inflection times and times to peak to the DSC curves correspond also within the limits of experimental error.

Table 3 Comparison of activation energy calculations: cure of TGDDM/DDS (25 phr) system

	E_a /kcal·mole		
	Dielectric		DSC
Isothermal	13.15	(240 Hz)	16.35
(From Fig. 6a)	12.82	(1 KHz)	
	12.94	(20 KHz)	
	12.97	Average	
Nonisothermal	16.25	(240 Hz)	15.31
(From Fig. 7a)	16.56	(1 KHz)	———
	15.47	(20 KHz)	
	16.09	Average	

Table 4 Comparison of activation energy calculations: cure of REX 373 dicyanate system

	E_a /kcal·mole		
	Dielectric		DSC
Isothermal (From Fig. 6b)	20.2	(100 KHz)	18.5
Nonisothermal (From Fig. 7b)	19.4	(100 KHz)	19.4

Arrhenius curves of the inverse peak times for both systems at each cure temperature are presented in Fig. 6. These curves are linear, further validating the model assumptions over a wide frequency range. The reaction activation energies calculated from these curves using Eq. 4 are summarized in Table 3 for the epoxy system and Table 4 for the dicyanate system.

The reaction activation energies for the two systems were also calculated from the nonisothermal dielectric data plotted in an Arrhenius manner in Fig. 7 using Eq. 8. Conduction effects again masked the peak in ε'', so the ε' inflection point was used to determine the peak temperature, T_p.

As with the isothermal data, the inflection and peak in ε' and ε'' were compared to the DSC data to verify the primary assumption in the method derivation. Table 5 summarizes the values of α_p and T_p at 20 KHz at each heating rate examined for the epoxy system. The values of α_p were difficult to accurately determine for the TGDDM/DDS system since the DSC exotherms were changing rapidly at T_p. Like in the isothermal case, however, the uniqueness assumption was verified with data from the dicyanate system. Table 6, which summarizes peak temperatures at different heating rates for both DSC and DEA, demonstrates that the uniqueness assumption is met within the accuracy of the experimental data.

Table 5 Comparison of TGDDM/DDS (25 phr) DSC extents of reaction at the 20 KHz ε' inflection during nonisothermal cure

$\Phi/\mathrm{deg}\cdot\mathrm{min}^{-1}$	T_p (20 KHz) /°C	α_p
1	226	0.91
5	252	0.75
10	299	0.99
	Average	0.88 ± 0.12

Table 6 Comparison of peak temperature of DSC curve and inflection point temperature of permittivity for REX 373 dicyanate

$\Phi/\mathrm{deg}\cdot\mathrm{min}^{-1}$	T_p, (100 KHz) /°C	T_p (DSC) /°C
1	226	229
3	254	263
5	269	267
10	300	293

The calculated activation energies from dielectric data for both systems examined are compared to those from DSC data in Table 3 and Table 4. For the TGDDM/DDS system (Table 3), values calculated using the isothermal dielectric method are lower than the DSC values by approximately 20%, but are within the accepted range of 12−15 kcal/mole for epoxy/amine reactions [8]. The nonisothermal values of activation energy are in excellent agreement with the DSC values, supporting the assumptions made in deriving Eq. 8. For

the REX 373 system (Table 4), the same trends were observed with activation energies calculated from DEA lower than those calculated from DSC in isothermal and higher than those from DSC in nonisothermal experiments. Compared with a value of 19 kcal/mole obtained from DSC kinetic studies on this system [10], the activation energies calculated from the proposed dielectric method are in excellent agreement with values obtained by established methodologies.

Conclusions

Classical thermoanalytical expressions were developed to calculate reaction activation energy E_a, from isothermal and nonisothermal dielectric measurements. The reaction activation energy may be calculated from either the times or temperatures at which the ε' inflection or ε'' maximum occurs. For both systems examined, epoxy and dicyanate, although the activation energies calculated from DEA are not exactly the same as those from DSC, in all cases, values were within or close to the accepted range of $12-15$ kcal/mole for the epoxy system and 19 kcal/mole for the dicyanate system. Collectively, when combined with earlier developments addressing nonreacting systems, this methodology provides a powerful new tool for quantitative analysis of dielectric data.

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Zusammenfassung — Es wurden Verfahren zur Berechnung der Aktivierungsenergien aus dielektrischen Messungen der isothermen bzw. nichtisothermen Aushärtung von Duroplasten entwickelt. Dabei wurde angenommen, daß die dielektrische Antwort bei einem einzelnen Wert der Reaktionswerte erfolgt. Die Aktivierungsenergie-Ergebnisse wurden für zwei Duroplast-Harze ermittelt: ein Epoxysystem - Tetraglycidyl-4,4'-diamonidiphenylmethan, gehärtet mit 25% 4,4'-Diaminodiphenylsulfonhärter; und ein Dicyanatmischharz aus 55 Gew.% Bisphenol A Dicyanat und aus 45 Gew.% Tetra-o-methylbisphenol F Dicyanat. Die Ergebnisse stehen in guter Übereinstimmung mit den aus DSC-Messungen erhaltenen Werten.