

Analysis of Temperature-Dependent AC Dielectric Loss Data

GYÖRGY BÁNHEGYI,* PÉTER HEDVIG,* and FRANK E. KARASZ, *Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003*

Synopsis

The analysis of dielectric loss data is frequently complicated by the presence of ohmic conductivity, especially at lower frequencies. Two simple methods are discussed for locating transition temperatures and for determining activation energies in such cases. In the first method the permittivity derivative $[d\epsilon'(T)/dT]$ is used; in the second, permittivity difference spectra $\epsilon'(T, \nu_1) - \epsilon'(T, \nu_2)$ ($\nu_1 \ll \nu_2$) are used. The latter technique, however, cannot be used for activation energy determination. The theoretical basis of these methodologies and an analysis of representative experimental data are presented. The data set include measurements of pure and filled polyurethanes and of radiation-cured unsaturated polyester resins. Finally, the advantages of data presentation in the form of ϵ' and ϵ'' instead of $\tan \delta$ are discussed.

INTRODUCTION

Dielectric spectroscopy is a useful technique for studying relaxation transitions in polymers complementary to thermal and mechanical methods.^{1,2} Dielectric measurements can be made in the time, frequency, and temperature domains. In the first two types of measurements, the temperature is fixed, and the step response (DC) or the response to sinusoidal (AC) stress is typically studied. In temperature domain dielectric spectroscopy, the measuring frequency is held constant, and the temperature is systematically changed, often in linear fashion. This measurement can be readily automated and has the advantage that it can be directly compared to other temperature domain methods, such as DSC, dilatometry, or thermomechanical analysis. If multiple fixed frequencies are used in the temperature domain, useful information concerning the activation energies can also be obtained.

Superposition of various relaxation mechanisms, especially in polymeric mixtures and phase-separated systems requires careful deconvolution of the data. The presence of ohmic conduction often obscures the locations of the transitions by masking the loss peaks. In this contribution two simple methods are discussed which can help to maximize the information that can be derived from temperature-dependent AC dielectric measurements.

*Research Institute for Plastics, H-1950, Budapest, Hungary.

THEORY

The step (DC) response $\epsilon(t)$ of a dielectric containing orientable dipoles is¹

$$\epsilon(t) = \epsilon_{\infty} + (\epsilon_s - \epsilon_{\infty})[1 - \phi(t)] \quad (1)$$

where ϵ_s and ϵ_{∞} are the equilibrium (static) and instantaneous (high frequency) limiting permittivities, $\phi(t)$ is the normalized response function [$\phi(0) = 1$, $\lim_{t \rightarrow \infty} \phi(t) = 0$]. The AC response can be calculated using the Boltzmann superposition principle^{1,2}:

$$\frac{\epsilon^*(\omega) - \epsilon_{\infty}}{\epsilon_s - \epsilon_{\infty}} = \int_0^{\infty} - \left[\frac{d\phi(t)}{dt} \right] \exp(-i\omega t) dt \quad (2)$$

where $\epsilon^*(\omega)$ is the Fourier transform of the time derivative of the dielectric response function. If $\phi(t)$ is described in terms of a continuous distribution of exponential responses

$$\phi(t) = \int_{-\infty}^{\infty} F(\ln \tau) \exp(-t/\tau) d \ln \tau \quad (3)$$

where the distribution function $F(\ln \tau)$ is normalized to 1, the dynamic response can be written as

$$\frac{\epsilon^*(\omega) - \epsilon_{\infty}}{\epsilon_s - \epsilon_{\infty}} = \int_{-\infty}^{\infty} \frac{F(\ln \tau) d \ln \tau}{1 + i\omega\tau} \quad (4)$$

The distribution function can be determined from the frequency dependence of the real and imaginary components of $\epsilon^*(\omega)$:

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) \quad (5)$$

In the first approximation³

$$F(\ln \tau) \approx \frac{2}{\pi} \epsilon''(\ln \omega) \Big|_{\omega=1/\tau} \quad (6)$$

and

$$F(\ln \tau) \approx - \frac{d\epsilon'(\ln \omega)}{d \ln \omega} \Big|_{\omega=1/\tau} \quad (7)$$

As the distributions of the relaxation times broaden, the accuracy of these relations increases. In this approximation $\epsilon''(\omega)$ and $-d\epsilon'(\ln \omega)/d \ln \omega$ are proportional. [The exact relationship between $\epsilon'(\omega)$ and $\epsilon''(\omega)$ is given by the Kramers-Kronig integral transformation.^{2,3}]

Another commonly used method of describing experimental AC responses is to assume a nonexponential response function, perform the Fourier transformation, and fit the parameters to the experimental data. As a recent example

of this procedure, Gény and Monnerie⁴ derived the orientational response function for a polymer chain in a tetrahedral lattice using the defect-diffusion model of Valeur et al.⁵:

$$\phi(t) = \exp(-t/\tau) \operatorname{erfc}(t/\tau_p)^{1/2} \quad (8)$$

where τ_p is the diffusion-correlation time of the local conformational motion of the chain, while τ describes out-of-lattice effects,⁶ and $\operatorname{erfc}(x)$ is the complementary error function:

$$\operatorname{erfc}(x) = 1 - \operatorname{erf}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-u^2} du \quad (9)$$

The function in eq. (8) has been derived by Hunt and Powles⁷ for one-dimensional spin diffusion in supercooled liquids and has the advantage that its Fourier transform can be written analytically⁴:

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = \frac{1 + [(\tau/\tau_p)(1 + i\omega\tau)]^{1/2}}{1 + i\omega\tau + [(\tau/\tau_p)(1 + i\omega\tau)]^{1/2}} \quad (10)$$

The single relaxation time limit is approximated if the diffusion process is very slow, i.e., if $\tau/\tau_p \rightarrow 0$. The shape of the response function and that of the corresponding Cole-Cole plot is defined by the single parameter τ/τ_p .

Havriliak and Negami⁸ have proposed an empirical two parameter function for $\epsilon^*(\omega)$:

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = \frac{1}{[1 + (i\omega\tau)^{1-\alpha}]^\beta} \quad (11)$$

By choosing proper values for the independent form parameters α and β practically any experimental Cole-Cole plot can be fitted. This relation provides, however, no physical insight for the parameters, and the inverse Fourier transform (the decay function) cannot be written analytically.

TABLE I
Dielectric Transition Parameters for a Hypothetical Polymer
with Two Relaxations

	1	2
N (mol/dm ³)	1.7	6.5
$g^{1/2}\mu_0(D)$	3.0	1.5
α	0.3	0.4
β	0.2	0.5
τ (20°C) (s)	10^{-3}	10^4
E_d (kJ/mol)	250	350

α , β , g , N , ϵ_∞ are assumed to be temperature-independent; conductivity data are given in the text.

To describe the shape of the loss peak, it is necessary to scan 5–10 decades of frequency, depending on the broadness of the distribution. Since a single experimental technique may only cover 3–4 decades,² several experimental techniques⁹ over wide temperature ranges and the temperature-frequency superposition principle^{1,2} may have to be employed in order to obtain a sufficiently wide frequency range. The latter technique utilizes the fact that τ , the time constant, is temperature-dependent. The functional form of this dependence can usually be described, at least over a limited temperature range, by an Arrhenius relation^{1,2}:

$$\tau = \tau_0 \exp E_d/RT \quad (12)$$

where τ_0 is the preexponential factor and E_d is the activation energy of the dielectric relaxation.

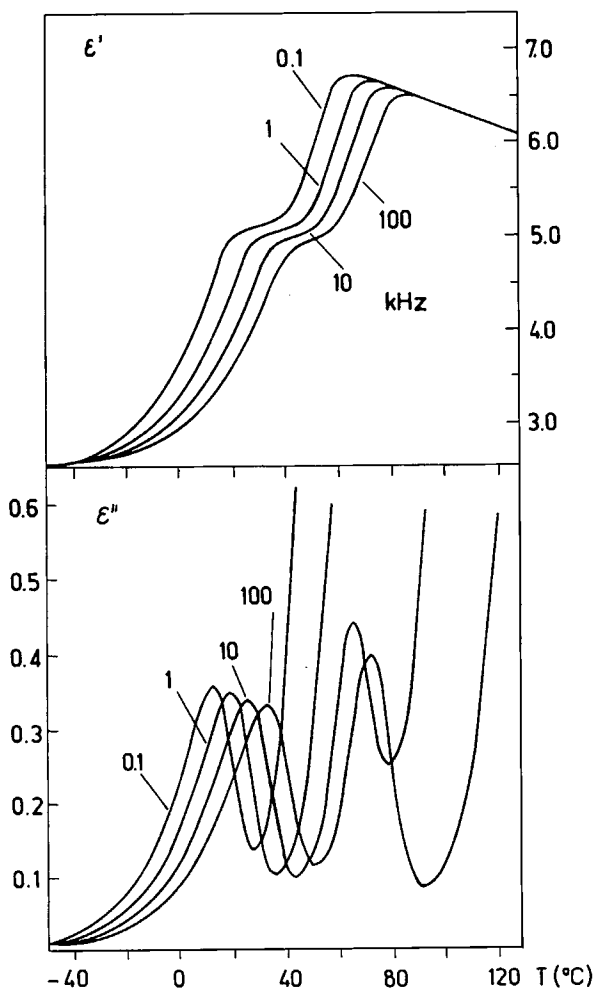


Fig. 1. Dielectric permittivity and loss in a model system with two independent transitions. Relevant parameters are given in Table I.

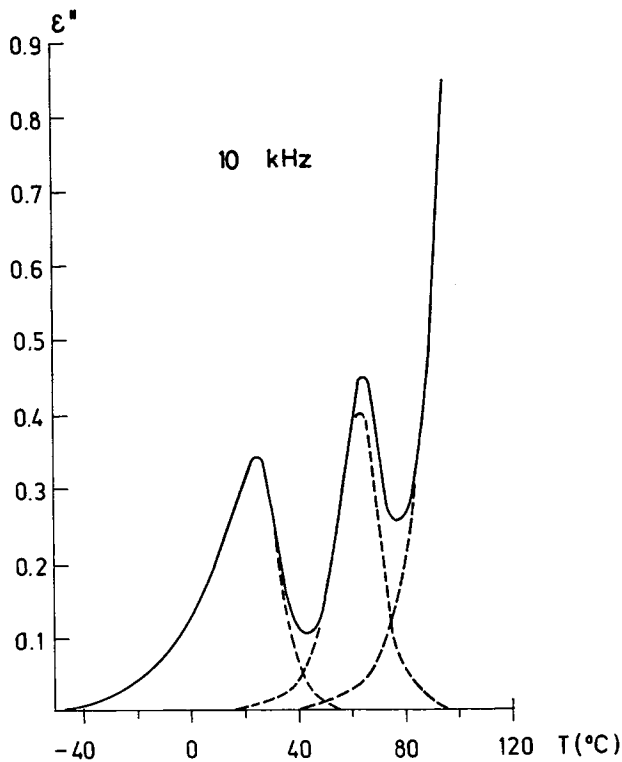


Fig. 2. Deconvolution of the 10 kHz loss curve shown in Figure 1 by extrapolation of the ohmic conductivity tail.

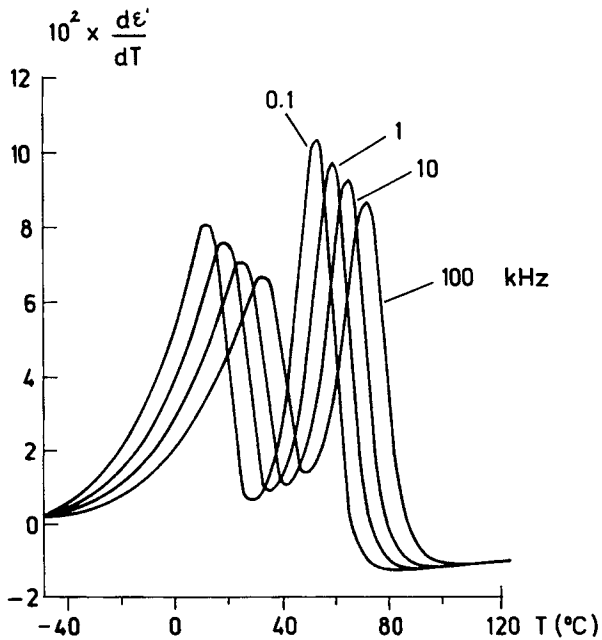


Fig. 3. Permittivity derivatives of the data shown in Figure 1.

Interpretation of temperature-dependent measurements is complicated by the fact that the relaxation strength ($\epsilon_s - \epsilon_\infty$) is itself temperature-dependent^{1,2}:

$$\epsilon_s - \epsilon_\infty = \frac{3\epsilon_s}{2\epsilon_s + \epsilon_\infty} \cdot \frac{N}{3\epsilon_0 RT} \left(\frac{\epsilon_\infty + 2}{3} \right)^2 g \mu_0^2 \quad (13)$$

where N is the number of orientable dipoles (mol/dm³), ϵ_0 is the vacuum permittivity, μ_0 is the gas phase dipole moment, and g is the Frölich-Kirkwood factor which takes into account the correlation of dipoles. As ϵ_∞ is only slightly temperature-dependent, the relaxation strength usually displays a T^{-1} type dependence. At structural transitions (e.g., glass-rubber transitions, melting, etc.) g , or even N , can change abruptly, resulting in complicated $\epsilon_s(T)$ functions.¹⁰

Another obstacle in interpreting temperature dependent AC losses is the presence of ohmic conductivity which may depend exponentially on temperature²:

$$\sigma(T) = \sigma_0 \exp(-E_c/RT) \quad (14)$$

where σ_0 is the preexponential factor and E_c is the activation energy of conduction and appears in phase with the dielectric loss:

$$\epsilon''_{\text{tot}}(\omega, T) = \epsilon''_{\text{diel}}(\omega, T) + \sigma(T)/\epsilon_0\omega \quad (15)$$

Let us consider a model situation of a polymer with $\epsilon_\infty = 2.5$ and with two independent relaxation processes described by a two-parameter Havriliak-Negami relation [eq. (11)]. The parameters for this model are summarized in Table I. The assumed room temperature ohmic conductivity is

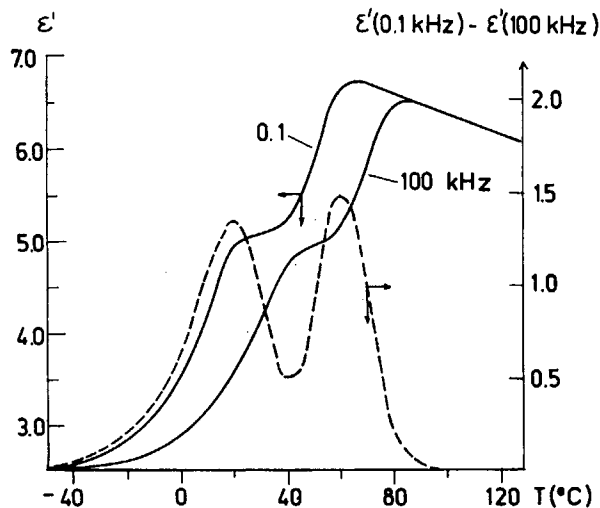


Fig. 4. 100 Hz and 100 kHz permittivities and the difference spectrum for the model system (see text and Table I).

$10^{-12} \Omega^{-1} \text{ cm}^{-1}$; E_c is 100 kJ/mol. Figure 1 shows simulated relaxation spectra at four different frequencies in the low audio-frequency range. One can see that at 10 and 100 kHz both transitions are readily observable as loss peaks. At lower frequencies, however, the high temperature peak is obscured by a conductivity tail. Maxima can be relatively easily "deconvoluted" using the extrapolation technique (see Fig. 2) if there is a temperature range in which the second term of eq. (15) is dominant; thus σ_0 and E_c can be determined.

Since ϵ'' is independent of the conductivity, the information contained in it can be used to locate the transitions. The theoretical background is as follows. The transition range can be scanned by changing the $\omega\tau$ product. If the temperature is fixed, ϵ'' and ϵ' are related to each other by eqs. (6) and (7). If

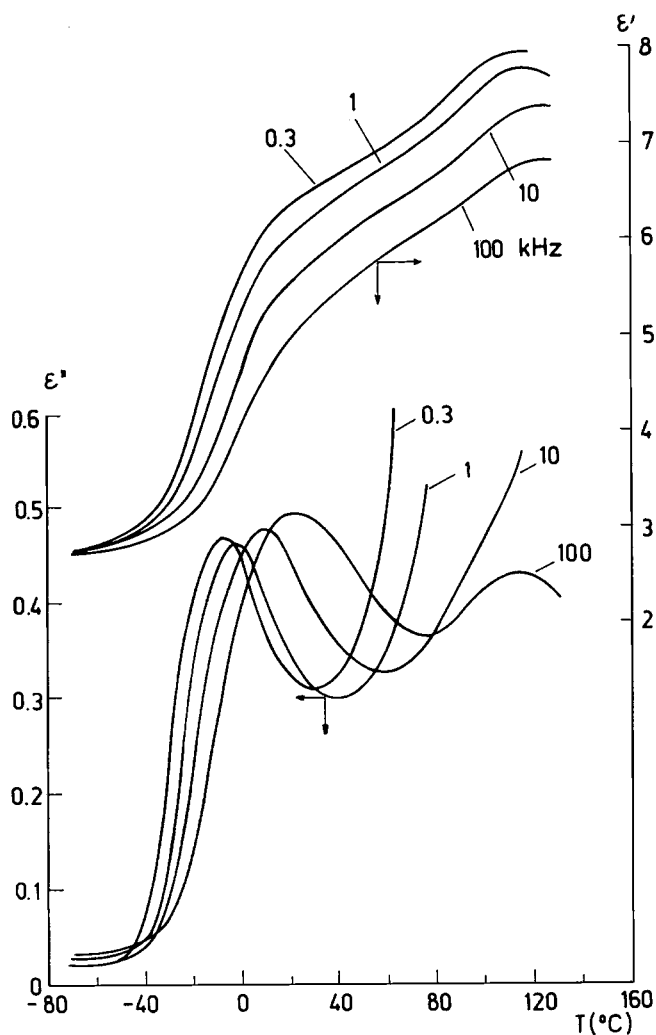


Fig. 5. Permittivity and loss in a segmented polyurethane sample at four frequencies (see text).

the frequency is constant and eq. (12) is valid, ϵ'' is roughly proportional to $-\frac{d\epsilon'(T)}{d(1/T)}$. For practical purposes an inspection of the simple temperature derivative $[d\epsilon'(T)/dT]$ is enough to locate the transition temperatures (Fig. 3). In this case both transitions are easily discernible; frequency shifts can be used to calculate the activation energies. If there are data at only two, widely different, frequencies, we can plot the permittivity difference spectra (Fig. 4). In this case the frequency dependence is diffuse, but the number and relative intensities of the transitions can be easily determined. Because of this additional information it is preferable that permittivity data be used together with ϵ'' instead of loss spectra or $\tan \delta$ alone.

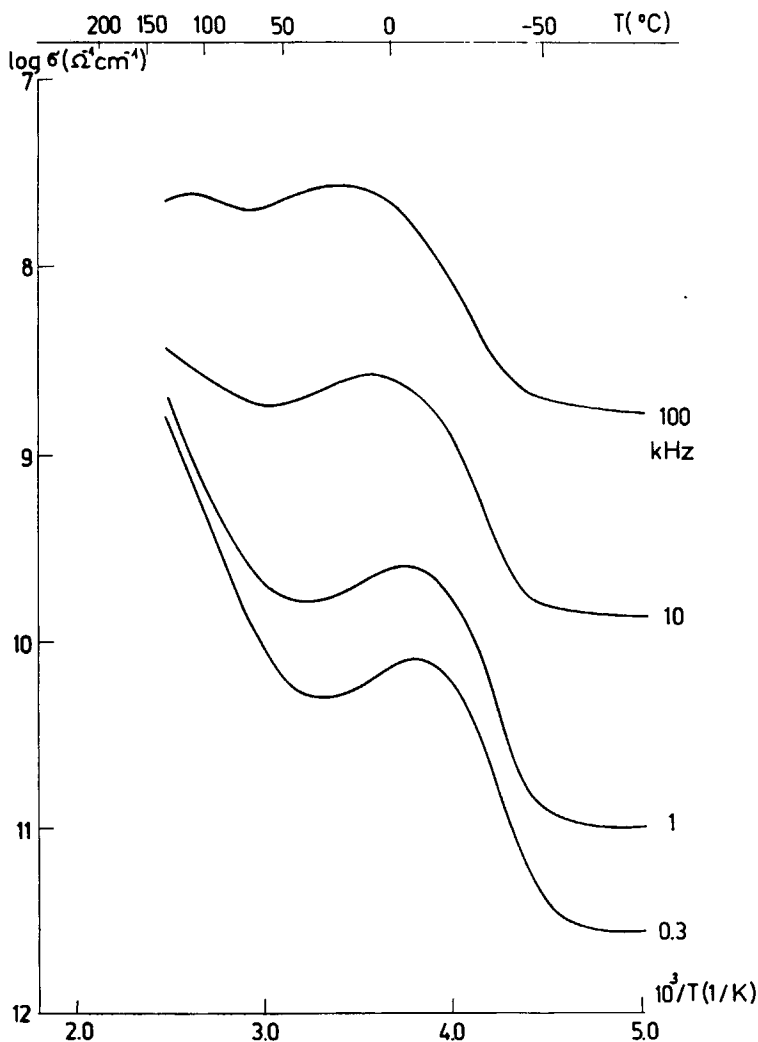


Fig. 6. Arrhenius plot of the AC conductivities of the system shown in Figure 5.

EXPERIMENTAL EXAMPLES

As a first example of the analysis of actual data, we consider temperature dependent AC dielectric data for segmented polyurethanes.¹¹ In this case the sample chosen contains polypropylene oxide as soft segment, 4,4'-diphenyl methane diisocyanate (MDI) as the hard segment, and the chain extender is *N,N'*-bis(2-hydroxyethyl)isophthalamide; for further experimental details (see Ref. 11).

Figure 5 shows the permittivity of the material at four different frequencies. In this case the situation is less favorable than in the hypothetical case discussed above since the two transitions can be observed separately only at the highest frequency (100 kHz). The extrapolation method cannot be used in this case, since the AC conductivity is frequency dependent over the whole temperature range. (Figure 6 shows the Arrhenius plot of the AC conductivity,

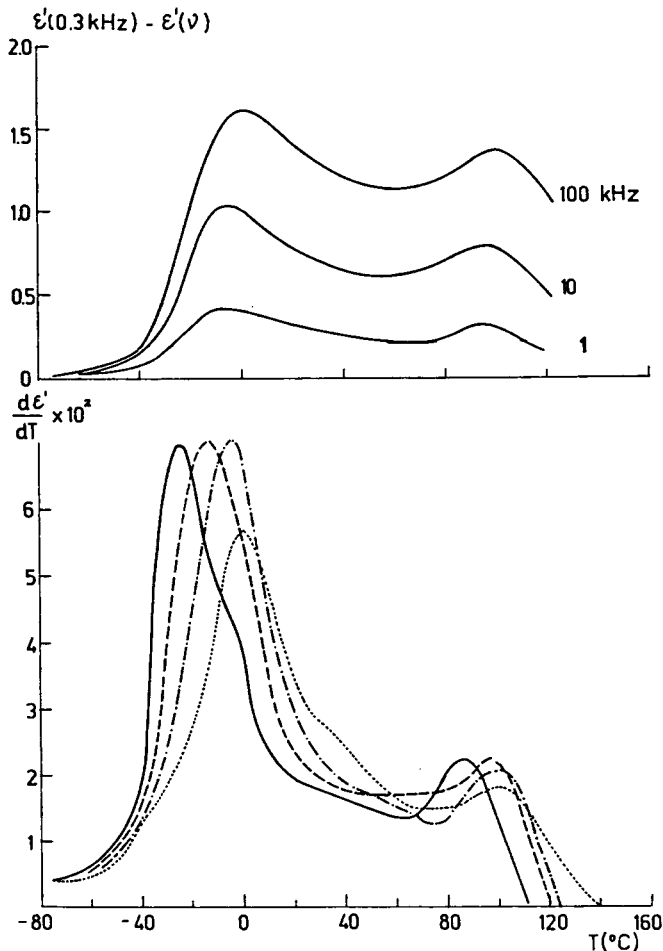


Fig. 7. Permittivity difference spectra (above) and permittivity derivatives (below) of the system given in Figure 5. ν (below) (kHz): (—) 0.3; (---) 1; (-·-) 10; (···) 100.

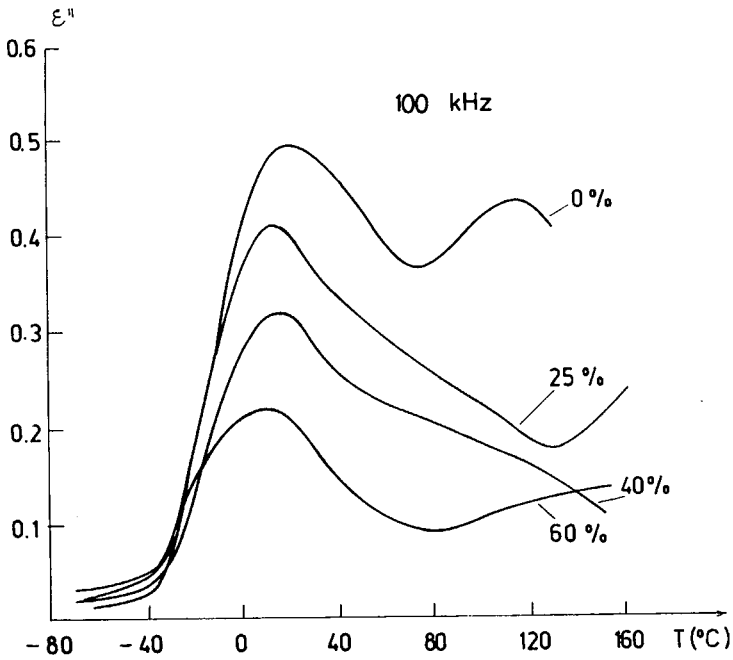


Fig. 8. 100 kHz dielectric losses for CaCO_3 -filled polyurethane samples. The polymer component is identical to that shown in Figure 5. Numbers are filler contents in vol %.

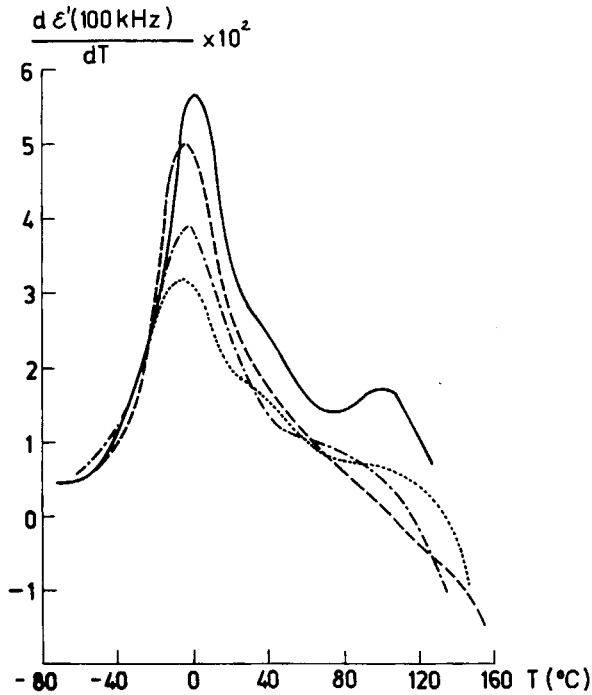


Fig. 9. 100 kHz permittivity derivatives for the data shown in Figure 8: (—) 0%; (---) 25%; (-·-) 40%; (···) 60%.

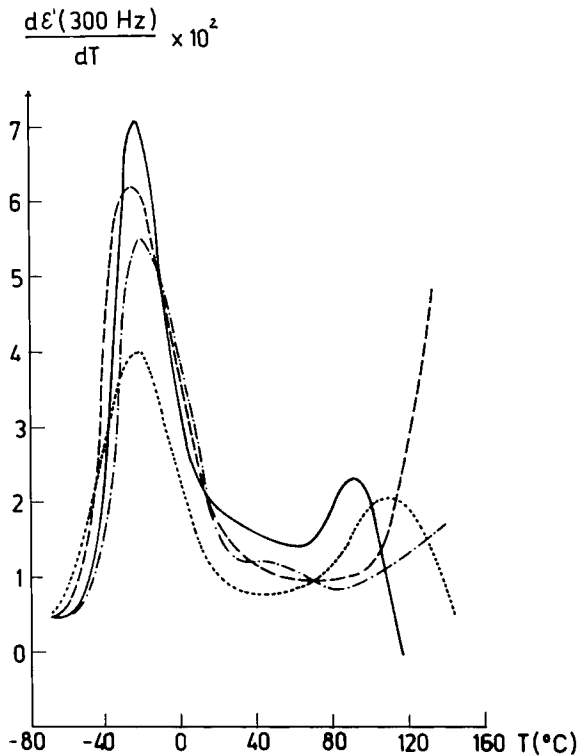


Fig. 10. 300 Hz permittivity derivatives for the data shown in Figure 8: (—) 0%; (---) 25%; (-·-) 40%; (···) 60%.

including dielectric loss.) Thus the dielectric and ohmic components cannot be separated. Permittivity derivatives and difference spectra, however, clearly show the presence of two transitions (Fig. 7). The intensities of the permittivity difference spectra increase with increasing frequency differences, but the qualitative behavior is unchanged.

As a second example we consider the same polyurethane sample filled with differing amounts of CaCO_3 .¹¹ Figure 8 shows the 100 kHz losses for the pure and for three filled samples. The presence of two transitions and intensity changes are clearly visible from the high frequency losses. The situation is quite similar if the 100 kHz permittivity derivatives are examined (Fig. 9). Low frequency permittivity derivatives (Fig. 10), on the other hand, show the onset of a new relaxation mechanism, probably due to interfacial relaxation (see Ref. 11) at the highest temperatures. Difference spectra (Fig. 11) corroborate this conclusion.

The final experimental example to be considered is from a dielectric study of the radiation ($\text{Co}^{60}\text{-}\gamma$) cure of unsaturated polyesters.^{12,13} The resins studied were commercially available materials (Chromos, Zagreb, Yugoslavia) and polypropylene glycol maleate resins with varying amounts of styrene (for further details, see Refs. 12 and 13). The uncured resins show a relatively high conductivity, of the order of $10^{-11}\Omega^{-1}\text{cm}^{-1}$ at room temperature, so that losses and $\tan \delta$ values were not satisfactory for monitoring the curing

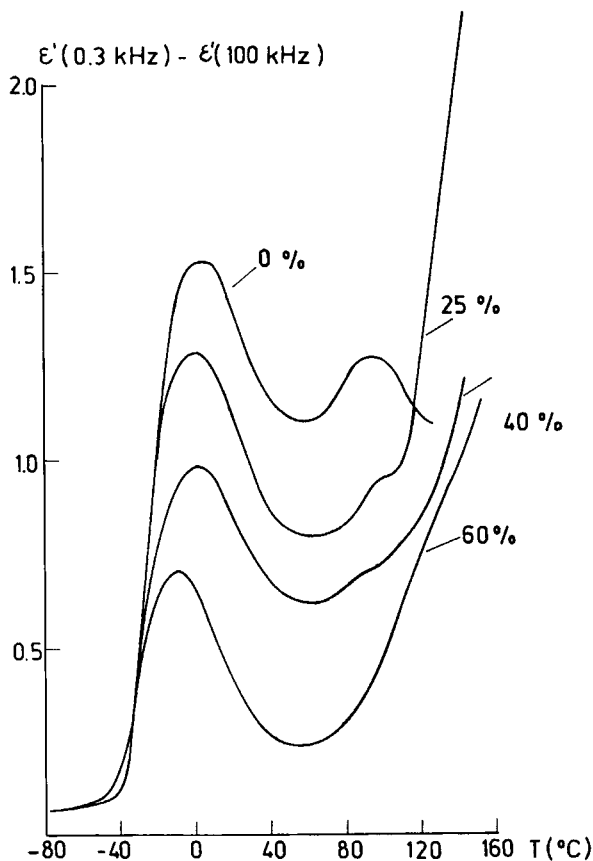


Fig. 11. Permittivity difference spectra of the data shown in Figure 8. Note the onset of the new relaxation mechanism at high temperatures.

reaction. $\tan \delta$ values are misleading in these cases since not only the permittivity but also the ohmic conductivity changes drastically upon curing. Figure 12 shows the permittivities of an uncured and of a cured resin at four different frequencies. The permittivities of the uncured resins can be well fitted by the Gény-Monnerie function [eq. (10)] assuming that the τ/τ_p parameter is independent of temperature. The lower part of Figure 12 clearly shows the effect of irradiation: the transitions become broader, and the transition temperatures shift to higher values. The permittivity derivatives clearly show the broadening and even splitting of the relaxation transitions (Fig. 13) at higher doses. In some cases even the deconvolution of these double transitions is possible: Figure 14 shows the 100 kHz experimental permittivity curve of a partially cured resin, the Gény-Monnerie fit of the components, and the derivatives of these components.

CONCLUSION

As shown by the analysis of a model system and of representative data, temperature-dependent permittivity data even in a limited frequency range

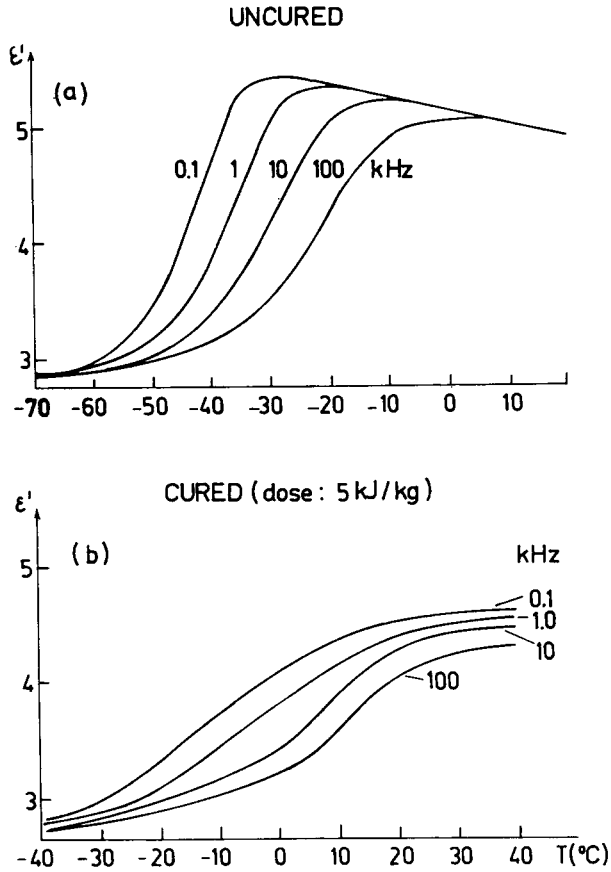


Fig. 12. Permittivities of an uncured and of a partially cured unsaturated polyester resin sample (see text) at four frequencies.

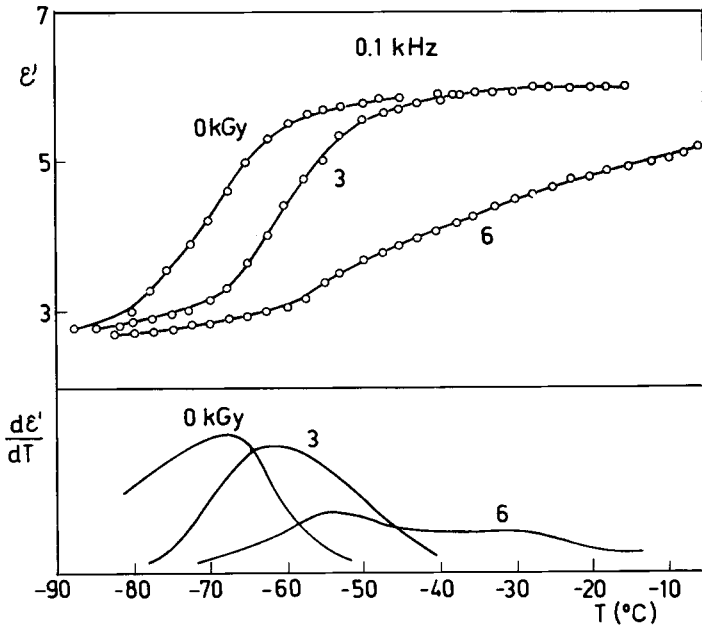


Fig. 13. Permittivities and permittivity derivatives at 0.1 kHz for an unsaturated polyester resin at three different levels of radiation cure.

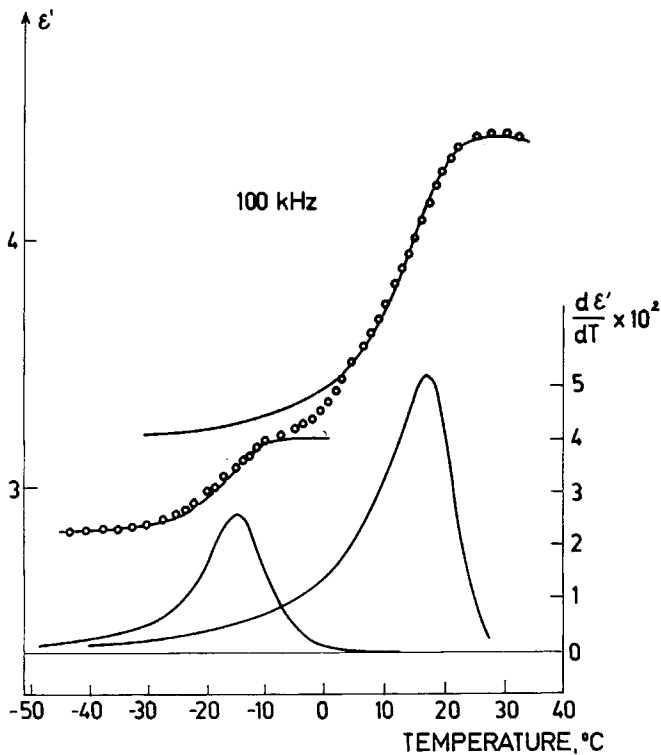


Fig. 14. Decomposition of a double transition in a partially cured polyester resin. Points denote the 100 kHz permittivity data; the continuous lines show the Gény-Monnerie fits and their derivatives.

may provide enough information to locate transitions regardless of the ohmic conductivity level. The applicability of the proposed methods has limitations, including experimental difficulties of acquiring appropriate data, as, normally with increasing resistive currents, bridge-balancing becomes increasingly difficult. For samples with substantial conductivities lock-in detection and balancing of the resistive currents is required. The advantage of the proposed methods is that the relative accuracy of AC bridge capacity measurements is much higher than that of the measurement of ϵ' itself. Some care must be taken in data processing, e.g., smoothing before taking derivatives, if the temperature data are closely spaced or application of spline functions if the temperature points are relatively far apart (see, for example, Ref. 14), and overinterpretation of apparent derivatives from smooth data is a potential problem.

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