# Using Two-Dimensional Dielectric Relaxation Spectroscopy To Study the Effect of Water on the Dynamics of Epoxy−Amine Networks

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The effect of moisture on the structure and properties of epoxy−amine networks has been studied on levels that range from molecular to macroscopic. But the interactions between the network and the absorbed moisture remain incompletely understood despite having been investigated by a battery of experimental (gravimetric, calorimetric, and spectroscopic) and computational techniques.[1−3] This report marks the first time that two-dimensional (2D) dielectric relaxation spectroscopy (DRS) has been employed to study the water−network dynamics.

The basic concept of constructing 2D spectra from the perturbation-induced fluctuations of one-dimensional (1D) spectra was first introduced by Noda in 1986.[4] In that pioneering work, the external stimulus was limited to a simple sinusoidal waveform with a fixed frequency. In 1993, Noda generalized his formalism to perturbations characterized by an arbitrary waveform.[5] Since then, the 2D correlation analysis has been applied to a host of spectroscopic techniques that include IR,[6−8] near-IR (NIR),[9] Raman,[6] UV−vis,[10] fluorescence,[11] and NMR.[12,13] An overview of 2D correlation spectroscopy is found in refs 14 and 15. The most important advantages of 2D over 1D spectroscopy are (1) the possibility of improving the resolution and enhancing the separation of overlapping molecular events and (2) the possibility of probing the relative rate of spectral intensity changes during the application of an external stimulus. The 2D spectra appear particularly promising in the studies of polymer dynamics where a precise identification of molecular mechanisms with different time and length scales is often the key goal.

In this Communication we report the initial results of a 2D DRS analysis of an epoxy−amine network with water content as external stimulus. The objective of this investigation was to explore the possibility that 2D DRS analysis may enhance our understanding of the complex relaxation mechanism that characterizes these networks.

The system we use is a stoichiometric mixture of diglycidyl ether of bisphenol A (DGEBA) and diethylenetriamine (DETA). Fully cured DGEBA−DETA samples were prepared, exposed to an aggressive environment at 80 °C and 98% RH, removed from the environment at selected time intervals, weighed, and tested. A Novocontrol α analyzer was used for DRS measurements in the frequency range from $10^{-2}$ Hz to 3 MHz. A 2D analysis requires that the external stimuli (varying water content in our case) be equally spaced, and our DRS spectra were adjusted accordingly by linear interpolation. "2D Pocha" software by Daisuke Adachi (Kwansei Gakuim University) was used in the analysis.

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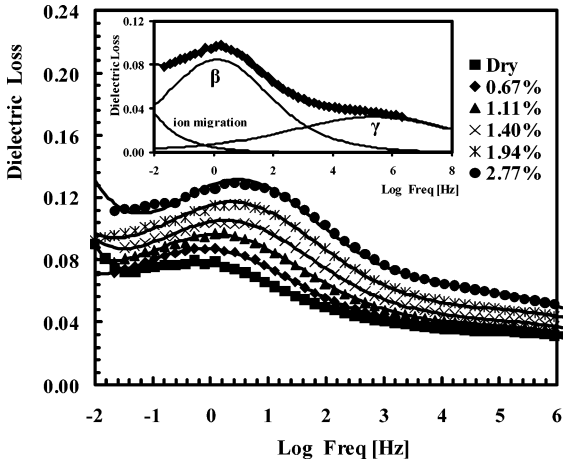


**Figure 1.** Dielectric loss in the frequency domain for DGEBA−DETA network with moisture content as a parameter, measured at −60 °C. The inset shows a deconvoluted spectrum (moisture content = 1.11%) composed of a low-frequency dc conductivity term and two Cole−Cole functional forms.

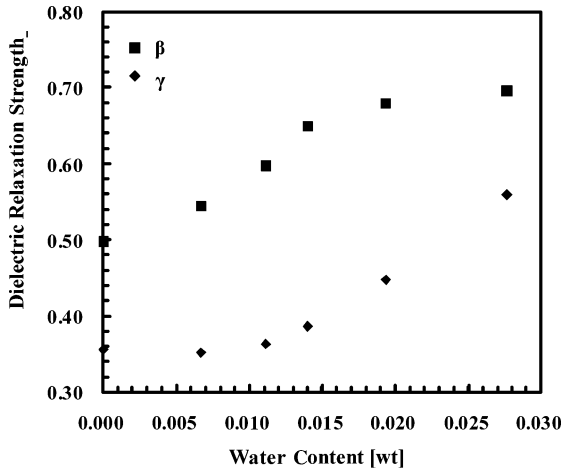


**Figure 2.** Dielectric relaxation strength of $\beta$ and $\gamma$ processes as a function of moisture content, measured at −60 °C.

The 1D DRS spectra (dielectric loss in the frequency domain) of a DGEBA−DETA network with different water content are shown in Figure 1. We observe a broad relaxation peak in the dry network which increases with increasing water content. The solid lines in Figure 1 are composite fits of the dc conductivity term and two Cole−Cole functional forms[16] that describe two relaxation processes (termed $\beta$ and $\gamma$, respectively, in the order of increasing frequency). The dielectric relaxation strength of $\beta$ and $\gamma$ processes, obtained from the fits, is shown as a function of water content in Figure 2; note that the $\beta$ process increases faster than the $\gamma$ process.

In the text below we refer briefly to the salient features of the 2D correlation analysis; a detailed description of the methodology is given in ref 5. Two types of spectra can be obtained from a 2D correlation analysis: synchronous and asynchronous. The synchronous 2D correlation spectrum reflects a simultaneous change in spectral intensities at two different frequen-

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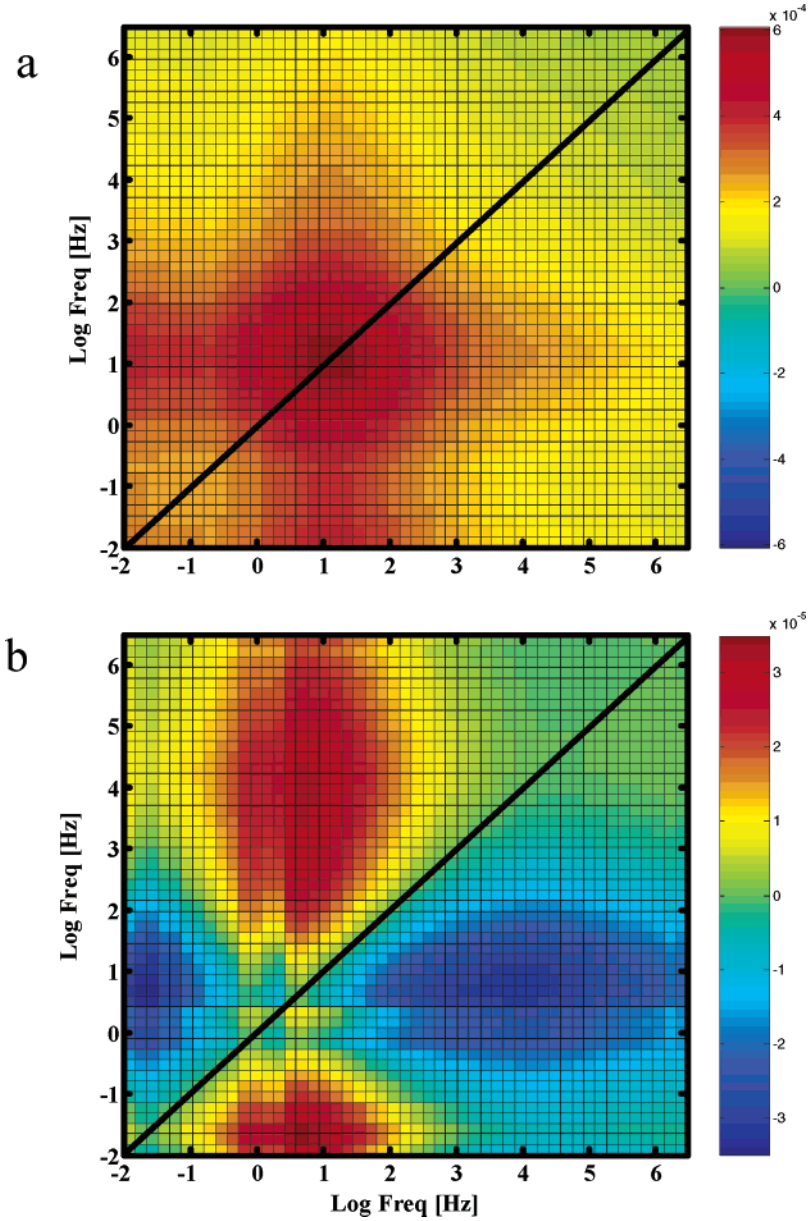


**Figure 3.** Synchronous (a) and asynchronous (b) 2D correlation DRS spectra.

cies, while the asynchronous spectrum depicts a sequential change. The synchronous and asynchronous 2D DRS spectra of our networks were generated from the data in Figure 1 and are shown in parts a and b of Figure 3, respectively. The color scale represents the correlation intensity, which increase from negative (blue) to zero (light green) to positive (red). The synchronous spectrum (Figure 3a) is symmetric with respect to the diagonal line, and the correlation peaks appear at both diagonal (autopeaks) and off-diagonal (cross-peaks) positions. The autopeaks identify the signals that undergo changes with the external stimulus and are always positive. The cross-peaks, on the other hand, are positive if the two signals change in the same direction (either increase or decrease) and are negative otherwise. In the synchronous spectra of Figure 3a, we observe one autopeak ($10^1$, $10^1$ Hz) and two cross-peaks ($10^{-2}$, $10^1$ Hz) and ($10^1$, $10^{-2}$ Hz). All those peaks are positive, which signifies that the measured parameter (dielectric loss) changes in the same direction with water content at all frequencies. In this case, on the basis of the underlying physics, we know that the dielectric loss in the frequency domain *increases* with increasing water content.

The asynchronous spectrum has a better resolution than the synchronous spectrum. Recall that the asynchronous correlation spectrum contrasts spectral intensities at two frequencies that change at different rates. The asynchronous spectrum is antisymmetric and contains no autopeaks but only cross-peaks at off-diagonal positions that appear when two dynamic spectral intensities are out of phase (either accelerated or delayed). A cross-peak with coordinates $f_1$ and $f_2$ is positive if the spectral intensity change at $f_1$ is accelerated with respect to that at $f_2$ and negative if the opposite is true. Let us focus on the upper left portion of the spectrum (above the diagonal line) in Figure 3b. We can see two peaks: one negative peak at ($10^{-2}$, $10^1$ Hz) and one positive peak at ($10^1$, $10^4$ Hz). The negative value at ($10^{-2}$, $10^1$ Hz) indicates that the rate of change of the process at $10^{-2}$ Hz is slower than that at $10^1$ Hz. The positive value at ($10^1$, $10^4$ Hz) means that the process at $10^1$ Hz changes faster than that at $10^4$ Hz. The absence of a peak at ($10^{-2}$, $10^4$ Hz) implies that the two

processes at $10^{-2}$ and $10^4$ Hz change at a similar rate. Thus, the 2D DRS spectra reveal the presence of three processes that vary with water content at $10^{-2}$, $10^1$, and $10^4$ Hz.

We next compare the information obtained from 1D and 2D analysis and draw the following principal conclusions. First, the hypothesis based on the 1D fits that the loss spectra comprise a charge migration process and two relaxation processes is corroborated by the 2D analysis. The three processes at $10^{-2}$, $10^1$, and $10^4$ Hz are clearly observed and identified with charge migration, $\beta$ relaxations, and $\gamma$ relaxation, respectively. Second, the 2D analysis reveals that the process at $10^{-2}$ Hz (charge migration) changes slower than that at $10^1$ Hz ($\beta$ relaxation), which could not be clearly deduced from the 1D spectra. Third, the 2D analysis confirms that the process at $10^1$ Hz ($\beta$) changes faster than that at $10^4$ Hz ($\gamma$), in agreement with the 1D findings (Figure 2). And finally, the 2D analysis also reveals that charge migration and $\gamma$ relaxation change at a similar rate with increasing water content—another observation that could not be made from the 1D spectra.

In summary, this Communication offers the first evidence of a successful use of 2D DRS correlation spectra in the analysis of relaxation processes in polymer networks. DRS is a powerful tool for the study of dynamics of solids (crystalline and amorphous), liquids, and gases, and the utilization of the 2D analysis adds a new dimension to this technique that should prove informative for the characterization of relaxation processes with different time and length scales. We anticipate an increased use of the 2D DRS analysis in the near future.

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