**Summary**

Calculation of the activation energy for molecular relaxations allows the scientist to:

- Identify the chemical nature of the thermal transition based on the magnitude of the barrier (energy) to molecular movement.
- Determine the temperature/frequency relationship of the transition.

Dielectric analysis (DEA) is an ideal technique for measuring the activation energies of molecular relaxations because of the technique’s high sensitivity and its capability to vary frequency over more than 7 decades during the experiment.

**Introduction**

Dielectric Analysis (DEA) measures capacitance and conductance changes of a material as it is subjected to a periodic electrical field. The capacitive nature of a material is its ability to store electric charge, and the conductive nature is its ability to transfer electric charge. While these properties are important in themselves, they have more significance when they are correlated to changes in the molecular and/or structural changes in a material. The actual parameters monitored during dielectric analysis are the permittivity ($\varepsilon'$) and loss factor ($\varepsilon''$). The permittivity measures the degree of alignment of the dipoles (both permanent and induced) to the electrical field. The loss factor is a measure of the energy required to align dipoles and to move trace ions.

Dielectric analysis offers high sensitivity, a wide frequency range, and the ability to accommodate a wide variety of samples. These qualities permit the characterization of subtle molecular transitions ($\alpha$, $\beta$, and $\delta$) which are not easily distinguishable by other thermal analysis techniques (ie. DSC). In addition, the frequency dependent nature of these transitions lends itself to further analysis. For example, the energy of activation can be obtained by performing a linear least squares analysis on the plot of $[\ln$ (frequency)] versus $[1/(T_{max})]$, where $T_{max}$ is the temperature which corresponds to the loss factor peak maximum at a certain test frequency. The slope of the resultant plot when multiplied by the gas constant $R$ (8.314 J/mole or 1.981 cal/mole) will reveal the Energy of Activation (Ea).

**Experimental**

In dielectric analysis, the sample is placed in direct contact with the sensor, or electrode array. The electrodes transmit an applied oscillating voltage to the sample and sense the response of the sample to the applied voltage. The optimum sensor arrangement for monitoring the bulk properties of a polymeric film is the ceramic parallel plate sensor. The parallel plate sensor consists of a lower and upper electrode. The lower electrode is the excitation electrode and contains an RTD (resistance temperature detector) for accurately monitoring sample temperature. The upper electrode is the response electrode and contains a guard ring to prevent fringing effects.

DEA results are affected by temperature, time, and frequency. In general, the ability to detect subtle changes in the material (sensitivity), as well as the ability to separate closely occurring changes (resolution) are optimized by using relatively low heating/cooling rates (ie. 3°C/minute or less) and by utilizing low analysis frequencies (ie. less than 10 Hz). In this study, since the shift of loss factor peaks with frequency is key to the measurement, a series of analysis frequencies were used.

A sample of polyethylene terephthalate (PET) (0.125mm thick) film was placed on the ceramic parallel plate sensors, and after purging for 5 minutes with dry nitrogen gas, the upper ram was lowered to exert 400 Newtons of force on the sample. Data was acquired while heating at a rate of 3°C/minute from -150°C to 200°C and multiplexing frequency (1, 3, 10, 30, 100, 300, 1000, 3000, 10000, 30000, and 100000 Hz).

**Results**

Figures 1 and 2 show the permittivity and loss factor data versus sample temperature obtained on the polyethylene terephthalate film, respectfully. The dielectric data reveals two relaxational, frequency-dependent transitions. The beta transition is detected in the subambient region and is attributed to main chain motions involving the ester group. The alpha transition or glass transition is seen starting in the temperature region of 100°C. The alpha transition is due to large scale rotational motion in the amorphous phase. (1).
The actual loss factor maximum at each frequency is determined using DEA Standard Data Analysis Software.

Arrhenius plots constructed for each transition (a and b) by plotting ln (frequency) versus $1/T_{\text{max}}$ are shown in Figures 3 and 4 respectively. Activation energies determined from the slope of these plots are 51.2 kJ/mole (12.3 kcal/mole) and 354.6 kJ/mole (84.8 kcal/mole). Both agree well with literature reported values of 13 kcal/mole and 90 kcal/mole. (2)

REFERENCES