Summary
Absorbed moisture can have a significant effect on polymer properties, particularly when the end-use form is a thin film. Dielectric Analysis (DEA) is an ideal technique for monitoring the plasticizing effects of moisture on polymer transitions (e.g., glass transition), as well as for estimating the amount of absorbed water.

Introduction
Dielectric Analysis (DEA) is a thermal analysis technique which measures two fundamental electrical characteristics of a material - capacitance and conductance - as a function of time, temperature, and frequency. The capacitive nature of a material is its ability to store electric charge. The conductive nature is the ability to transfer electric charge.

While these electric properties are important in themselves, they have more significance when they are correlated to changes in the molecular state of the material. The actual parameters monitored using DEA are permittivity ($\varepsilon'$), which measures the alignment of molecular dipoles in the material and loss factor ($\tan \delta$), which represents the energy required to align the dipoles or move trace ions. Since water is a dipolar material, absorption of even small amounts of water into a material affects these measured dielectric properties. With close attention to experimental procedures, it is possible to not only see the effects of absorbed moisture but also to estimate the absorbed moisture based on the changes in dielectric properties particularly $\varepsilon'$.

One aspect of good experimental procedure for DEA evaluations is maintaining suitable contact between the instrument's measurement electrodes and the sample material. Dry nitrogen, which is normally used as the purge gas during DEA experiments is a good dielectric material. Thus any nitrogen present at the sample/measurement electrode interface creates an interference that affects results. Obviously, this effect is more noticeable with thin films since the interfering nitrogen layer becomes a more significant portion of the region being evaluated.

One way to improve sample/measurement electrode contact is to sputter coat, under vacuum, a metallic electrode directly onto the sample surface. In sputter coating, the sample is placed in a vacuum to remove any interfering gas molecules. The sample surface is then exposed to a plasma of metal ions (usually gold) which deposits onto the sample surface. This forms a conducting layer on the sample that provides excellent contact with the DEA measurement electrodes.

Experimental
The DEA results were obtained under the following conditions:

- $\varepsilon'$ results: isothermal at 25°C, 100kHz, nitrogen purge
- $\tan \delta$ results: 3°C/minute heating from -150 to 200°C, 10Hz, nitrogen purge

Samples were prepared by cutting 2.5cm x 2.5cm sections from 25 µm and 50 µm polyamide films. (Polyamides were selected for their ability to absorb moisture). After drying in a vacuum oven at 100°C for several days to remove residual water, one section of each polymer was stored in a desiccator while the other sections were conditioned at known temperature/humidity conditions for three weeks. The result was four samples of different "equilibrated" moisture contents. (See Table 1.) The water content of the conditioned films was determined by weight gain on an analytical balance for comparison to the DEA permittivity results.

Before positioning in the DEA, the samples were gold sputtered on both sides using a Denton Desk II (1) System. Each film was covered by a mask overlay which controlled the region of the sample surface exposed to sputtering. This yielded a well-defined electrode area. Control of the sputtered area is important because it is one of the parameters used to calculate quantitative results.

The DEA sensors used to actually evaluate the samples are a variation on the standard parallel plate configuration. These ceramic sensors (Figure 1) have smaller gold electrode areas than the standard arrangement. The lower electrode applies a voltage to the sample, polarizing it. The upper electrode measures the generated current. There is no guard ring on these sensors because edge (fringing field) effects are negligible. A platinum resistance thermometer is contained on the lower sensor to provide accurate temperature measurements.
Results

Polymers generally have weak conductive and capacitive dielectric properties, whereas water is highly conductive. Hence, polymers that absorb moisture with time should exhibit dielectric permittivities ($\varepsilon'$) which increase on exposure to higher humidity environments. If both the constituent contributions from the polymer and water ($\varepsilon_p'$ and $\varepsilon_w'$) add in parallel, the following equations apply:

$$\varepsilon'_t = f_p \varepsilon'_p + f_w \varepsilon'_w$$

where $\varepsilon'_t$ is total permittivity, $\varepsilon'_p$ is dry polymer permittivity, $\varepsilon'_w$ is water permittivity, $f_p$ is weight fraction polymer, $f_w$ is weight fraction water.

Table 1 shows the water absorbed by two polyamides under various humidity conditions as determined by the above equation with $\varepsilon'_w$ being 78 (at 25°C and 100kHz). The DEA results compare favorably with the weight gains measured by an analytical balance. Only polyamide B at high temperature and relative humidity (38°C/90%RH) exhibits an $\varepsilon'$ which is widely divergent from the weight gain result. This lower than expected $\varepsilon'$ can be explained by the theory of Aldrich et al (2) which hypothesizes that water in polymers can exist as droplets within polymer crystalline defects or as individual molecules. As droplets, the water builds interfacial polarization which reduces its normal polarizability.

Figures 2 and 3 show the $\tan \delta$ ($\varepsilon''$) results for polyamide A and polyamide B films respectively. In both polymers, the $\alpha$ and $\beta$ relaxations are shifted to lower temperature with increased humidity. The shifts in polyamide A are reasonably proportional to moisture gain. The $\alpha$ relaxation shift for polyamide B at the highest humidity is larger than expected, considering the lower than expected $\varepsilon'$ mentioned previously. However, this shift agrees well with the large amount of absorbed moisture determined by the weight gain method. This large shift may reflect the fact that absorbed water existing as droplets within the polymer is more effective in reducing main chain interaction so that the $\alpha$ relaxation can readily occur. The $\beta$ transition shifts in polyamide B with moisture are also more pronounced than in polyamide A. This transition, however, is more affected by absorbed water molecules within the polymer which can hydrogen bond to amide groups. Hence, the largest shifts are seen at low moisture levels.

Reference

1. Denton Vacuum Inc., Cherry Hill, NJ.
DIELECTRIC TAN $\delta$ RESULTS FOR POLYAMIDE A

Figure 2

Figure 3

*Brief is based on studies performed by Dr. Mimi Keating, DuPont Company, Wilmington, DE and published as "Moisture Content in Polymers - Estimated by Dielectrometry," NATAS Proceedings 1991.

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