TA Instruments

Thermal Analysis & Rheology

Thermal Analysis Application Brief

Characterization of Ethylene Vinyl Acetate Copolymers by Dielectric Analysis

Number TA-107

SUMMARY

Ethylene-vinyl acetate (EVA) is a generic name used to describe a family of thermoplastic polymers ranging from 5 to 50% by weight of vinyl acetate incorporated into an ethylene chain. Increasing the level of vinyl acetate in EVA polymer reduces the overall crystallinity level associated with the polymer, which increases its flexibility and reduces its hardness. The resultant mechanical and electrical properties exhibited by EVA polymers are therefore very dependent on the level of vinyl acetate in the material. Suppliers and users of EVA polymers need to be able to control the vinyl acetate level to tailor the material for specific end-use applications such as flexible packaging, tubing & hoses, gaskets, or wire coatings. Dielectric analysis (DEA) provides an easy-to-use method for determining this valuable product quality information.

INTRODUCTION

The rubber-like characteristics of EVA polymers are a function of the level of vinyl acetate in the material. Higher levels of vinyl acetate result in a polymer which exhibits a higher degree of rubberlike behavior. The level of vinyl acetate required in the EVA material depends on its particular end-use application. EVA polymers with lower levels of vinyl acetate are utilized in packaging applications, while higher levels of vinyl acetate are needed for hot melt adhesive and coating applications. It is important, therefore, to be able to control and determine the level of vinyl acetate present in the material.

Dielectric analysis, which measures a material's response to a time - varying voltage signal, provides an excellent means to characterize the vinyl acetate level of EVA polymers. The high sensitivity of DEA allows the technique to detect subtle differences in the amorphous vinyl acetate phase of the polymer which can not be detected by more traditional thermal analysis techniques such as DSC or TMA.

Dielectric analysis measures the two fundamental electrical characteristics of a material — capacitance and conductance — as a function of time, temperature and frequency. The capacitive nature is the ability of the material to store an electrical charge and dominates the electrical response at temperatures below the glass transition event. The conductive nature is the ability to transfer an electrical charge and this component becomes important when the material is heated above its glass transition or melting temperature. While these two electrical properties are important in themselves, they have more significance when they are correlated to changes in the molecular and/or structural state of the material. The actual parameters monitored using dielectric analysis are e' (permittivity), which is a measure of the degree of alignment of the molecular dipoles to the applied electrical field; and e" (loss factor), which reflects the energy required to align the dipoles or to move trace ions.

EXPERIMENTAL

In dielectric analysis, the sample is placed in contact with the sensor, or electrode array. The electrodes transmit an applied oscillating voltage signal (at a frequency ranging between 0.003 and 100000 Hz) to the sample and measure the response of the material to the applied voltage. The optimal sensor arrangement for studying the properties of EVA is the ceramic single surface sensor since EVA is usually supplied in the form of pellets. The single surface sensor contains an array of interdigitated excitation and response electrodes on a planar surface. The sensor is easy to use with meltable materials (such as EVA) and is disposable (avoiding the need for tedious clean-up procedures after the sample softens or melts). Samples supplied in the form of pellets are best analyzed by softening the pellets (after placement on the DEA sensor) and then compressing the softened polymer using a force applied by a

ceramic ram located directly above the sensor. The exertion of the force ensures that the sample is in good contact with the electrodes.

A series of EVA polymers, with varying levels of vinyl acetate, was analyzed using the Dielectric Analyzer 2970 with the ceramic single surface sensor. The EVA polymers contained the following levels, by weight, of vinyl acetate; 14, 18, 25, 28 and 33%. The pellets were placed to cover (as best as possible) the electrode array on the sensor. The upper ceramic ram was then lowered to exert 400 Newtons of force on the pellets. The DEA cell was programmed to heat the pellets to 130°C which softened the polymer sufficiently to allow it to flow under the applied force, forming a uniform coating (with a thickness of 0.6 mm) on the sensor. The ram force was removed, the softened EVA polymer was cooled down to -85°C, and the ram force was reapplied once the temperature reached 40°C during cooling. The sample was then heated from -85 to 130°C at a rate of 3°C/min. The following frequencies were applied to the samples during the analysis: 1, 3, 10, 30, 100, 300, 1000, 3000 and 10000 Hz. The use of multiple frequencies permits the assessment of the effects of short time scales on the properties exhibited by the material. The DEA cell was purged with dry nitrogen gas adjusted to a flow rate of 500 ml/min.

RESULTS

Displayed in Figures 1, 2, 3, 4 and 5 are the loss factor (e") curves for EVA samples containing 14, 18, 25, 28 and 33% vinyl acetate, respectively. The peak in each of the loss factor curves between -25 and 0°C is the glass transition (Tg) for the polymer. This transition is frequency dependent and shifts to higher temperatures as the DEA measurement frequency is increased. This is as expected for a non-equilibrium, time-dependent event such as the Tg, and explains the series of slightly different curves in each figure. To directly compare results between samples, therefore, a single frequency which yields a well-defined loss peak must be chosen. Figure 6 is the comparative data at 1000 Hz. The comparative plot shows that the glass transition temperature is relatively insensitive to the level of vinyl acetate in the EVA polymer. However, the magnitude of the loss transition is very dependent on the concentration of vinyl acetate. As the level of vinyl acetate increases, the magnitude of the loss factor peak increases. This is consistent with the fact that increasing the level of vinyl acetate increases the flexibility associated with the polymer. Hence, a DEA analysis based on calibration with a series of known EVA formulations could be used to follow vinyl acetate content.

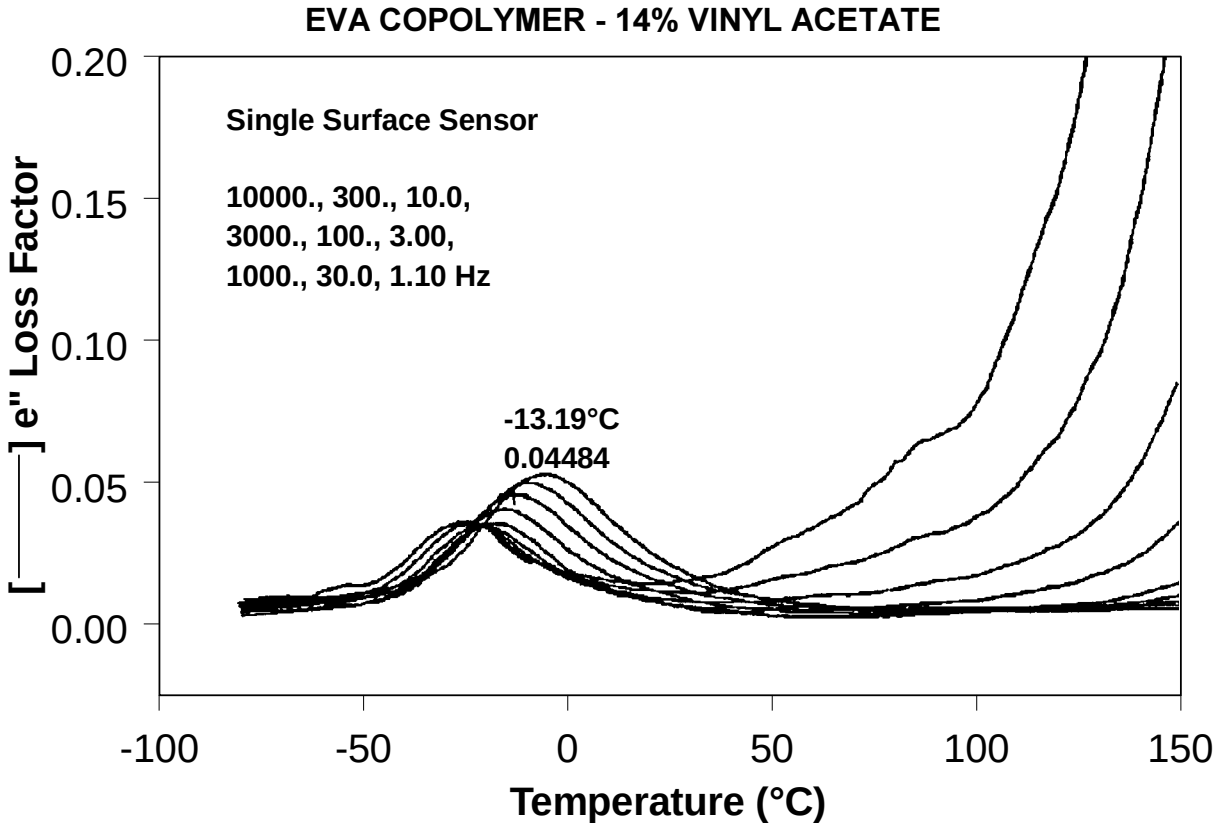

Figure 1

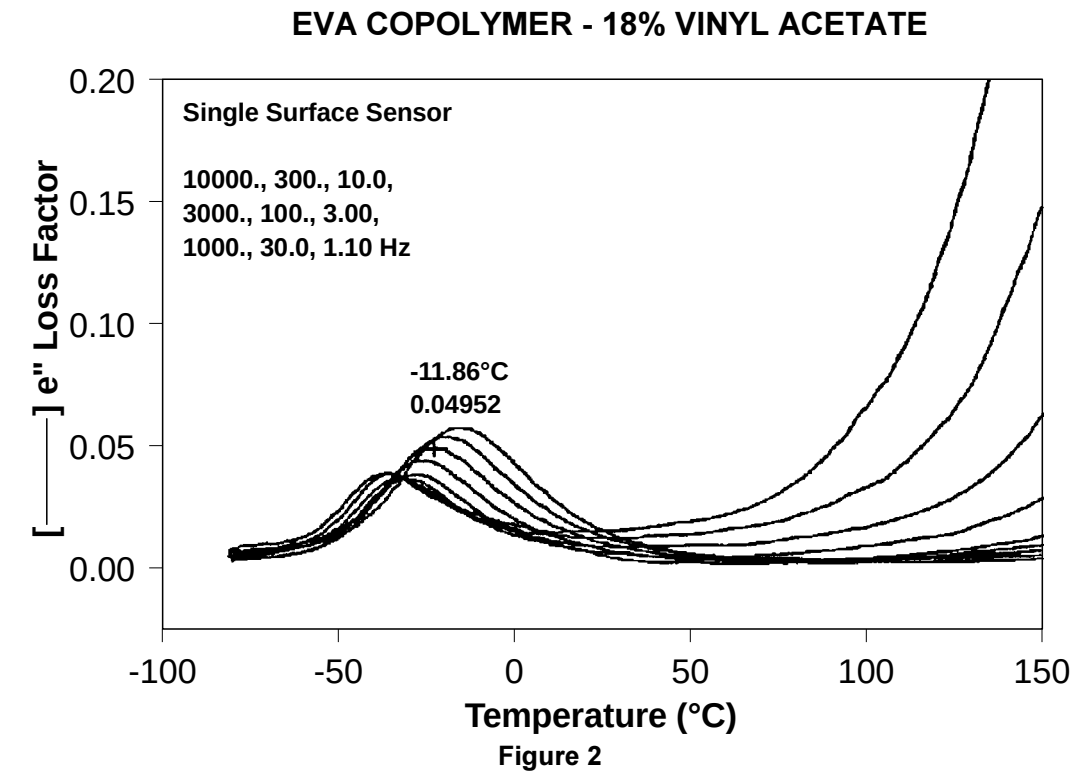

Figure 2

These results are particularly significant because DSC and TMA, which are most commonly used for evaluating polymer Tg's, cannot detect differences in these materials at the Tg. TGA has also been used to measure vinyl acetate content in EVA polymers, but is a more difficult measurement.

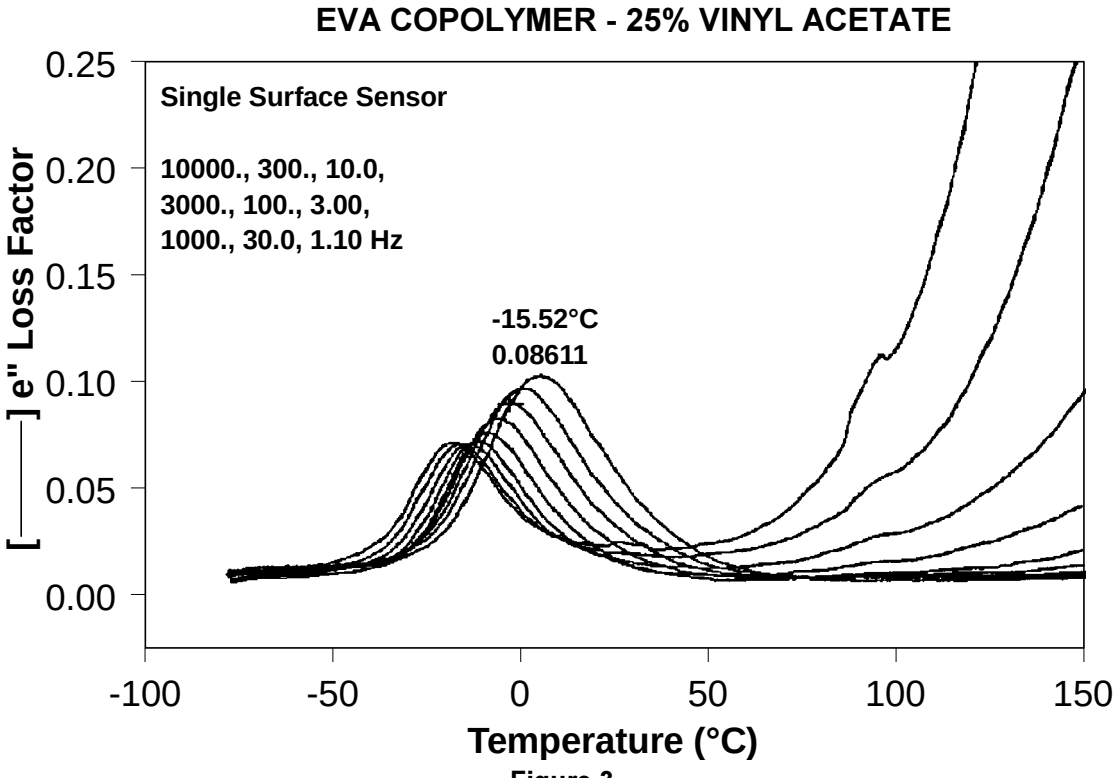

Figure 3

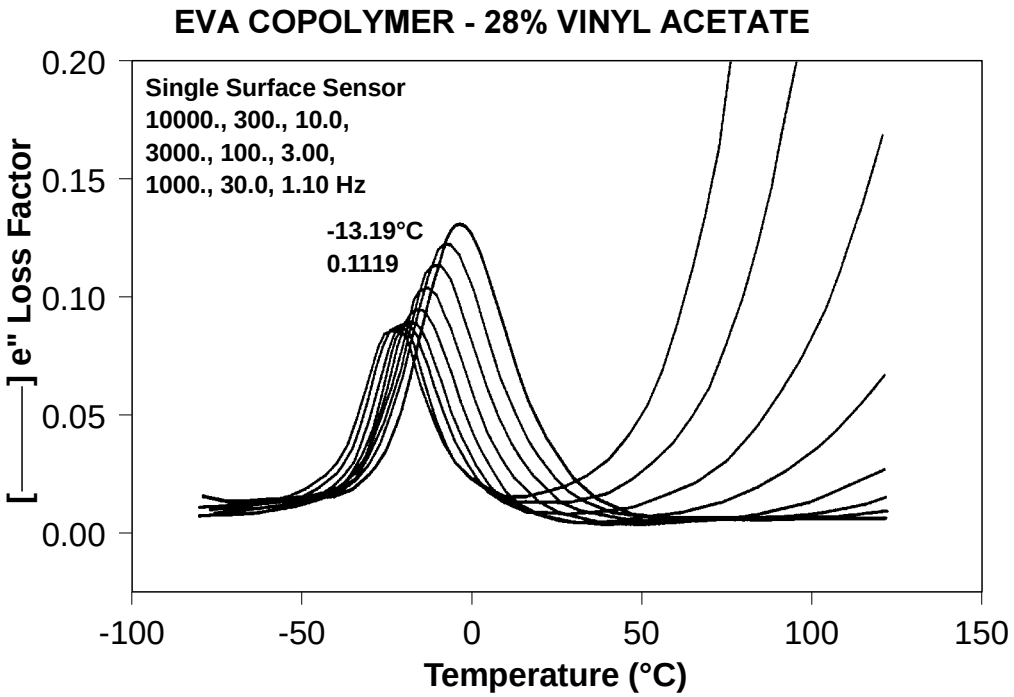

Figure 4

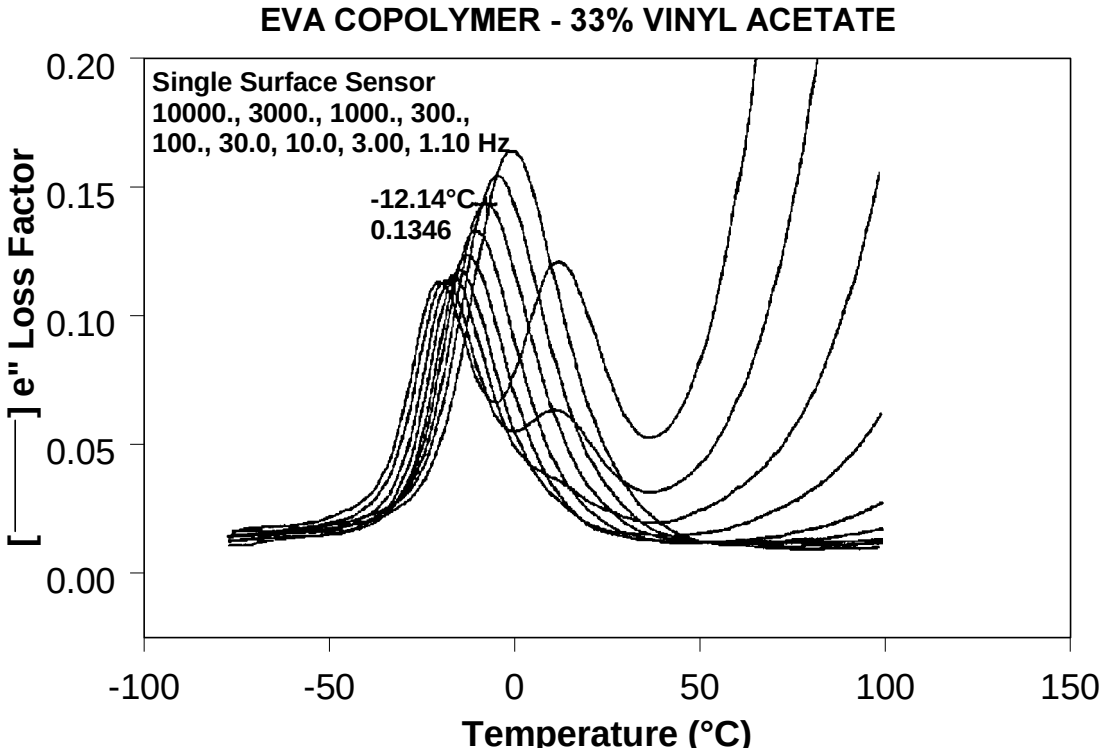

Figure 5

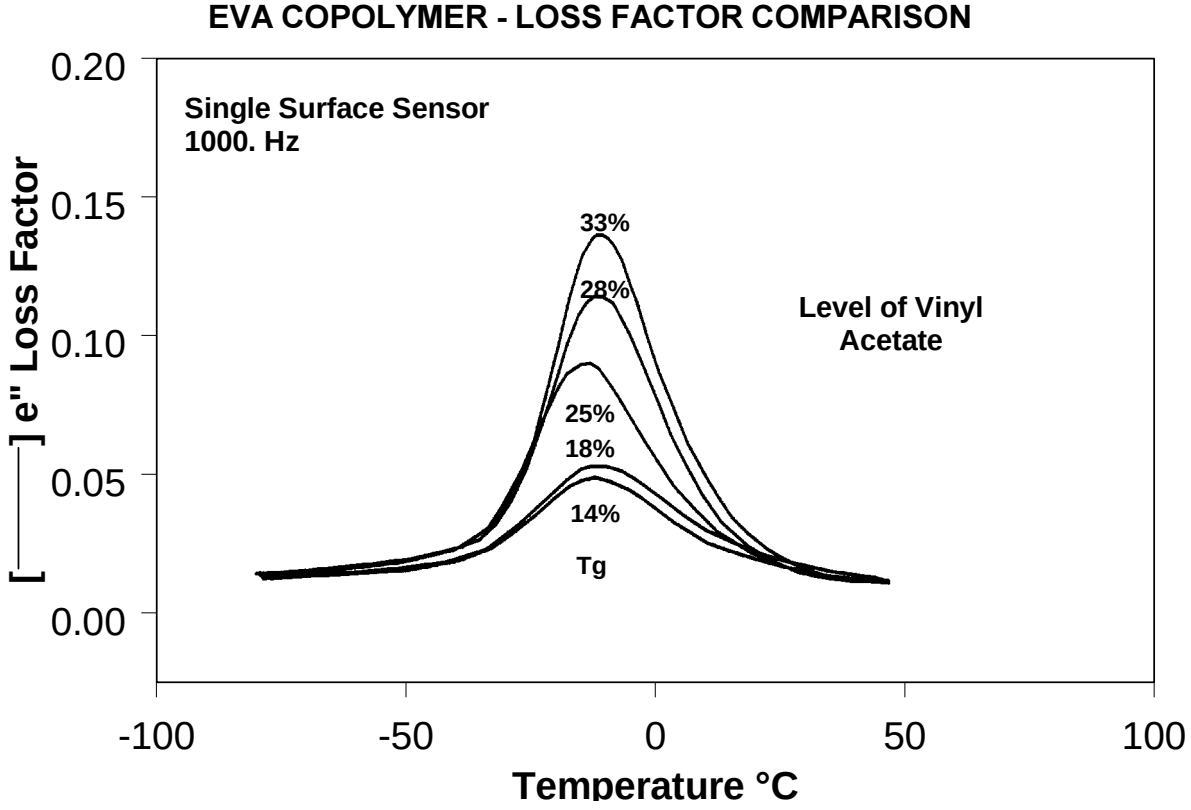

Figure 6

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