TRITON
TECHNOLOGY

What is Dielectric Thermal Analysis, DETA?

Introduction

Dielectric measurements are the electrical analogue of dynamic mechanical measurements. The mechanical stress is replaced by an alternating voltage across the sample (a.c.field) and the alternating strain becomes the stored charge (Q) in the sample. The sample in effect behaves as a simple capacitor. Q is always measured as its derivative dQ/dt = a.c.current.

The dielectric data is obtained from phase and amplitude measurements of current and voltage to resolve the components ε^* = Capacitance with sample/Capacitance with an identical air gap.

Theory

A material such as a polymer can exhibit a capacitive behaviour (its ability to store an electrical charge) and a conductive behaviour (its ability to pass an electrical charge). Under a given set of conditions, the material under test can be represented by a resistor (conductor) and a capacitor in parallel, as shown in Fig.1

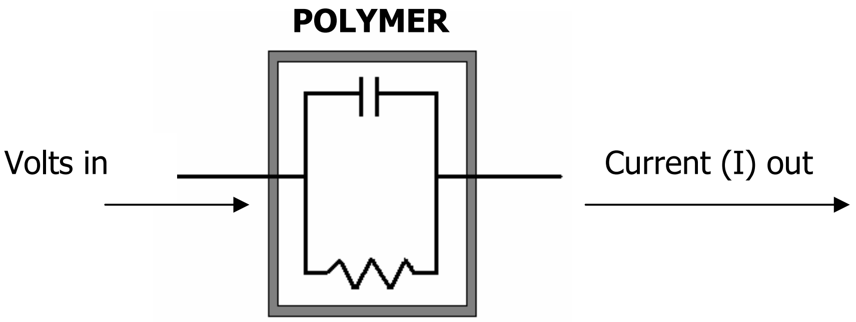


Figure 1

If a sinusoidal voltage is applied to a resistor (conductor), the resulting current that is measured is in phase with the applied voltage. There is no storage of any charge by the resistor.

When the same periodic voltage is applied to a capacitor, there is some storage of the charge and as a result, the measured current appears out of phase with the applied voltage. The phase shift, denoted by delta, δ is 0° for a true conductor and 90° for a true capacitor. (Fig.2) Polymeric materials exhibit both capacitive and conductive properties. The result is a phase shift somewhere between 0° and 90°.

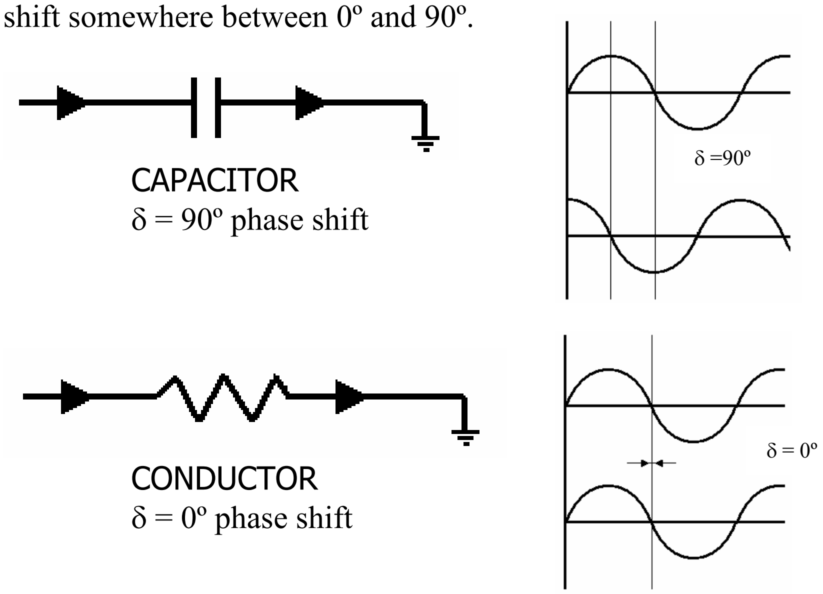


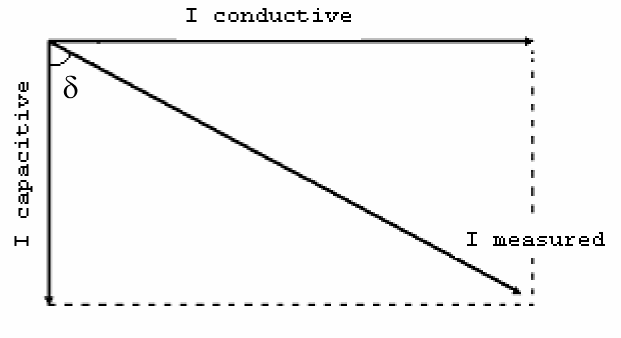
Figure 2

The measured current (^{I}meas) for a polymeric material can be separated into its capacitive component and its conductive component. The Argand diagram (Fig.3) illustrates as follows:-

$$^{I}\text{conductive} = {}^{I}\text{meas x cos(phase)}$$

$$^{I}\text{capacitive} = {}^{I}\text{meas x sin(phase)}$$

The Argand diagram shown in Fig 3 shows that this parallels the complex modulus treatment used on DMA data. The tanδ values are not equal for the same mechanical and electrical process.



$$^{I}\text{conductive} = {}^{I}\text{meas x cos}\delta$$
$$^{I}\text{capacitive} = {}^{I}\text{meas x sin}\delta$$

Figure 3

The materials capacitance and conductance are then calculated using the following equations:-

Capacitance = ^{I}meas x sinδ/V_{in} x $2\pi f$

Conductance = Resistance -1 = ^{I}meas$^{\cos\delta}$ V_{in}

where $2\pi f$ = angular frequency
f = frequency

If the geometry of the sample is known, then it's [possible to express the capacitive and conductive responses of the material as the dimensionless quantities:-

e′ dielectric constant or permitivity

e″ loss factor

Another commonly used term for expressing dielectric response is the dissipation factor or loss tangent:-
tan delta = e″/ e′

For parallel plate electrodes, e′ and e″ can be calculated from the measurements of capacitance and conductance respectively, for a homogenous sample, as follows:-

$e' = Cd/e_0A$

$e'' = d/RAW\ e_0$

where:
C = Capacitance
R = Resistance
A = Electrode plate area
D = Plate spacing
W = Angular Frequency ($2\pi f$)
e_0 = Absolute permittivity of free space (8.85 x 10^{-12} F/M)

Several phenomena cause polymeric materials to have capacitive (e′) and conductive (e″) components.

These are:-

- **Induced dipoles**. The charge separation on non polar bonds due to the presence of an electrical field. They react so quickly to an electric field that they are frequency independent.
- **Static dipoles**. These require molecular motion to orientate to the applied electric field and are therefore frequency dependant.
- **Ionic conduction**. This is caused by the flow of ions, usually impurities, within the electric field. Their mobility is independent of frequency.

Figures 4 and 5 illustrate the effect of applying an electrical field to a polymeric material. When the field is applied, the dipoles attempt to align with the field and ions migrate to the oppositely charged electrode.

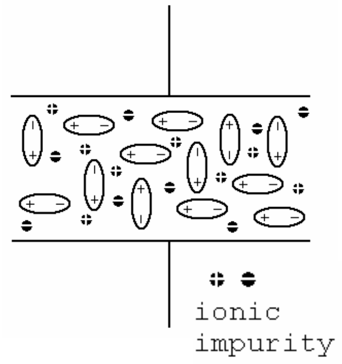


Figure 4

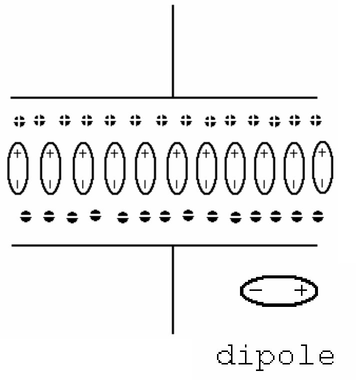


Figure 5

Values for e′ and e″ are calculated by equations which quantify these relationships:

e′ = permittivity due to induced dipoles + permittivity due to alignment of dipoles

e″= dipole loss factor + ionic conductance

e′ represents the amount of alignment of the dipoles to the electrical field. e′ is low for polymers at low temperature, below thermal transitions, because the molecules are frozen in place and the dipoles cannot move to align themselves with the electrical field. Likewise, e′ is low for highly crosslinked thermosetting resins.

e″ measures the amount of enery needed to align the dipoles and move ions. Ionic conduction is not significant until the polymer becomes fluid (e.g. above Tg or Tm). e″ represents the energy required to align dipoles below and through Tg. e″ displays a peak as the polymer passes through Tg. Above Tg, e″ is used to calculate the bulk ionic conductivity;

$$\sigma = e''We_o$$

where σ = Ionic conductivity
W= angular frequency
e_o= absolute permittivity of free space
(8.85×10^{-12}F/M)

Bulk ionic conductivity (sigma) can be used to follow the rheological changes that take place during the processing of thermoplastics and the curing of thermosets. Ionic conductivity is related to viscosity, because fluidity is identified by the ease with which ionic impurities can migrate through the sample.

Experimental Procedure

Samples are typically thin sheets, films or liquids which are held between parallel plate electrodes as shown in Fig 6.

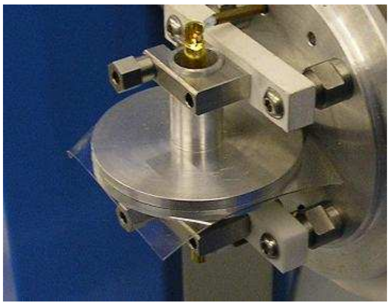


Figure 6

It is important to ensure that perfect contact between the sample and the electrodes is achieved, therefore samples ideally need to be smooth surfaced with no undulations. Generally, thinner samples are better than thicker ones. 2mm or less is ideal in many cases.

If the sample is not smooth, it will be necessary to sputter coat the sample with a coating of a conducting medium. Gold is ideal but can be expensive. Silver or aluminium work just as well but the surface can oxidise quickly and so analysis should be made as quickly as possible after sample preparation.

This coating will eliminate any air gaps between the sample and effective electrode (which is now the sputter coated metal) and will eliminate spurious data.

Alternatively, a coating of a dielectrically inert material can be applied to the sample to eliminate air pockets. Such a material is petroleum jelly.

The electrodes of the Triton DETA are normally spring loaded to maintain a positive contact with the sample through the thermal profile. They can be locked into place if required to avoid squeezing fluid samples out.

Typical Result