



Analysis of plastics

by John Gearing - [Gearing Scientific](#)

Introduction

Polymer analysis takes many forms and two general areas are:

Thermal Analysis, and GPC or SEC.

Thermal analysis (TA)

This is seeing what happens to a small amount of material when it is heated or cooled or iso-thermed at a particular temperature or several.

The most common methods are:

DSC (Differential Scanning Calorimetry) or DTA which gives you the melting points or gelation and sometimes the glass transition T_g , which is when the material softens from being a plastic into a rubber or elastomer. Only a few milligrams are needed in a sample pan which can be open, closed or with a pin-hole in the lid. Pressure DSC allows this to be done at higher than ambient pressures, and modulated DSC is a little more sensitive particularly to mixtures or co-polymers where 2 things may happen at once.

TGA (Thermal Gravimetric Analysis) shows the temperatures at which gases are given off when heated in a controlled environment which is usually nitrogen or air, and when connected to a mass spectrometer (TGA-MS) to identify what the products of degradation are. (TGA-IR is also used). EGA (Evolved Gas Analysis) is usually TGA-MS.

STA (Simultaneous TA) consists of DSC or DTA with TGA at the same time on the same sample in the same pan.

DMA or DMTA (Dynamic Mechanical Thermal Analysis) is one of the most useful techniques for polymers having about 1000 times the sensitivity of DSC, so that the glass transitions of even minor components are easily seen and also any other phase transition or melting. The sample needs to be larger than in DSC and this has been extensively used for co-polymers and blends.

As the sample is vibrated in tension, compression, shear or bending a range of frequencies can be used at constant stress or strain, so that the modulus (stiffness) and damping (tangent delta) in real operating conditions can be measured. e.g., Engine mountings on vehicles in Alaska need to be still rubbery at -30°C at frequencies up to 100Hz (6000rpm).

This might be equivalent to a DSC glass transition of -70°C as the T_g is frequency- and often strain-dependant! Most filled polymers are strain dependant so that the modulus and damping change with increasing stress or strain. For these samples with larger forces,

constant temperature step iso-therms are often used and the frequencies or strains swept. If DMA is done in tension or compression then the expansion/contraction can be measured which is also called TMA, (Thermal Mechanical Analysis) and will depend on the static force and time taken for the experiment - as creep is there too. See Chapter 24 of Handbook of Polymer Testing 1998 M Dekker (Ed R Brown).

TMA is rarely performed now as DMA can do it. It was a very small force on a small sample and could see the Tg and melting points usually as well as expansion.

Di-electric Thermal Analysis (DETA) shows how the di-electric constants and tangent delta (V to i) change and is analogous to DMTA, except that the frequency range can be much higher. However not all polymers can be studied and traces of water or other ionic species can be over-emphasised in the results. It works very well for thin coatings on metals.

Thermal Conductivity needs rather larger samples which are often 10 to 50mm thick by 200mm square or larger. For solid polymers several layers may be stacked up to make 10mm and the results will depend on the porosity of the sample and the foaming gas used or the fillers. Foams are in the range 0.017 to 0.05, whilst solid polymers from 0.12 to 0.80W/m.K typically one thousand times lower than metals.

Curing timers and gel timers are usually simple DMTAs designed to cover a liquid resin or adhesive as bulk or as a thin film at fixed different temperatures. It shows how the resin gels and then solidifies with time.

The Cureometer is a standard in rubber labs for QC and the Strathclyde Rheometer or Trombomat are typical at between a quarter and half the price of a DMTA! Several companies used to manufacture TBAs (Torsion Braid analysers) which were DMAs for curing of resins.

Contract testing on most of the above or advice as to where to purchase your own can be given by contacting gearingsci@yahoo.com

GPC (Gel permeation chromatography) or SEC (size- or steric-exclusion C)

This is a form of HPLC which is very simple in principle but quite difficult to do well! The molecular weight averages and distribution can be measured, and using calibration standards of similar polymers overcomes the problem of very different solvation of the molecules of say LLDPE or PS. Up to 250°C may be needed to dissolve some polymers or to melt them, and some such as PEEK cannot be measured at all.

Contract testing with an expert is recommended unless you can afford your own specialist. Several detectors can help to understand the distributions of co-polymers and the modern mixed bed column makes choice much simpler. Pre-mixed standard packs for calibration of PMMA, PEO, PS and autosamplers speed up the analysis.

Contract testing and one of the widest ranges of polymer standards in Europe is available from Gearing Scientific.

© John Gearing. January 2000