A campaign for real thermal analysis

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Thermal analysis is concerned with what happens to a material when it is subjected to a change in temperature. Used in isolation, it is a very poor form of analysis in the sense of identification of chemical structure but a very good way of quickly characterizing a sample in terms of its performance. Commonly, the property being measured (e.g. heat capacity, weight or stiffness) does not yield much useful information regarding the composition of the sample – it is the change in property with temperature that gives an insight into the behaviour of the sample under the test conditions employed (e.g. identifying the glass transition temperature or evaluating thermal stability). For example, the DSC curve of a polymer will not conclusively identify it as PET but similar measurements on different grades of PET will quickly reveal differences in crystallinity, molecular weight, etc. Often it may be more appropriate to use other techniques, such as X-ray diffraction or size exclusion chromatography to determine absolute values for these parameters. Despite this disadvantage, thermal methods present the benefits of being quick, cheap and simple to perform.

However, it is all too easy to report a point extracted from a plot of weight loss or heat flow against temperature as a unique parameter defining the properties of a material. Even with the greatest attention to experimental detail, a single number (or kinetic equation) does not really reveal how a polymer will behave in the outside world, where poorly characterized materials are often exposed to even less well-controlled environments. What the customer really wants to know is whether the Research Department's new wonder polymer will make a better fuel-transfer line than the current material. The question is not whether the properties of the polymer measured under laboratory conditions make it suitable for making into flexible tubing, it is "can the material cope with the environment that it is expected to come into contact with?".

This situation can be easily addressed by the scientist who is prepared to employ a little ingenuity (and sometimes bravery!) with his equipment – many thermal analysis techniques lend themselves to performing measurements under the sort of conditions that the sample might experience during manufacture, post-processing and end-use. Thermomechanical and dynamic mechanical analysers, in particular, are not greatly affected by the sample atmosphere (unlike DSC cells, which require recalibration when purged with different gases and which may be plagued by thermal changes caused by the condensation or evaporation of volatile components). It is entirely possible to carry out experiments in solvent-saturated atmospheres, or even with the sample completely submerged in a solvent, with little modification to equipment[1].

Several workers have modified dynamic mechanical analysers to operate with the sample clamped in a bath of liquid. Depending on the instrument, various means have been used to achieve this, ranging from continuously overflowing baths of heated liquid[2], extensions to the clamping assembly" or by turning the whole instrument on its side[4].

A good example of the importance of studying the interaction of a polymer with its environment is the effect that moisture can have on different classes of materials. Many hydrophilic polymers, such as cellulose and nylon, are plasticized by water-yet, under certain conditions of humidity and temperature, antiplasticization can occur through suppression of relaxation mechanisms and this can result in the sample being stiffer and more brittle than the untreated material[5]. Even hydrophobic materials, such as acrylic fibres, are plasticized by water – otherwise it would be almost impossible to dye them[6]. This can also lead to problems, for example when a garment is washed at too high a temperature and inadvertently turns the rest of the laundry pastel pink!

Thermal analysis is a poorly publicized area, yet the way the properties of a material change with temperature are vital to its processing and applications. Adding the new dimension of how a polymer interacts with its environment gives an additional insight into the physics and chemistry of polymer science, as well as being of great practical value. An example of this is some work that I recently presented at the 11 th International Congress for Thermal Analysis and Calorimetry (ICTAC) (Philadelphia, USA, 12-16 August 1996) on the use of dielectric measurements to monitor the photodegradation of pressure-sensitive adhesives employed in the construction of 'solar control' window films. Stuck to the inside surfaces of windows, these are used to reduce heat build-up in buildings and automobiles by rejection of TR radiation, and to limit fading of interior upholstery by absorption of UV light. Because these products are to be used in vehicles, any blemishes in the film brought about by degradation of the adhesive are extremely undesirable. By mounting dielectric sensors directly on the adhesive layer whilst it is still on the glass substrate, it was possible to monitor the effectiveness of different stabilizer packages in preventing the deterioration of the polymer during accelerated weathering. Studies like this also have great educational value by illustrating the utility of these techniques to nonspecialists in an easily understood and pertinent way.

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Studies of the interaction of a material with its surroundings raise a more general point – it is more important to attempt an appropriate measurement crudely than to perform an unsuitable measurement with high precision. When faced with a particular problem, it is often tempting to grasp at easily accessible 'straws' rather than try to do the correct experiments that might make the greatest contribution to addressing the issue. The correlation of thermal measurements with impact properties comes under this category[7]. Even well-informed scientists will measure the glass transition temperature of a polymer (or some other relaxation process) using DSC, dynamic mechanical or dielectric methods (depending on what is most convenient) and try to make some predictions about the impact resistance of the material. Whilst, in some cases, there is agreement between measurement and performance[8], would it not have been better to do impact testing in the first place?

The philosophy of carrying out appropriate measurements under relevant environmental conditions is an important, but often overlooked, aspect of thermal analysis. Like all tools, the methods are open to abuse and misuse. Most importantly, the scientist must not lose touch with reality. However, with a little forethought, ingenuity and a critical appraisal of what is required from the work, then perhaps, as Michael Brown said at the recent ICTAC, we can all try to establish 'not what is true, or what is false, but what is useful'.

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