A CAMPAIGN FOR REAL THERMAL ANALYSIS

Duncan M. Price

IPTME, Loughborough University, Loughborough, Leics. LE11 3TU, UK.

d.m.price@lboro.ac.uk

ABSTRACT

There is a great tendency to "dumb down" thermal analysis (particularly from instrument vendors who seem to package thermal analysis like a soap powder). Often a point on the property-temperature plot from a thermal analyzer is selected as a unique parameter defining the properties of a material with little regard as to the influence of experimental variables, sample preparation or technique used. Most materials are not subjected to the same "tests" in the real world and there is little correlation between predicted and observed performance. Users should be encouraged to understand the task and think laterally in order to do the right experiments. Finally, one should critically examine the data in order to translate them into a useful and useable result.

INTRODUCTION

Thermal Analysis is the measurement and interpretation of the relationship between the physical and/or chemical properties of a sample and its temperature. Several methods are commonly used - these are distinguished from one another by the property which is measured eg. heat capacity, mass, length, stiffness *etc.* Sometimes different properties may be measured at the same time or concurrently (e.g. heat capacity & mass or mass & exchanged gases). It is usual to control the temperature in a predetermined way - either by a continuous increase or decrease in temperature at a constant rate (linear heating/cooling) or by carrying out a series of determinations at different temperatures (stepwise isothermal measurements). More advanced temperature profiles have been developed which use an oscillating (usually sine or square wave) heating rate (Modulated Temperature Thermal Analysis) or modify the heating rate in response to changes in the system's properties (Sample Controlled Thermal Analysis).

Used in isolation, thermal analysis 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, stiffness *etc.*) 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 sample's behavior under the test conditions employed (*e.g.* glass transition temperature, thermal stability *etc.*). For example, the DSC curve of a polymer will not conclusively identify it as polypropylene, but similar measurements on different grades of polypropylene 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.

THERMAL ANALYSIS IN THE "REAL WORLD"

Thermal analysts spend a great deal of time measuring melting points, glass transition temperatures, etc. Even with the greatest attention to experimental detail, a single number (or kinetic model) doesn't really reveal how a material will perform in the outside world where poorly characterized materials are often exposed to even less well controlled environments. All that the results of an exhaustive study on the degradation kinetics of some material tell you is how it behaves in your thermobalance under dry nitrogen. What the user really wants to know is whether the Research Department's new wonder polymer would 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 or her 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 analyzers, in particular, are not greatly affected by the sample atmosphere (unlike DSC cells which require re-calibration when purged with different gasses and which may be plagued by thermal effects brought about 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 analyzers 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 *(3)* or by turning the whole instrument on it's side *(4)*.

A good example of the importance of studying a polymer's interaction with the 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, anti-plasticization can occur due to suppression of relaxation mechanisms resulting in the sample being stiffer & more brittle than the untreated material *(5)*. Even hydrophobic materials, such as acrylic fibers 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 a material's properties 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 the use of dielectric measurements to monitor the photodegradation of pressure sensitive adhesives employed in the construction of 'solar control' window films *(7)*. Stuck to the inside surfaces of windows, these are used to reduce heat build-up in buildings and automobiles by rejection of infra-red radiation and to limit fading of interior upholstery by absorption of ultraviolet light. Since 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 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 non-specialists in an easily understood and pertinent way.

DOING THE RIGHT MEASUREMENT

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 right experiments that might make the greatest contribution to addressing the issue. The correlation of thermal measurements with impact properties comes under this category *(8)*. Even well-informed scientists will measure a polymer's glass transition temperature (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 material's impact resistance. Whilst, in some cases, there is agreement between measurement and performance *(9)* wouldn't it have been better to do impact testing in the first place?

Often, the tasks addressed by thermal analysis are "problems in principle" rather than "problems in practice" *(10)*. For example, the author once refereed a paper in which examined the thermal degradation of polyethylene and predicted the lifetime of this material at room temperature. Despite the oversight that the kinetic model had been developed using data obtained above the material's melting point, the reviewer was forced to comment that "degradation of the material via other means *e.g.* exposure to sunlight, chemicals or other mishap, was more likely."

GETTING THE RIGHT ANSWER

Even when doing the right measurements one often faces the question "what is the right answer?" Consider the glass-rubber transition, for example: it is a phenomenon which can be observed in a wide variety of systems. Polymers are probably the most familiar class of glass forming materials (apart from "glass" itself), but it is also true that metals, pharmaceuticals, etc. can be prepared in the glassy state. It could be argued that since not all materials can be formed into perfect crystals but all materials can be made into a glass, then the glassy state is a universal state of matter. In order to determine the glass transition temperature

(T_g) of a system, one usually has to change its temperature. How does the result depend upon the measurement?

It turns out the T_g is a "moveable feast" - *i.e.* the conditions under which a glass is formed (*e.g.* cooling rate) and is subsequent thermal history all affect the properties of the sample and the outcome of any measurement. The timeframe over which measurements are made also affect the result. Therefore, in reporting the glass transition temperature of a specimen one should specify how the sample was prepared and measured. Even then, one faces a difficulty - it is all too easy to report an arbitrary point extracted from a plot of some property against temperature as a unique parameter defining the behavior of a material. For as many different properties that can be used to measure T_g as there probably just as many ways of "defining" T_g based upon the way the property changes with temperature. With DMA data for example: does one use the peak in damping factor or loss modulus? Or does one use the extrapolated onset in decay in storage modulus on a linear or logarithmic scale? The most popular approach seems to be to use "Sinatra's Method" *(11)*.

CONCLUSIONS

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 mis-use. 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, perhaps, as Prof. Michael Brown put it, we can all try to establish "not what is true, or what is false, but what is useful" *(12)*.

REFERENCES

1.	D. M. Price, *Thermochim. Acta* **1997** 294 127.
2.	T. Murayama and A. A. Armstrong, Jr*., Journal of Polymer Science: Polymer Physics Edition* **1974** 12 1211.
3.	A. B. Desai and G. L. Wilkes, *Textile Res. J.* **1975** 45 173-178.
4.	S. H. Dillman and J. C. Seferis, *Polymer Eng. Sci.* **1991** 31 253.
5.	R. W. Seymour et al., *J. Macromol. Sci. Phys.* **1979** B16 337.
6.	D. Aitken et. al., *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1991** 47 263.
7.	D. M. Price, *J. Thermal Anal.* **1997** 49 953.
8.	L. E. Nielsen, *"Mechanical Properties of Polymers & Composites"*, Vol. 2, Marcel Dekker Inc., New York **1974.**
9.	R. M. Evans et. al., *Soc. Plast. Eng. J.* **1960** 16 76.
10.	M. Reading, *personal communication*.
11.	F. A. Sinatra, *"My Way"*, Reprise Records **1969.**
12.	M. Brown, 11th International Conference for Thermal Analysis & Calorimetry, Philadelphia, USA, **1996**.