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Application of Thermal Analysis Techniques (TGA, DSC, TMA and Evolved Gases FTIR) in Understanding New Materials

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Abstract

Thermal analysis of both traditional and new advanced building materials can provide valuable information on their behaviour under different environmental conditions. This type of analysis involves techniques that look at changes in the physical, chemical and mechanical properties of a material as a function of temperature. The Advanced Materials Characterisation Facility (AMCF), located at Western Sydney University's Parramatta campus, is home to a suite of thermal analysis instrumentation that are able to carry out various thermal analysis techniques on small scale samples. These techniques include Thermo-Gravitation Analysis (TGA), Differential Scanning Calorimetry (DSC), Infra-Red (FTIR) analysis of evolved gasses from TGA/DSC and Thermo-Mechanical Analysis (TMA). Properties that can be analysed include mass changes, material phase transitions (e.g. crystalline, amorphous, melting, etc), heat capacity, expansion, tension, young's modulus, sintering, softening points, evolved gases and much more.This paper will provide an overview of each of the thermal analysis instruments housed at the AMCF. Examples of thermal analysis previously undertaken on various materials will also be given in order to show the potential of thermal analysis techniques on future construction materials.

Keywords: Thermal analysis, Thermal properties, Material properties, Instrumentation, New materials

1. INTRODUCTION

With a growing awareness of environmental issues and energy management, there is an increasing need for new advanced building materials with improved properties and more efficient manufacturing processes in the construction industry. In order to better understand and assess these innovative materials, it is important to analyse the structure, durability and damage that may occur.

Thermal analysis of materials can provide valuable information on the behaviour of materials under different environmental conditions, with techniques that look at changes in the physical, chemical and mechanical properties of a material as a function of temperature. A lot of new materials being researched rely heavily on thermal processes and chemical reactions taking place.

Example 1, Phase Changing Materials (PCMs) which are able to store and release thermal energy when necessary as the material changes phase (i.e. melting and solidifying), need to work in a particular temperature range. It is also possible to mix PCMs with flame retardants, and then impregnate them into structural materials (e.g. concrete floors, blocks and plasterboard). It is imperative to know thermal properties such as melting and solidification temperatures, ignition points, absorption/dissipation of thermal energy and how these properties are affected when mixed with other materials (Pielichowska and Pielichowska, 2014).

Example 2, Self-healing polymeric composites are being designed to replace traditionally heavy metal alloys. These new materials possess an intrinsic matrix of capsules or a vascular network which can

release a polymer healing agent when damage occurs. In order to be used as structural materials, an understanding of their thermal strength and stability are needed at different temperature conditions, as well as analysis of glass transition temperatures, polymer curing temperatures and their reliability (Hia et al 2016, Guadago et al 2014).

Example 3, Adhesives containing thermally expandable particles, allow for strong adhesion in building materials, but can be easily separated under heat for recycling of parts. For any product using adhesives it is important to look at the product's final structural qualities, particularly the flexibility of the adhesive in both cold and hot temperature environments. Thermal expansion, Young's modulus and glass transition temperatures are important to understand (Banea et al 2014).

Example 4, Geopolymer concretes make use of a mixture of "geopolymer", polymerised chains of inorganic molecules (eg. silica and alumina) that create a hardened binder, industry by-products containing silicate materials such as fly ash, and various aggregates (Noushini and Castel, 2016). This concrete is more resistant to fire, harsh environments and, most importantly, more "green" in terms of production CO_2 emissions. The composition and microstructure has an influence on the thermal properties of the final product. It is important to analyse thermal properties such as curing temperatures, coefficients of thermal expansion (CTE), creep, and phase stability of the final products (Vickers 2015, Kovarik et al 2017, Dey 2014)

Example 5, there is also a need to understand potential hazards associated with new building materials. Recent events such as the Grenfell Tower fire in London (2017) saw the rapid spread of fire due to the use of highly flammable exterior cladding which also reportedly resulted in the production of cyanide gas (Razzall and Moralioglu, 2017). Thermal analysis coupled with evolved gas analysis can be used to identify the gasses produced from heating of modern building materials and at what temperature these gasses occur. This information may also be beneficial in assessing how these materials influence fire dynamics.

2. TECHNIQUES AND EXAMPLES

Thermal analysis includes a number of techniques which monitor and analyse material physical and chemical changes under different temperature conditions. For all types of analysis, samples can be heated or cooled at a consistent rate, multiple times if needed to test durability (dynamic temperature), or held at a particular temperature of interest for testing (isothermal temperature). The temperature can also be programmed to include both dynamic and isothermal sequences.

Samples can be tested at different heating rates, in different atmospheres (e.g. air, nitrogen, argon). A selection of crucibles is available (Figure 1b), and will depend on the temperature range that is to be used, and compatibility with the sample itself. Care also needs to be taken when considering sample size and the reaction of the sample to heat (Figure 1c).

Table 1. A comparison of properties each thermal analysis technique can measure.

TGA	DSC	TMA
Mass change Decomposition Moisture content Thermal stability Sample composition	Melting/solidification Crystallisation Glass transition Heat of fusion Purity analysis Specific heat Phase transition Curing temperature Sample composition	Expansion/shrinkage Compression/tensile strength Young's Modulus Load deformation Penetration Softening point Sintering temperature Hardness/softness Creep under load Coefficient of thermal expansion
FTIR		
Evolved gas analysis Sample identification		

Simultaneous Thermal Analysis (STA) is the simultaneous running of two or more thermo-analytical techniques (e.g. TGA, DSC and FTIR) on one sample at the same time. The advantage here is that the results from STA, which is a TGA plot and DSC plot, can be directly compared on the same graph with the knowledge that the sample and test conditions are identical. The following sections are an explanation of the most common thermal analysis techniques. A comparison of properties each thermal analysis technique can measure is shown in Table 1.

2.1. Thermo-Gravimetric Analysis (TGA)

TGA measures a sample's change in mass during heating in a furnace. As a sample undergoes a thermal event (e.g. moisture loss, decomposition, etc.) a mass change will occur and is detected by a microbalance located at the base of the instrument (Figure 1a).

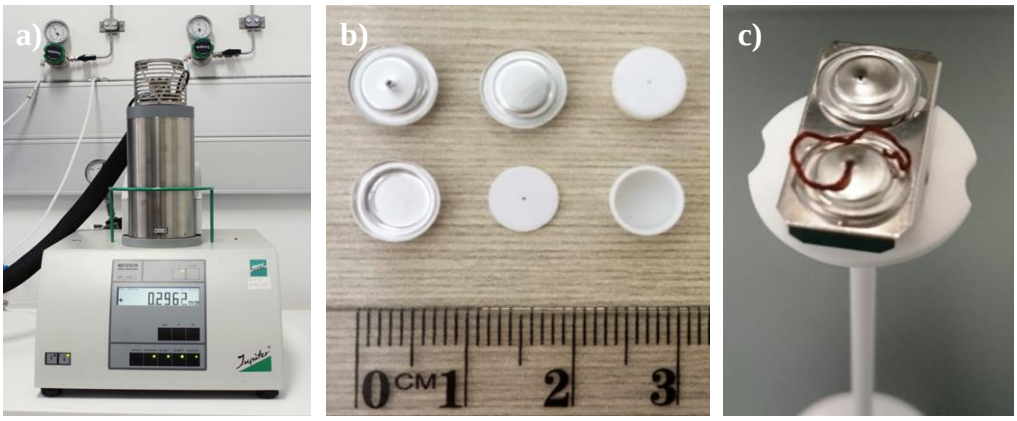

Figure 1. a) TGA setup, b) a selection of crucibles for TGA/DSC analysis (aluminium and alumina), and c) a STA sensor which measures TGA and DSC, with reference crucible (back) and sample crucible (front). Note it is important that sample size is small enough that if it expands, it does not extrude out the top of the crucible as shown above.

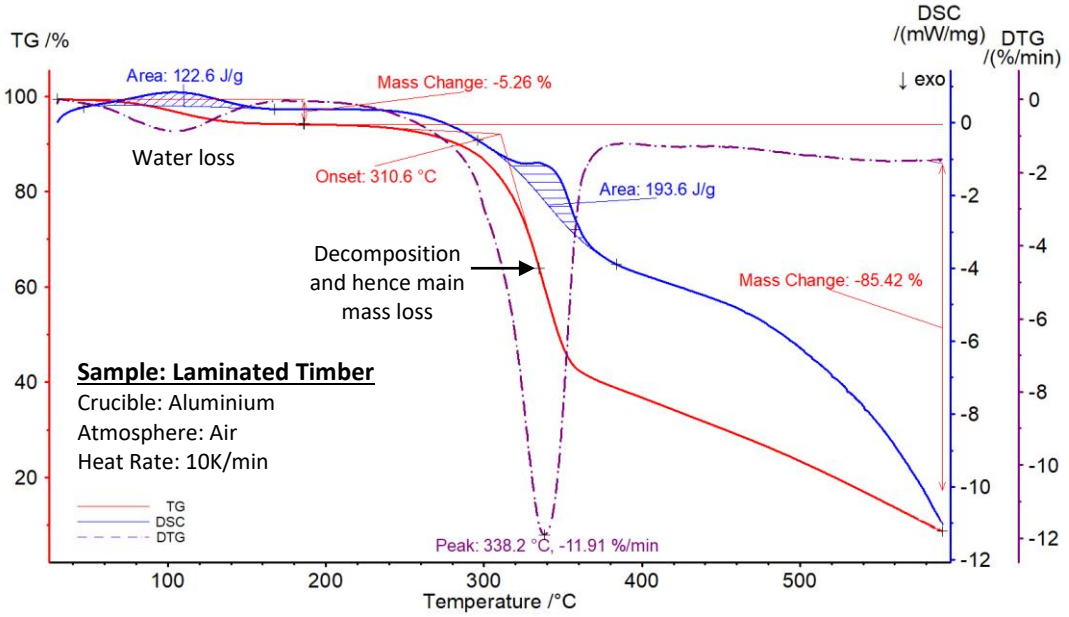

Figure 2. Simultaneous TGA and DSC analysis of a laminated timber sample. The TG curve (red line) shows the loss of mass as the sample was heated. This is compared with the first derivative of the TG curve (dotted line, DTG) which shows the rate of mass loss, and the DSC curve (blue line) which shows the mass loss is associated with an endothermic reaction. The associated heat absorbed can be calculated.

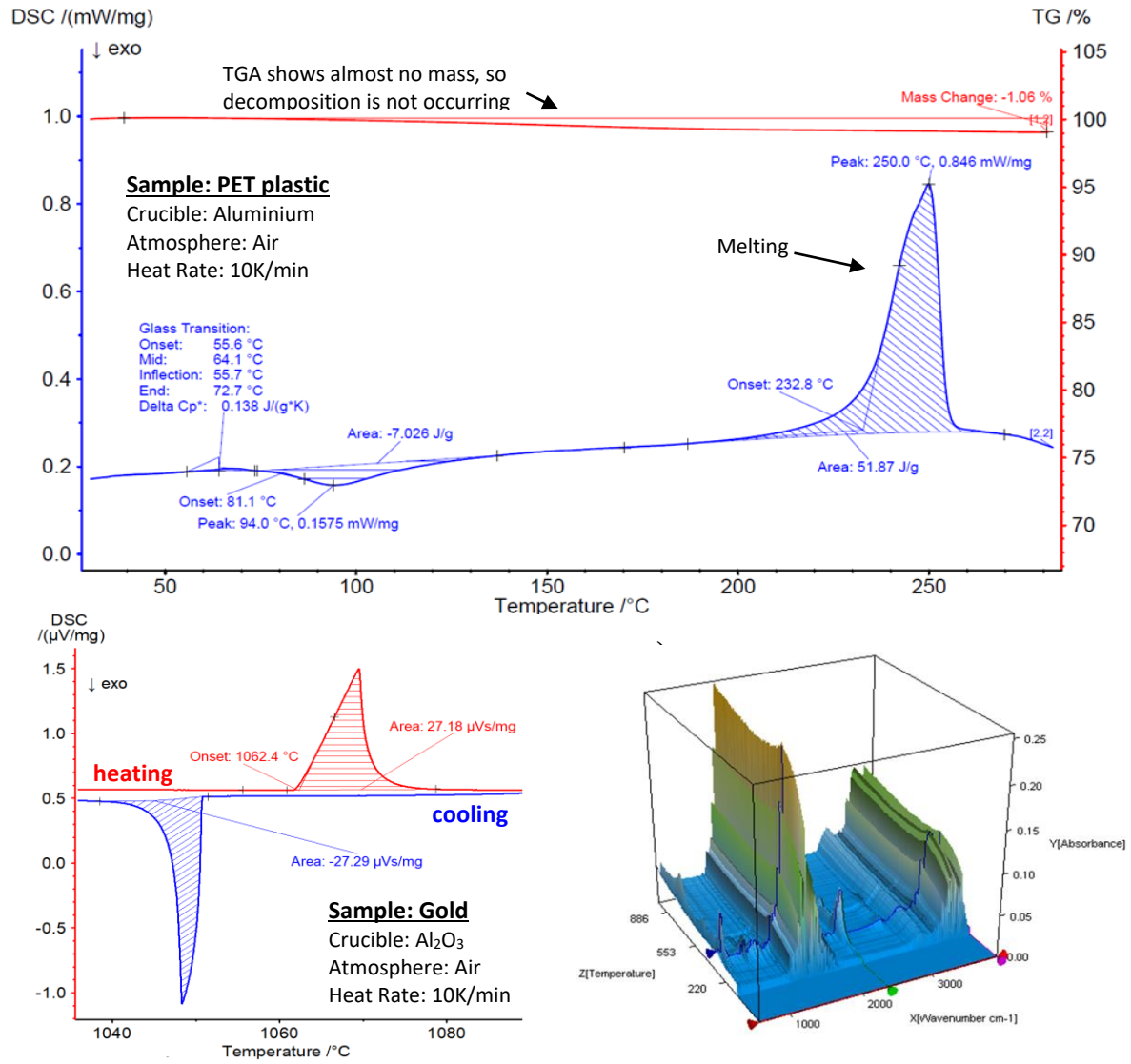

Figure 3. a) STA analysis (TGA and DSC) of a PET plastic sample showing the phase transition, recrystallisation and melting temperatures, b) DSC of a standard gold sample (the heat absorbed/released due to melting/solidification is almost identical, showing the sample is of very high purity), c) an evolved gas FTIR spectrum taken during TGA analysis of an algal material (different gases are coming of at 300ºC).

2.2. Differential Scanning Calorimetry (DSC)

DSC measures the heat into or out of a sample relative to a reference (usually an empty crucible identical to the one holding the sample). A linear heating rate is usually used (e.g. 10°C/min) so the particular temperature at which a thermal event occurs can be found (e.g. melting points, glass transitions, etc.). There are two main types of thermal events; endothermic (where heat is absorbed by the sample, such as melting) and exothermic (where heat is released by the sample, such as crystallisation).

During analysis the sample and reference are maintained at the same temperature, even when the sample undergoes a thermal event. The energy required to maintain a zero temperature difference between the sample and the reference is measured. It is important to note on any graphical results from DSC, which direction represents exothermic or endothermic heat (e.g. in Figures 2 and 3 exothermic heat is down the y-axis).

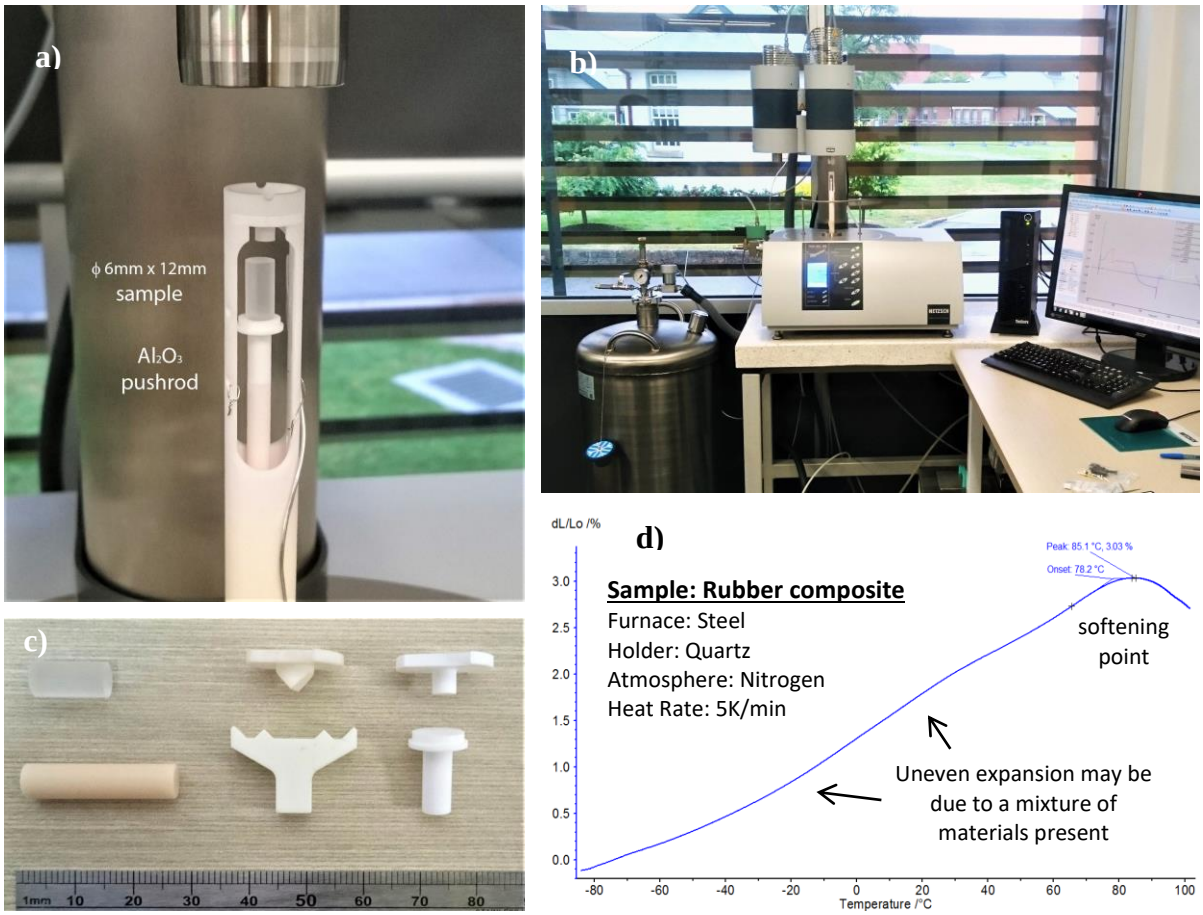

Figure 4. a) TMA setup for high temperature expansion experiments, b) TMA with two furnaces and pressurised liquid nitrogen dewar for negative temperature experiments, c) standard samples (left), and the attachments for high temperature 3-point bending (middle) and expansion (right), and d) results of an expansion experiment (-85 to 100ºC) for a rubber sample showing the material's softening point.

2.3. Fourier Transform Infra-Red (FTIR) Analysis of Evolved Gasses

As a material decomposes under high temperatures, volatile gases may be released. As a TGA or DSC analysis is undertaken, the gases that evolve during the experiment can be collected and sent through a FTIR gas cell for analysis using a special transfer tube. This transfer tube is kept short and at a relatively high temperature (e.g. 200ºC), so gases do not condense on the way to the FTIR detector. The FTIR spectrum can be used to identify gases evolved during the thermal analysis, and at what temperatures they evolved. Figure 3c shows an example of a 3-dimensional representation of the evolved gas FTIR collected from an algae based material.

2.4. Thermo-Mechanical Analysis (TMA)

This versatile instrument determines material dimensional changes under different temperature regimes and different mechanical forces (both static and dynamic). The instrument shown in Figures 4a and 4b, has a choice of two furnaces (Silicon-Carbide and Steel) which can be easily interchanged, two thermocouples types (K and S-type) and two sample holder materials (alumina and quartz). These choices allow for a wide range of materials to be tested under temperatures ranging from -160°C to 1600°C.

The sample holders and push rods also come in different configurations (Figure 4a and 4c), allowing for different testing modes, such as expansion, penetration, compression, tensile and 3-point bending. The vertical design of the TMA's furnace with motorized hoist allows maximum flexibility regarding sample geometries (rods, squares, plates, films, fibres, powders, liquids).

3. CONCLUSIONS

As many new building materials and composites make use the material's inherent thermal properties, thermal analysis techniques such as TGA, DSC, TMA and evolved gas FTIR are essential in order to fully understand their stability and durability when put into use. Simultaneous thermal analysis is preferable, as the sample and conditions are identical. The results from each detector are also complimentary, helping to fully explain any thermal events that occur during analysis, and hence the sample's chemical and physical properties. Care must be taken however, to consider experimental conditions and how they affect results and relate to real-world applications.

4. ACKNOWLEDGMENTS

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