Journal of Thermal Analysis and Calorimetry, Vol. 90 (2007) 3, 653–662

SELECTED THERMOANALYTICAL METHODS AND THEIR APPLICATIONS FROM MEDICINE TO CONSTRUCTION
Part I.

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There are many thermoanalytical techniques but only several of them such as thermogravimetric analysis (TG), high resolution thermogravimetric analysis (Hi-Res^{TM} TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA), calorimetry, differential scanning calorimetry (DSC), modulated differential scanning calorimetry (MDSC), evolved gas analysis (EGA), transient thermal analysis (TTA) and thermal conductivity (*k*) have selected to be discussed in this paper. Simultaneous thermal analysis (STA) is ideal for investigating issues such as the glass transition of modified glasses, binder burnout, dehydration of ceramic materials or decomposition behaviour of inorganic building materials, also with gas analysis. Selected applications of various thermoanalytical techniques from medicine to construction have also been discussed in this paper.

Keywords: *applications of TA, DSC, DTG, EGA, TG, thermal conductivity, TTA*

Introduction

Thermal Analysis (TA) is a well-established set of techniques for obtaining qualitative and quantitative information about the effects of various heat treatments on materials of all kinds, including new chemical compounds, plastics, ceramics, alloys, construction materials, minerals, foods and medicines. Heating is performed under strictly controlled conditions and can reveal changes in structure and other important properties of the material being studied. Such studies are of great practical importance in the use of materials [1]. TA determines transformations in a subject under study by noting the temperatures at which thermal arrests occur. These arrests are manifested by changes in slope of the plotted of mechanically traced heating and cooling curves. When such data are secured under nearly equilibrium conditions of heating and cooling, the method is commonly used for determining certain critical temperatures required for the construction of equilibrium diagrams.

The structures of the various materials as well as the study of the influence of their compositions on the process of thermal decomposition are of great interests. Therefore, it is not surprising that many authors have investigated numerous materials with different origins and compositions and also studied their thermal, structural, spectral, microscopic and many other properties [3–64].

Selected thermo-analytical techniques

Thermal conductivity (k) and thermal diffusivity (α)

Thermal conductivity is the property of matter by which heat energy is transmitted through particles in contact (SI units: W m^{-1} K^{-1}) [2]. Thermal diffusivity (α) is the ratio of thermal conductivity to volumetric heat capacity. The SI unit for thermal diffusivity is m^2 s^{-1}. Both *k* and α are the most important thermophysical parameters for characterizing the thermal transport properties of a material or component [2].

Laser flash technique (LFA) over the broadest temperature range

The LFA is currently the most widely accepted method for precise measurement of the thermal diffusivity and the LFA 427 (NETZSCH) is one of the most useful instruments on the world market at present. High precision and reproducibility, short measurement times, variable sample holders and defined atmospheres are outstanding features of LFA measurements over the entire application temperature range from –70 to

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1388–6150/$20.00

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2000°C. The laser power, pulse width, gas and vacuum are variable over a wide range, making it possible to set the optimum measurement conditions for the very different sample properties. The LFA 427 is the most powerful and versatile LFA system for research and development as well as all applications involving characterization of standard and high-performance materials in automobile manufacturing, aeronautics, astronautics and energy technology.

Significance of thermal conductivity measurement

Accurate and reliable thermal conductivity data of fluids are essential to evaluate convective heat transfer coefficient for safe and economical design of heat exchangers involving heat transfer across a fluid-solid interface. In such heat transfer processes, convective heat transfer coefficient is a very important parameter and can be evaluated from the following dimensionless equation [65a]:

$$\overline{Nu}=C\mathrm{Re}^{\mathrm{m}}\,\mathrm{Pr}^{\mathrm{n}} \qquad (1)$$

where C, m and n are empirical parameters. For heat transfer in a tubular geometry, these parameters, C and the exponent m and n, are either constant or expressed by empirical relations [65b]. In Eq. (1), the dimensionless quantities Nusselt number (Nu), Reynolds number (Re) and Prandtl number (Pr) are defined by:

$$\overline{Nu}=\frac{\overline{h}_{\mathrm{c}}D}{k};\ \mathrm{Re}=\frac{\rho VD}{\mu};\ \mathrm{Pr}=\frac{c_{\mathrm{p}}\mu}{k} \qquad (2)$$

where $\overline{Nu}$, Re and Pr are expressed in terms of the fluid properties and fluid flow and the geometrical characteristics of the physical system. Accurate thermal conductivity measurements can also be utilized for other applications such as detection of impurities and quality control in mixtures as well as to develop and verify theoretical models for thermophysical properties of dense fluids. However, in the absence of any accurate theoretical model for dense fluids, experimental measurement is the only reliable method for determination of the thermal conductivity of fluids. In addition, one of the experimental techniques provides simultaneous measurement of the thermal diffusivity and determination of the specific heat of fluids.

Transient thermal analysis (TTA)

TTA takes one-tenth the time using a simplified h-model rather than running a full CFD (computational-fluid-dynamics) analysis which significantly reduces computation effort with no loss in accuracy. TTA determines the heat-transfer coefficient (h). The main applications of TTA are in architecture, automotive, defence and in electronics.

Determination of heat-transfer coefficient (h)

Convection heat transfer occurs between a fluid in motion, in this case air, and a boundary surface, when the two are at different temperature. For natural or free convection, two values are typically used to calculate the h: the Rayleigh number (Ra) and the Nusselt number (Nu). The Ra is used to choose the flow regime – either turbulent or laminar. The flow is laminar if $\mathrm{Ra}<1\cdot10^{9}$. Ra is a function of the temperature difference between the fluid and the solid-model surface. The Nu is a function of the Ra. The h can be calculated from the Nu as follows: $h=Nu*k/L$, where k is the thermal conductivity of air, and L is the length of the plate.

The experimental techniques for accurate measurement of thermal conductivity of fluids fall into the following two broad categories, steady-state method and transient technique which are described below.

Steady-State Method: This method employs a thin layer of fluid between two smooth isothermal surfaces maintained at two different temperatures. Guarded hot-plate apparatus, concentric cylinder apparatus and concentric shell apparatus fall in this category. Guard heaters are used in the first two methods to maintain the desired direction of heat flow. The heat flux and temperature difference across the fluid layer is accurately measured and the thermal conductivity (k) of the fluid is calculated from the Fourier's heat conduction relation [65c]:

$$q=-kA\frac{\mathrm{d}T}{\mathrm{d}x} \qquad (3)$$

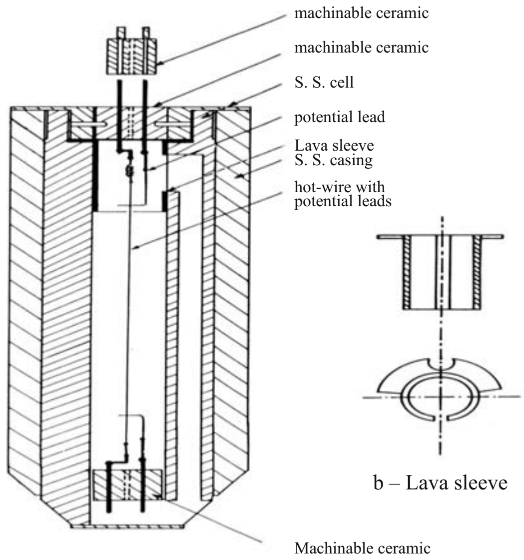
where q is the heat transferred by conduction through area A and $\mathrm{d}T/\mathrm{d}x$ is the temperature gradient in the direction (x) of heat transfer and normal to the surface area A. Steady-state methods are inherently time consuming and slow as thermal systems take long time to reach steady-state conditions. The influence of parasitic heat losses and the radiation effects, if present, can significantly influence the measurements [66].

Transient Method: The most widely used transient technique utilizes a very fine wire stretched vertically and surrounded by the test fluid. A constant current through the wire results heat dissipation from the wire into the surrounding fluid. As a result of this process, the fine wire undergoes a transient temperature rise which depends on the thermal conductivity of the surrounding fluid. The thermal conductivity of the fluid is, therefore, obtained from the transient temperature response (ΔT_{w}~time) of the wire. This technique was first proposed by Stalhane and

Pyk [67]. A complete solution by van der Held [68, 69] led to a mathematical formulation of an ideal model of the transient line-source technique and an absolute measurement of the thermal conductivity (k) of the fluid from the following equation:

$$\Delta T_{\mathrm{w}} = \frac{q_\ell}{4\pi k}\ln\left(\frac{t_2}{t_1}\right) \tag{4}$$

where ΔT_{w} is the temperature rise of the wire during the time period t_1 to t_2 and q_ℓ the heat dissipation rate per unit length of the wire. There are two variations of this apparatus – potential-lead type [70–72] and compensated-wire type [73–75] which have been used to closely model the ideal line-source. Figures 1 and 2 shows the schematic diagram of these hot-wire cells [72, 74].



a – Hot-wire cell

b – Lava sleeve

Fig. 1 Schematic diagram of the hot-wire cell – Potential lead type

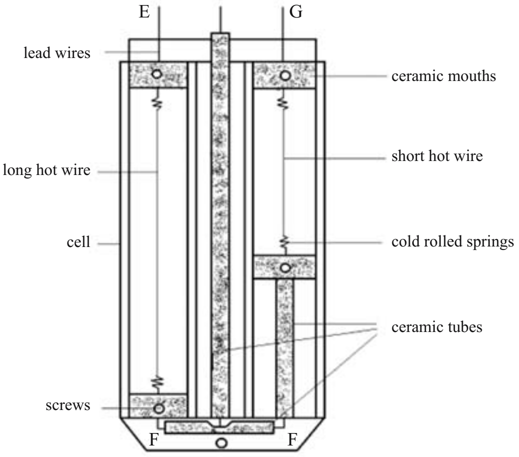


Fig. 2 Schematic diagram of the hot-wire cell – Compensating wire type

The ideal line source model employs a fine wire of infinitely small radius $a\rightarrow 0$ and infinite length $\ell\rightarrow\infty$. In the actual model, however, the wire has a finite diameter and a finite length which is attached to thick wires at the ends in a hot-wire cell. The use of potential leads as well as the compensating wire allows the ideal line source to be realized in a hot-wire cell. At small radial distance $r=a$, the temperature rise at time t is approximated by [76].

$$\Delta T_{\mathrm{w}}\ (a,t) = \frac{q_\ell}{4\pi k}\left(\ln\frac{4\alpha t}{a^2 C}\right) + \frac{a^2}{4\alpha t} + \ldots \tag{5}$$

If the wire radius is very small, the above solution (Eq. (5)) can be further simplified to [75]:

$$\Delta T_{\mathrm{w}}\ (a,t) = \frac{q_\ell}{4\pi k}\left(\ln\frac{4\alpha t}{a^2 C}\right) = G\ln(t) + A \tag{6a}$$

where

$$G = \frac{q_\ell}{4\pi k} \text{ and } A = \frac{q_\ell}{4\pi k}\ln\frac{4\alpha}{a^2 C} \tag{6b}$$

Equation (6a) shows a straight line relationship of ΔT_{w} (a, t)~ln(t) with slope G and intercept A. The slope G and the intercept A both can be determined experimentally from accurate and precise measurement of the transient temperature response of the wire. The transient hot-wire technique, therefore, provides an experimental method of simultaneous measurement of the thermal conductivity and the thermal diffusivity of fluids from the following equations obtained from Eq. (6b):

$$k = \frac{q_\ell}{4\pi G} \text{ and } \alpha = \frac{a^2 C}{4t_0}\mathrm{e}^{A/G} \tag{7}$$

In addition, the specific heat of fluids can also be determined from the following equation:

$$\alpha = \frac{k}{\rho c_{\mathrm{p}}} \tag{8}$$

if the density (ρ) of the fluid is known either directly or from its Equation of State.

The hot-wire instrument, measurement technique and data processing have to be ensured to account for various deviations of the actual line-source model from the ideal model. Convection and radiation heat transfer, if present, can result in significant error. Proper experimental procedure [74–79] has to be followed in order to avoid convection effects and correct for radiation effects.

The transient line source technique provides an absolute, rapid, accurate and reliable measurement of the thermal conductivity of fluids. It also provides a simultaneous measurement of the thermal diffusivity of fluids and specific heat determination. This technique permits convection-free measurements. In addition, the influence of radiation effect, if present, is less pronounced in comparison to the steady-state methods as the surface area of the hot wire is very small compared to the isothermal surfaces in the steady-state techniques.

TG, DTG and DSC measurements

Thermogravimetric analysis (TG) and derivative thermogravimetry (DTG) on powder samples (~20 mg) were carried out using a TG Q500 T.A.I. instrument at 10°C min^{-1} from room temperature (*rT*) to 700°C under nitrogen atmosphere using a flowing rate 60 mL min^{-1}.

Differential scanning calorimetry (DSC) experiments were conducted in sealed aluminum pans on powder samples (5–10 mg) using a simultaneous DSC Q1000 T.A.I. instrument at 5°C min^{-1} from room temperature (*rT*) to 250°C under nitrogen atmosphere using a flowing rate 60 mL min^{-1}.

Thermogravimetric analysis (TG)

In thermogravimetry, the sample mass is monitored as it is subjected to a temperature programme. The atmosphere is controlled, and includes either oxidising (oxygen/air) or inert conditions (argon, nitrogen, helium, etc.). To measure mass loss or gain, TG uses heat to force reactions and physical changes in materials. It provides quantitative measurement of mass change in materials associated with transition and thermal degradation. It records change in mass from dehydration, decomposition, and oxidation of a sample with time and temperature. Characteristic thermogravimetric curves are given for specific materials and chemical compounds due to unique sequence from physicochemical reactions occuring over specific temperature ranges and heating rates. These unique characteristics are related to the molecular structure of the sample. A schematic diagram of a thermogravimetric analyzer can be found in [80]. The TG curve of wheat straw is given in Fig. 3 as an example. The TG curve exhibits two mass loss steps between *rT*-250°C and 250–600°C. The first step between *rT* and 250°C is accompanied by 5.17% mass loss (measured from the TG curve by TA instrument software). The second step (main decomposition step) took place between 250 and 600°C and is accompanied by 80.84% mass loss. It is attributed to the decomposition of wheat straw. The decomposition temperature may also vary on experimental conditions.

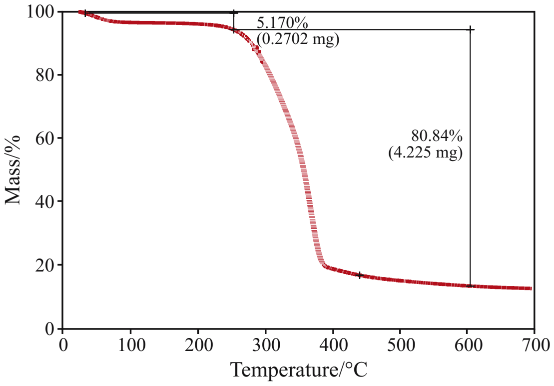


Fig. 3 The TG curve of wheat straw

High Resolution TG (Hi-Res$^{\text{TM}}$ TG)

Hi-Res$^{\text{TM}}$ TG is a novel TG mode, introduced by TA Instruments. It increases the resolution while often decreasing the time required for experiments. Hi-Res$^{\text{TM}}$ TG has two novel non-isothermal modes of operation

- Variable heating rate mode: the heating rate is dynamically and continuously varied to maximize resolution.
- Constant reacting rate mode: an attempt is made to keep the reaction at a specific constant value by changing the heating rate.

Hi-Res$^{\text{TM}}$ TG allows the determination of kinetic parameters such as E_a, reaction order of each step in multiple component materials using 4 different TG approaches: constant heating rate, constant reacting rate, dynamic heating rate, and stepwise isothermal.

Evolved gas analysis (EGA)

EGA is a technique in which the nature and/or amount of volatile product(s) released by a substance subjected to a controlled temperature program is (are) determined. The method of analysis should always be clearly stated. To obtain more information, the evolved gases can be analysed using a FTIR, MS and/or GC/MS coupled to the thermal analysis apparatus.

Thermogravimetric analysis – FTIR spectroscopy (TG-FTIR)

When used in combination with FTIR, TG-FTIR is capable of detailed FTIR analysis of evolved gases produced from the TG. An example of the typical EGA result using MS and FTIR coupled to the TA apparatus can be found in [81].

Thermogravimetric analysis – Mass Spectrometry (TG-MS)

To obtain more information, the evolved gases can be analysed using a mass spectrometer coupled to the TA apparatus. The molecular mass of the gases can either be scanned over a particular range, or the analyser set to look for specific fragments such as water (18) and carbon dioxide (44).

Derivative thermogravimetry (DTG)

Derivative thermogravimetry (DTG) is a method of expressing the results of TG by giving the first derivative curve as a function of temperature. The use of DTG curves to characterize calcium silicate hydrate (C–S–H), poly(vinyl alcohol) (PVA), calcium silicate hydrate (C–S–H)-polymer nanocomposite (C–S–HPN) materials with different polymer contents has been discussed in [82]. The DTG curve of wheat straw is presented in Fig. 4. The DTG curve exhibits an intensive peak at 369.56°C corresponding to the decomposition of wheat straw.

Calorimetry

One method of determining the energy exchange between the reaction system and its environment is to conduct a calorimetric analysis. A calorimeter is a thermally insulated container where a reaction system can be performed and the energy exchange between the system and its environment can be measured. The calorimeter and its contents are considered the environment. The reaction system is a chemical or physical process that occurs within the confines of the calorimeter.

$$Q_{\mathrm{surr}}=Q_{\mathrm{cal}}+Q_{\mathrm{contents}}$$

$$Q_{\mathrm{cal}}=\text{Heat Capacity }(T_{\mathrm{final}}-T_{\mathrm{initial}})$$

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC)

DTA measures temperature difference (ΔT) between a sample and reference material. DTA shares much in common with DSC. In this technique it is the heat flow to the sample and reference that remains the same rather than the temperature. When the sample and reference are heated identically phase changes and other thermal processes cause a difference in temperature between the sample and reference. Both DSC and DTA provide similar information; DSC is the more widely used of the two techniques [83–85]. DTA studies of basic $Li_2O{\cdot}SiO_2$ glass, heating rate 10°C min^{-1}, for studying the surface and voluminous crystallization in observed systems of crystallizing glasses are discussed in [86]. The DTA curve of $[Cu(CH_3COO)_2{\cdot}mpc]_2{\cdot}2H_2O$ together with TG curve are presented in Fig. 5. There are two endothermic and an exothermic peaks on DTA curve, corresponding to the respective decomposition steps of $[Cu(CH_3COO)_2{\cdot}mpc]_2{\cdot}2H_2O$.

DSC measures the differential heat flow between a sample and reference material. The degree of purity of pharmaceutical active ingredients derived from melting behaviour, the oxidation of fats and oils, or the curing of adhesives and powder paints are only some of the many topics that can be studied with DSC. DSC monitors the thermal response of a sample to temperature changes, or isothermally. The same temperature program is applied to a sample and a reference pan, and the difference in heat flow to each pan is measured. The transitions appear as endothermic peaks if heat is absorbed or as exothermic peaks if heat is given out. Examples of both types of transition are shown in the Fig. 7. Both the sample and reference are maintained at very nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will need to flow to it than the reference to maintain both at the same temperature. Whether

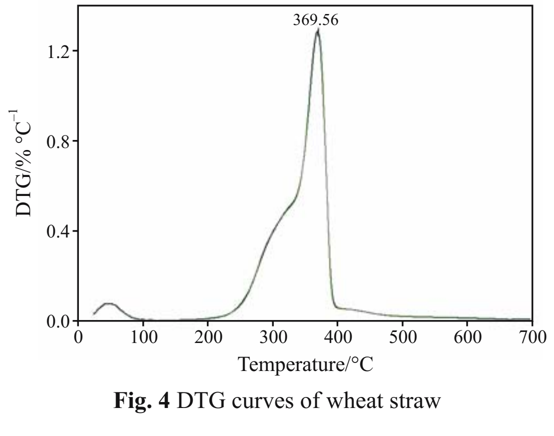


Fig. 4 DTG curves of wheat straw

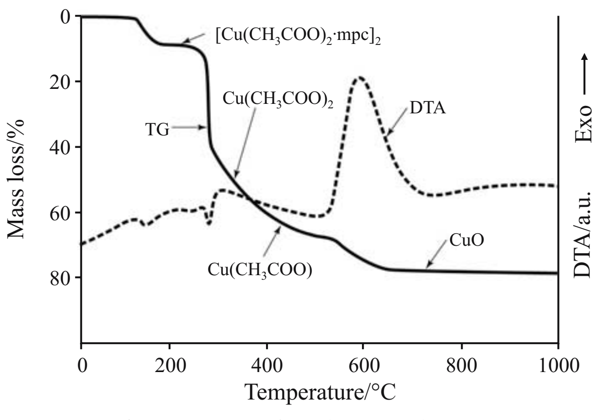


Fig. 5 TG and DTA curves of $[Cu(CH_3COO)_2{\cdot}mpc]_2{\cdot}2H_2O$, reproduced with permission from [87]

more or less heat must flow to the sample depends on whether the process is exothermic or endothermic. For example, as a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of energy absorbed or released during such transitions. DSC may also be used to observe more subtle phase changes, such as glass transitions. DSC is widely used in industrial settings as a quality control instrument due to its applicability in evaluating sample purity and for studying polymer curing [83–85]. There are two main types of differential scanning calorimeters: power compensation DSC and heat flux DSC.

Power Compensated DSC: In power compensated calorimeters, separate heaters are used for the sample and reference [80]. This is the classic DSC design pioneered by the PerkinElmer® company. Both the sample and reference are maintained at the same temperature while monitoring the electrical power used by their heaters. The heating elements are kept very small (weighing about 1 gram) in order to ensure that heating, cooling, and thermal equilibration can occur as quickly as possible. The sample and reference are located above their respective heaters, and the temperatures are monitored using electronic temperature sensors located just beneath the samples. Generally platinum resistance thermometers are used due to the high melting point of platinum.

Heat Flux DSC: In a heat flux DSC, heat is transferred to the sample and reference through a disk made of the alloy constantan [80]. The heat transported to the sample and reference is controlled while the instrument monitors the temperature difference between the two. In addition to its function in the heat transfer, this disk serves as part of the temperature-sensing unit. The sample and reference reside on raised platforms on the disk. Under each of these platforms there is a chromel (chromel is an alloy containing chromium, nickel and sometimes iron) wafer. The junction between these two alloys forms a chromel-constantan thermocouple. The signal from these sensors is then used to measure the differential heat flow. The temperature is typically monitored by chromel-alumel thermocouples attached beneath the chromel wafers [83, 85].

DSC curves

The result of a DSC experiment is a heating or cooling curve. This curve can be used to calculate enthalpies of transitions. This is done by integrating the peak corresponding to a given transition. It can be shown that the enthalpy of transition can be expressed using the following equation: $\Delta H=KA$, where ΔH is the enthalpy of transition, K is the calorimetric constant, and A is the area under the curve. The calorimetric constant will vary instrument to instrument, and can be determined by analyzing a well-characterized sample with known enthalpies of transition [84]. DSC can be used to measure a number of characteristic parameters of a sample. Using this technique it is possible to observe fusion and crystallization events as well as glass transition temperatures (T_g). In addition to these applications, DSC can also be used to study oxidation as well as other chemical reactions [83–85].

Glass transitions occur as the temperature of an amorphous solid is increased. A glass transition is characterized by a decrease in viscosity. These transitions appear as a step in the baseline of the recorded DSC signal. This is due to the sample undergoing a change in heat capacity, but no formal phase change occurs [83, 85]. As the temperature increases, an amorphous solid will become less viscous. At some points the molecules will obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This is known as the crystallization temperature (T_c). This transition from amorphous solid to crystalline solid is an exothermic process, and results in a peak in the DSC signal. As the temperature increases the sample eventually reaches its melting temperature (T_m). The melting process results in an endothermic peak in the DSC curve. The ability to ascertain transition temperatures and enthalpies makes DSC an invaluable tool in producing phase diagrams for various chemical systems [83].

DSC may also be used in the study of liquid crystals. As matter transitions between solid and liquid it often goes through a third state, which displays properties of both phases. This anisotropic liquid is known as a liquid crystalline or mesomorphous state. Using DSC, it is possible to observe the small energy changes that occur as matter transitions from a solid to a liquid crystal and from a liquid crystal to an isotropic liquid [84].

The study of the oxidative stability of samples using DSC generally requires an airtight sample chamber. Usually, such tests are done isothermally (at constant temperature) by changing the atmosphere of the sample. First, the sample is brought to the desired test temperature under an inert atmosphere, usually nitrogen. Then, oxygen is added to the system. Any oxidation that occurs is observed as a deviation in the baseline. Such analyses can be used to determine the stability and optimum storage conditions for a compound [83].

DSC is widely used in the pharmaceutical and polymer industries. For the polymer chemists, DSC is a handy tool for studying curing processes, which allows the fine tuning of polymer properties. The cross-linking of polymer molecules that occurs in the curing process is exothermic, resulting in a positive peak in the DSC curve that usually appears soon after the glass transition [83–85]. In the pharmaceutical industry it is very important to have well-characterized drug compounds in order to define processing parameters. For instance, if it is necessary to deliver a drug in the amorphous form, it is desirable to process the drug at temperatures below those at which crystallization can occur [84]. DSC curves may also be used to evaluate drug and polymer purities. This is possible because the temperature range over which a mixture of compounds melts is dependent on their relative amounts. This effect is due to a phenomenon known as freezing point depression, which occurs when a foreign solute is added to a solution. (Freezing point depression is what allows salt to de-ice sidewalks and antifreeze to keep our car running in the winter.) Consequently, less pure compounds will exhibit a broadened melting peak that begins at lower temperature than a pure compound [83, 85].

Modulated differential scanning calorimetry (MDSC)

The principle of MDSC is determination of the enthalpy of caloric processes by measuring the heat flow between sample and reference with temperature modulated heating (cooling). Using modulation spectra, high sensitivity and resolution can be obtained, and reversible and irreversible processes can be separated. The main applications of MDSC are determination of phase transitions, glass transitions and reaction enthalpies [88].

Pressure differential scanning calorimeter (PDSC)

PDSC is a kind of differential scanning calorimetry under either high- or low-pressure conditions. Raw materials and finished products are often processed or intended for use at conditions other than ambient temperature and pressure. Conventional calorimetry characterizes well the physical and chemical properties of materials.

DSC studies of polylactic acid (PLA)

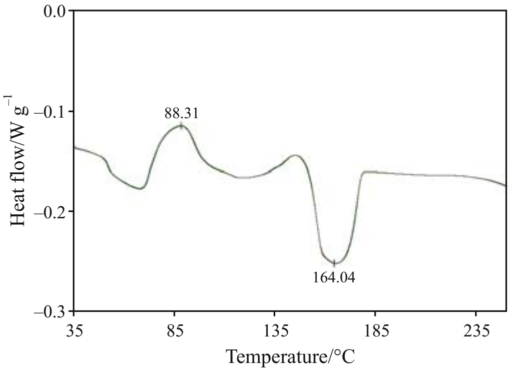


Fig. 6 DSC curve for polylactic acid (PLA)

Figure 6 shows a DSC curve for polylactic acid (PLA) sample following heating up to 250°C. It has been noted that PLA is characterized by a glass transition temperature (T_g), crystallization peak (T_c) and melting peak (T_m), typical of semi-crystalline polymers at 59, 88 and 164°C, respectively.

Selected thermal analysis applications overview

Applications of TA in determination of composition and/or structure

Many of us may think that the applications of TA are limited to gaining the information on thermal properties of materials. However, thermal analysis in combination of other analytical techniques such as elemental, spectral and complexometric titration can also be used to determine the compositions and/or structures of many chemical compounds and materials. Here is a great example of that. We have successfully used the thermal decomposition information in determining the structure of $[Cu(CH_3COO)_2{\cdot}mpc]_2{\cdot}2H_2O$ without getting suitable single crystals in the following way:

At the beginning we were not able to get the suitable single crystal to solve the crystal structure but the compound exhibited unique antimicrobial activities and many other important properties which had prompted us to determine the composition/structure of the compound. But the elemental, complexometric titration and spectral analysis are not sufficient enough to conclude the structure of the compound. Therefore, we also applied the results of TG-DTG-DTA analysis. From the TG curve (Fig. 6), we can see that there are solvent molecules and according to the mass loss we were able to easily conclude that there were two water molecules.

We also used the % of the residue (CuO) and individual intermediate products. After careful consideration of the % of all mass loss steps together with the elemental, complexometric titration and spectral analysis, we were able to easily conclude the structure of the compound $[Cu(CH_3COO)_2{\cdot}mpc]_2{\cdot}2H_2O$. Approximately, one year latter, we were lucky enough to get the suitable single crystal to solve the crystal structure. We were very happy to see that the crystal structure [87]. confirmed the composition/structure of the compound we predicted one year earlier using TA, elemental, complexometric titration and spectral analysis. This gave us enough confidence and a useful way to determine the composition/structure of the hundreds of compounds even without having crystal structure. Since it is very difficult to gain suitable single crystal to solve crystal structure, TA can also be used in combination with other techniques to determine the composition/structure of many very important compounds.

Pharmaceutical

Potential applications of TA in the pharmaceutical industry are numerous. Amongst others these include method development, characterization and specification of active and inactive ingredients, safety analysis or routine analysis in quality control and stability studies. TA can also be used in pharmaceutical industry for studying the decomposition at the melting point, melting behaviour and decomposition, polymorphic modifications by annealing, DSC 'Fingerprint', magnesium stearate, purity using DSC and HPLC, solvent detection by TG-MS and pharmaceutically active substance quantification.

Applications of TA in biomaterials

Traditionally, materials used in medicine and dentistry have been achieved entirely by trial and error. One type of materials is being used regardless of the age of the patient, or the quality of the bone or connective tissue of the patient. We have never known enough to think about solving the problem at a patient-by-patient level. We now have a starting point for doing that. Bio-glass was the first man-made material to bond living tissue. Thus, the idea of a 'bionic person' in which living organs, such as lungs, can be manufactured using biomaterials is becoming very realistic. Composites including glass ceramics containing dispersed biocompatible hydroxyapatite or fluoroapatite phases are very important in medicine and TA is very useful to characterize various biomaterials and thus can play key roles in biomaterials development [87, 89, 90].

Inorganics

With DSC and STA, the primary areas of investigation include melting, crystallization, phase transitions, specific heat, oxidation, and thermal stability of non-metallic, inorganic compounds and elements. Desorption and adsorption behaviour of minerals and catalyzers also are important application areas for TG or STA. The coefficient of thermal expansion and the expansion rate as well as phase transitions are measured with dilatometry. Knowledge of the thermal diffusivity and conductivity of geological layers is becoming increasingly important for studies regarding global warming. The expansion and shrinkage behaviour of technical ceramics during sintering can be measured with dilatometry.

TG-DTA methods is also of great importance for the estimation of hydrate phase quality formed in concrete [91]. The ratio between gel-like hydration products having the fine and non-permeable pore structure and crystal $Ca(OH)_2$ creating the coarse pore structure rich in capillary pores with increased permeability is primary determined from the TA studies. Hence the dependence between the formed hydrate phase (given as percentage of water bound in gel-like hydration products) and the concrete permeability on water (given as permeability coefficient calculated from the results of mercury intrusion porosimetry) is derived. It is clear that the concrete with lower permeability has the higher strength. This is important from the viewpoint of the concrete service-ability expectations, which are nowadays planned over 100 years even up to 500 years. The figure shows the mutual dependencies between bound water content and permeability coefficients of different types of the concrete exposed to 20°C/60%, 80% and 100% – R.H. – cure. As well, the mutual dependence between TG-DTA results on the one hand, strength, Young's modulus of elasticity and carrying capacity of the concrete that are typical construction properties can be determined on the other hand [91].

Conclusions

Thermal analysis has numerous applications almost in all areas from medicine to construction. TA belongs to an evolving technology that has the potential to have an impact on an incredibly wide number of industries and markets. More new TA techniques, combined with other techniques will become more familiar and the applications of TA will increase significantly in future. Consequently, more researchers will use various TA techniques. It is not possible to make a complete conclusion of any research work without knowing its thermal properties in the most of the research fields starting from medicine to construction. Only selected TA techniques and applications are discussed in this paper; however, more thermoanalytical methods and more applications of TA will be discussed in a future paper.

Nomenclature

a	radius of the wire
A	parameter in Eq. (6)
C	a constant (exponential of Euler's constant)
c_p	specific heat of fluid
D	characteristic dimension of the pipe/tube
G	parameter in Eq. (6)
h_c	convective heat transfer coefficient
K	thermal conductivity of fluid
$\overline{Nu}$	Nusselt number
Pr	Prandtl number
q_ℓ	heat dissipation rate per unit length of wire
Re	Reynolds number
V	velocity of fluid
t	time
t_0	reference time (=1 s)
T	temperature
α	thermal diffusivity of fluid
ΔT	temperature difference
μ	viscosity of fluid
ρ	density of fluid
Subscripts:	
ℓ	per unit length
w	wire
0	reference
1	initial
2	final

Acknowledgements

The authors would like to thank the Canada Foundation of Innovation (CFI) for financial support.

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DOI: 10.1007/s10973-007-8518-5