AN OVERVIEW OF THERMAL ANALYSIS OF POLYMERS

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SUMMARY

This article presents an up-to-date overview of the application of thermoanalytical methods in the study of polymers with special focus on thermogravimetry, differential thermal analysis, differential scanning calorimetry and thermomechanical analysis. The working principles behind the various thermoanalytical methods together with modes of operation are described. Their usefulness in the characterisation of polymers is covered comprehensively with examples cited in the literature. The question of validity of data obtained from thermokinetic studies of polymers is examined and it is felt that the kinetic parameters generated carry little physical meaning about the kinetic of the polymer reaction.

INTRODUCTION

The introduction of modern thermal analytical instrumentation into the laboratory in the last fifteen years has taken thermal analysis from a technique known to only a small number of mineralogists using home made equipment to highly sophisticated machines used routinely both in research and production today. The number of publications relating to thermal analysis is increasing at an exponential rate. A number of journals are available today dealing exclusively with thermal analysis.

There is the need, however, to acquaint more workers in the scientific community with the fundamentals of thermal analysis and to describe a few of the ways in which these techniques can be utilised. While thermal analysis as a group of techniques is used in a broad spectrum of scientific disciplines, it is at present one of the primarily utilised methods in the characterisation of polymeric materials to give information often unobtainable by other techniques. It is for this reason that this article will focus its attention on the thermal analysis of polymers.

1. Thermal analysis

1.1 Classification

There are literally hundreds of techniques which can be loosely called thermal analysis. The arrangement adopted for the defined techniques as recommended by the International Confederation of Thermal Analysis (ICTA) (1) is summarised in Table 1.

Table 1 Classification of thermoanalytical techniques

Physical property	Derived technique (s)	Accepted abbreviation
Mass	Thermogravimetry	TG
	Isobaric mass-change determination	
	Evolved gas detection	EGD
	Evolved gas analysis	EGA
	Emanation thermal analysis	
	Thermoparticulate analysis	
Temperature	Heating-curve determination	
	Differential thermal analysis	DTA
Enthalpy	Differential scanning calorimetry	DSC
Dimensions	Thermodilatometry	
Mechanical characteristics	Thermomechanical analysis	TMA
	Dynamic thermomechanometry	
Acoustic characteristics	Thermosonimetry	
	Thermoacoustimetry	
Optical characteristics	Thermooptometry	
Electrical characteristics	Thermoelectrometry	
Magnetic characteristics	Thermomagnetometry	

The table shows clearly the inter-relationship between the methods and can be readily adapted to incorporate additional physical properties/or techniques as necessary. By far the most widely used thermal analysis techniques today are TG, DTA, DSC and TMA on which this article will be based.

1.2 Definition

Thermal analysis (TA) – a group of techniques in which a physical property of a substance is measured as a function of temperature whilst the substance is subjected to a controlled temperature programme.

Thermogravimetry (TG) – a technique in which the mass of a substance is measured as a function of temperature whilst the substance is subjected to a controlled temperature programme.

Differential thermal analysis (DTA) – a technique in which the temperature difference between a substance and a reference material is measured as a function of temperature whilst the substance and the reference material are subjected to a controlled temperature programme.

Differential scanning calorimetry (DSC) – a technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature whilst the substance and reference material are subjected to a controlled temperature programme.

Thermal mechanical analysis (TMA) – a technique in which the deformation of a substance under non-oscillatory load is measured as a function of temperature whilst the substance is subjected to a controlled temperature programme.

Thermodilatometry – A technique in which a dimension of a substance under negligible load is measured as a function of temperature whilst the substance is subjected to a controlled temperature programme.

Dynamic Mechanical Analysis (DMA) – A technique in which the dynamic modulus and/or damping of a substance under oscillatory load is measured as a function of temperature whilst the substance is subjected to a controlled temperature programme.

2. Individual Thermal Analysis Methods

2.1 Thermogravimetry (TG)

TG, one of the most widely used, matured measuring techniques of thermal analysis, is suitable for following processes accompanied by mass transport, both in dynamic and isothermal mode of operation. It can also be used for following virtual mass change in magnetic transitions when external field is used. The first derivative of the TG signal recorded can also be generated directly during the measurement, to obtain thus the derivative TG (DTG) signal, which does not contain new information, but only facilitate visual evaluation in first approximation. A schematic diagram of the TGA machine is shown in Fig. 1 which depicts the combination of a suitable electron microbalance with a furnace and associated temperature programmer. The balance should be in a suitably enclosed system so that the atmosphere can be controlled. Several types of weighing mechanisms have been incorporated in commercially available instruments and there is also a choice of sample, and hence furnace position relative to the balance beam, as either toploading (Mettler), horizontal (Dupont), or suspended (Cahn, Perkin Elmer and Stanton Redcroft). Characteristically, TG devices are manufactured by these companies in forms to suit individual or simultaneous measuring techniques, or they are placed on the market as a modular system, together with devices of other TA methods.

The usual temperature range of operation is from room temperature up to 1000 – 1500°C. Above this range precise operation requires special materials and special design. The rate of heating of the sample can be selected from slow (1°C/min) to fast (100°C/min) and those in between.

Figure 1 Schematic Diagram of a Horizontal Balance

The sample temperature, T_s , will usually lag behind the furnace temperature, T_f , and T_s can not be readily measured without interfering with the weighing mechanism. The lag can be as much as 30°C, depending on the operating conditions (2).

The main types of TG curves obtained are illustrated in Fig. 2. The interpretation are as follows:

Figure 2 Types of TG Curves

The type (i) curve shows that the sample is stable over the temperature range shown (although phase change may occur). The rapid initial mass-loss in type (ii) curve is characteristic of desorption or drying. Type (iii) curve represents a single-stage decomposition with fairly stable intermediates, which are not formed in the type (v) decomposition curve. In type (vi) curve, there is a gain in mass as a result of the sample reacting with the atmosphere, eg., oxidation of polymers in air. Resolution of stages may generally be improved by examined of the DTG curve.

2.2 Differential Thermal Analysis (DTA)

In DTA, the difference in temperature, ΔT , between the sample and the reference material is recorded while both are subjected to the same heating or cooling program-

me. The apparatus is represented schematically in Fig. 3. Should an endothermic thermal event (ΔH +ve, such as melting) occur in the sample, the temperature of the sample, T_s , will lag behind the temperature of the reference, T_r , which follows the heating programme. If the output of the thermal couple, $\Delta T = T_s - T_r$, is recorded against T_r , (or the furnace temperature, $T_f \cong T_r$), the result will be similar to Fig. 4. An exothermic reaction (ΔH -ve, such as oxidation) will give an opposite effect as shown also in Fig. 4. The area under the endotherm or exotherm is related to the value of the enthalpy change, ΔH , for the event.

Figure 3 Essential Elements of the Calorimetric DSC Cell

Abrupt changes in slope or position of the base line usually indicate second order transition. The enthalpy changes for such transitions are usually zero, but there is a change of heat capacity. Examples of this type are glass transition in polymers and the Curie point transition in ferromagnetic materials.

The reference material should obviously undergo no thermal changes over the operating temperature range, and its thermal conductivity and heat capacity should be similar to those of the sample.

The measured area, A , of the endotherm or exotherm is related to the enthalpy change, H , for the thermal event by

$$\Delta H = A/m \times K$$

where m is the sample mass and K is the calibration factor. This factor has to be determined by relating a known enthalpy change to a measured peak area. Usually the melting of a pure metal, such as indium, is used for calibration. The calibration factor contains contributions from the geometry and thermal conductivity of the sample/reference system and is thus specific to a particular instrument under one set of operating conditions. The value of K is critically dependent on temperature, so that calibration has to be carried over the whole temperature of interest.

Figure 4 A typical DTA Curve

2.3 Differential Scanning Calorimetry (DSC)

In DSC, the sample and the reference are kept at the same temperature through out the controlled temperature programme. Any power difference in the independent supplies to the sample and reference is then recorded against the temperature. The apparatus is shown schematically in Fig. 5. There are many similarities between DSC and DTA, including the appearance of the thermal analysis obtained and the kind of information they provide. The principle of operation of DSC, however, is quite different to that of DTA (3).

Figure 5 Essential Elements of a DSC Cell

Thermal event in the sample appears as deviations from baseline, in either an endothermic or exothermic direction, depending on whether more or less energy has to be supplied to the sample, relative to the reference material.

Again the area under the endotherm or exotherm is proportional to the enthalpy change, ΔH , for the process occurring.

$$\Delta H = A/m \times K'$$

A significant advantage of DSC over DTA is that the proportional constant K' is independent of temperature and calibration is thus much easier.

From the viewpoint of gaining information, i.e., from the aspect of the user, modern DSC (power compensation) and modern DTA (based on the measurement of heat flux difference) can be considered as equivalent and sharp polemics were published about it in certain papers (4,5). The operating temperature range of DSC instrument is generally more restricted than that of DTA instruments. The upper limit is around 700°C; for measurement above this temperature, DTA apparatus of classical arrangement is suitable, but it yields considerably less accurate calorimetric data. Low temperature attachments are available for extending the starting temperature to as low as -175°C.

2.4 Thermomechanical Methods (TMA, DMA)

The techniques described so far are based on the response of the sample to heat in the absence of another applied stimulus, except possibly control of the sample atmosphere. Further, these techniques generally employ small samples, often finely divided, whose physical shape is not critical to the measurement, although it may influence the results. In contrast, the shape of the specimen is very important in thermomechanical methods, and the measured property of the specimen is its response to an applied mechanical stress as well as heat.

Three thermal mechanical methods are usually employed:

- (i) thermomechanical analysis (TMA), in which the applied stress is non-oscillatory and usually constant; the deformation under load is measured;
- (ii) dynamic thermomechanometry, in which an oscillatory stress is applied; the dynamic modulus (stiffness) and mechanical damping of the specimen are measured;
- (iii) thermodilatometry, in which no external load is applied and the specimen is allowed to expand or contract under its own mass; the dimensional change is measured.

In thermodilatometry the bulk effect of the sample molecular response to changes in thermal energy is measured. These responses include lattice vibration, changes in crystal structure, changes of state and chemical changes, all of which can result in the expansion or contraction of a solid sample. Most dilatometers are designed to measure the change in length of a specimen as its temperature changes.

Similar expansions and contractions occur in TMA where measurements are made under an applied stress, but in addition to the temperature the stress may result in changes of shape or size as a result of either dissipation of energy by relative motion of molecules (viscous response) or storage of energy, which is released on the removal of the stress (elastic responses).

The viscous response is time dependent but the elastic response is independent of time; thus, the viscoelastic effect can be resolved into its two components by the use

of a 'time probe', i.e., in dynamic thermomechanometry the frequency of the oscillatory stress. If a continuous oscillatory stress is applied to a viscoelastic material, the resulting strain in the material will be oscillatory with the same frequency, but will be out of phase with the stress by an amount that depends on the relative elastic and viscous responses. For a purely elastic response, the phase difference would be zero. The two responses are interrelated by

$$E = E' + jE'' \quad (1)$$

where E is the appropriate bulk modulus for the type of applied stress (tensile, torsional, etc.), E' is the elastic component and E'' is the viscous component. $E' = E \cos \delta$ and $E'' = E \sin \delta$, being the phase difference, whence

$$E''/E' = \tan \delta \quad (2)$$

which gives a measure of the relative energy dissipation per cycle.

Hence the three techniques are closely related in the mechanical properties on which they give information. Dilatometry, the oldest, was traditionally applied to such materials as metals, glasses and ceramics, all of which show a basically elastic response. Consequently, dilatometers have been developed for operation over a wide range of temperature range encountered in the use and processing of these materials i.e., from temperature approaching absolute zero to 2500°C or more.

Instrument for dynamic thermomechanometry, in contrast, has been developed recently and benefit from advances in microprocessor technology that permit rapid data analysis. These generally cover smaller temperature ranges, typically to 850°C and have been applied principally in polymer studies where a considerable viscous behaviour can be found.

Thermomechanical analysis spans the two techniques in the sense that it gives limited information on viscoelastic responses as well as dimensional changes. Again, polymer studies are the commonest applications for the technique, and it is operated over a restricted temperature range.

A typical thermomechanical analyser is shown schematically in Fig. 6. The heart of the instrument is a moveable-core linear variable differential transformer (LVDT) whose output is proportional to the linear displacement of its core. A thermocouple in direct contact with or in close proximity to the sample measures the sample temperature. The sample and probe are surrounded by a temperature-controlled cylindrical heater and Dewar assembly. The final output is a plot of probe displacement or its derivative versus sample temperature or time.

Various probe configurations allow the TMA to be operated in differing modes such as expansion, compression, penetration, tension, dilatometric, stress relaxation, and fibre tension. Some of these accessories are shown in Fig. 7.

Various construction principles can be used in studying the viscoelastic response of a polymer under oscillatory load (6):

- (i) the load may be applied continuously and the modified oscillatory response of the specimen measured; alternatively, the load may be applied intermittently and the decay of oscillation through viscous damping monitored;
- (ii) the specimen may be driven in forced oscillation to assume its natural frequency;
- (iii) the stress may be applied in flexure, tension/compression or torsion.

All of these design variables have resulted in a multiplicity of instruments, some readily applicable to thermoanalytical studies. In the Du Pont Dynamic Mechanical

Figure 6 Schematic Diagram of a Thermomechanical Analyser

F = Fixed Member M = Movable Member

Figure 7 TMA Probe Configurations

Figure 8 Schematic Diagram of the Du Pont DMA Analyser

Analysers (Fig. 8), a flexural stress of fixed amplitude is applied to the specimen; the modulus is related to the resonant frequency of the system and the damping to its power absorption (7). Microprocessor data-reduction techniques provide graphical and tabular output of these properties as functions of time and temperature. The values determined are: E' (tensile storage modulus), $\log E'$, E'' (tensile loss modulus), $\log E''$, $\tan \delta$ (loss factor E''/E'), frequency and damping. Similar information can be obtained from the Stanton Redcroft Dynamic Mechanical Analyser which operates on the principle of forced vibration using flexural stimulation.

TMA is a valuable technique for the thermal characterisation and quality control of materials. Primarily, this is because it provides a sensitive measure of temperature dependent properties, which are extremely important in practice but are not sensed by enthalpic thermal analysers such as DSC, DTA or by thermogravimetric techniques, such as TG. By measuring dimensional changes (expansion and extension modes) or viscoelastic changes (penetration and compression modes), properties such as coefficient of expansion, modulus, heat distortion temperature, softening temperature, deflection temperature, and heat shrink behaviour can be determined precisely and rapidly.

3. Applications for Thermal Analysis in Polymers

3.1 Thermogravimetry

In polymer science, TG is mainly applied to the study of:

- (i) thermal degradation of polymers (kinetics and mechanisms);
- (ii) thermal stability;
- (iii) oxidative degradation;
- (iv) solid state reaction;
- (v) determination of moisture, volatiles and ash;

- (vi) absorption, adsorption, and desorption processes;
- (vii) composition of plastics and composites;
- (viii) identification of polymers

One of the most important application of TG is to give a quick indication of the thermal stability of polymers. The TG scan of fluorinated polymers vs. their parent compounds in nitrogen (8), shown in Fig. 9, yielded some surprising and extremely informative results : whereas fluorinated polyethylene (PTFE) was more stable than the normal polyethylene (PE), the corresponding fluorinated polypropylene (PHFP) was less stable than the unfluorinated polypropylene (PP).

Figure 9 Thermal Stability of Polymers

A typical composition analysis utilising TG is shown in Fig. 10. This analysis of PTFE-carbon black-silica mixture shows how the entire composition may be obtained directly from a single TG run. The initial portion of the scan was run in nitrogen, in which both the carbon and SiO_2 are inert. After the PTFE weight loss was complete, air was introduced and the carbon black oxidised to CO_2 but the SiO_2 remains inert to either atmosphere. This example points out the usefulness of being able to control sample atmosphere.

Recently TG has been used in the field of polymer flame retardancy (9, 10). The choice of flame retardant is dependent on the polymer substrate and the flame retardant must be able to act in the condensed or vapour phase at the right time i.e., at the maximum rate of decomposition of the polymer. The easiest way to match the flame retardant with the polymer is to compare their TG curves as shown in Fig. 11. The TG curves show very clearly that compounds 1, 2 and possibly 3 are ineffective as they are too unstable while compounds 4 and 5, are commercially available flame retardants especially for use in polyurethane.

Figure 10 TG of silica and carbon-filled PTFE

Figure 11 TG curves of flame retardants: 1. Stauffer's Fyrol CEF-tris (2-chloroethyl) phosphate; 2. Stauffer's Fyrol FR-2-tris (2,3-dichloropropyl) phosphite; 3. Monsanto Phosgard C-22-R; 4. Michigan Chemical's Firemaster T-23-P (2,3-dibromopropyl) phosphate; 5. Monsanto's Phosgard 2XC-20

3.2 Differential Thermal Analysis/Differential Scanning Calorimetry

DTA-DSC techniques are commonly used to measure:

- (i) glass transition temperature (T_g);
- (ii) melting point (T_m);
- (iii) decomposition temperature (T_d).

DTA-DSC methods can also be applied in the direct measurement of the energy absorbed or evolved in studies of:

- (i) heats of fusion;
- (ii) heats of vaporisation;
- (iii) heats of crystallisation;
- (iv) heats of reaction;
- (v) specific heats;
- (vi) activation energy;
- (vii) solid state transition energy.

Schematic DTA-DSC curves are given in Fig. 12 with all the important thermal events labelled. The enthalpy involved in each event can also be calculated as discussed.

Figure 12 Schematic DTA and DSC curves

An experimentally obtained DTA curve is shown in Fig. 13. In this sample of cis-polybutadiene, four transitions are discernible. The two transitions at -133°C and -104°C are second order (observed as baseline shifts); the one at -104°C can be attributed to the glass transition. The other two are first order transitions (observed as peaks), the one at -72°C being a crystallisation exotherm, whereas the one at -23°C is the crystalline melting.

The thermal history of the polymer sample has a profound effect on its thermal characteristics and an illustration of this effect is shown in Fig. 14. The first-run scan shows both the glass transition and the crystalline melt of a Neoprene sample. The sample after melting was quench-cooled in liquid nitrogen at such a rate that formation of crystallites was prohibited and an amorphous glass resulted. A run on this glassy material indicated the complete absence of any crystalline melt, even though the glass transition is still obvious.

Figure 13 Low temperature DTA transitions of cis-polybutadiene

Figure 14 Thermal history of Neoprene W

In DSC, the area under the thermogram is directly proportional to the total amount of energy (q) transferred in or out of the sample. This ability to measure quantitative energy flow is useful in a wide variety of applications. The area under the curve for the scan of polyethylene shown in Fig. 15 can be used to determine the heat of fusion (ΔH_f). Comparing the ΔH_f found for this sample (51.6 cal/g) to that reported for 100% crystalline polyethylene (68.4 cal/g) allows a calculation of % crystallinity which is in excellent agreement with that found by x-ray crystallography (11).

Figure 15 Polymer crystallinity by DSC

The curing of thermosetting polymers can easily be monitored by DSC and the energy involved in the exothermic reaction calculated by DSC. Fig. 16 depicts the thermal events in the curing of a resol resin by using the hermetically sealed sample container. Sometimes the exothermic cure reaction may be altered or masked by competitive thermal events such as the vaporisation of water of condensation. In such cases pressure DSC can be used (12).

3.3 Thermomechanical Analysis/Dynamic Thermomechanical Analysis

TMA technique is commonly used to measure:

- (i) expansion coefficient;
- (ii) viscosity/flow;
- (iii) stress relaxation/viscoelasticity;
- (iv) composite delamination;
- (v) glass transition temperature (T_g);
- (vi) polymer creep;
- (vii) fibre or film shrinkage and
- (viii) polymer softening temperature.

Figure 16 DSC curve of cure of Resol resin by using the hermetically sealed sample container

The measurement of T_g and expansion coefficient is of particular significance in the manufacture of composites and laminates to ensure compatibility. Fig. 17 illustrates such an example for a printed circuit board laminate using a Du Pont 943 Thermal Mechanical Analyser.

Figure 17 Determination of T_g and change of specific heat of epoxy printed circuit board

A typical example of the use of DMA for characterisation of a polymer composite is illustrated in Fig. 18.

DMA technique is commonly used to study:

- (i) curing of thermosets;
- (ii) polymer blend compatibility
- (iii) correlation of impact stability with damping;
- (iv) observation of plasticisers effect;
- (v) measurement of subtle transitions;
- (vi) tensile properties;
- (vii) characterisation of stiff polymer composites;
- (viii) characterisation of supported systems (coatings, preregs, adhesives).

Figure 18 Epoxy glass laminate by dynamic mechanical analysis

Such a scan immediately shows several phenomena associated with change in the viscoelastic properties of the materials, as well as the quantitative magnitude of these properties; In one such scan, the modulus-temperature profile disclosed three distinct events, each of which resulted in a decrease in stiffness associated with changes in the epoxy material.

The first of these changes, the one occurring at subambient temperature (-80°C to -20°C), is attributed to the B-relaxation process in the epoxy. It is caused by the motion in the crosslinks of the three dimensional network.

The second is the well known glass transition (T_g) phenomena occurring at about 103°C , which results in a dramatic modulus decline from 2.9 to 0.58×10^6 psi at about 130°C as the material changes from a glass to the rubbery state. The kind of information concerning the engineering integrity is vital to the successful application of epoxy in the printed circuit board where high temperatures are encountered. The third change in the viscoelastic properties of the composite is associated with the onset of polymer decomposition.

4. Kinetic Calculation in Thermal Analysis

For the kinetic study of transformation and decomposition proceeding in the solid or melt phase, thermoanalytical methods, particularly TG and DTA-DSC, seem to be applicable in first approximation. With these methods, coupled with appropriate data gathering and processing methods, data can be obtained on the reaction rate, the rate constant, the activation energy (E^*) of the process, the order of reaction (n), the frequency pre-exponential factor (A).

The main problem is that kinetics in thermal analysis differ in many ways from homogeneous fluid phase kinetics. There is no homogeneous distribution of concentration and the system is not truly isothermal. The procedural conditions, the thermal history of the sample as well as sample size and geometry play an important role and it is often difficult to decide which is the rate determination step in the overall transformation or decomposition. Moreover, researchers substitute experimental data in one of the available mathematical models more or less arbitrarily. The most common models are those derived for liquid phase kinetics for their simplicity, and as a number of workers (15, 16, 17) argued, in many cases of polymer decomposition it is not always permitted or possible to interpret calculated kinetic parameter in the same way as accepted in fluid phase, isothermal kinetics. Sestak also pointed out some obvious deficiencies of non-isothermal kinetics in his survey (18, 19).

The opinion of the present author is that notwithstanding the fact that thermokinetic does not yield unambiguously evaluable kinetic results at its present level of development, some of the calculated parameters may be characteristic of overall description of simple processes, at least on a comparative level. As for polymers, the basic rate equation $d\alpha/dt = k(1-\alpha)^n$ cannot strictly be applied to a heterogeneous solid state reaction (polymers normally transform through such a state). The kinetic parameters obtained such conditions are best treated as approximate algebraic description of the reaction which carries little physical meaning about the kinetics of the reaction.

Conclusions

Thermal analysis is a technique that can contribute significantly to the understanding of material characterisation. It is at present perhaps the most widely used group of techniques in polymer research and development to provide insights into the correlation between structure, properties and processing of polymeric materials. This brief overview on an extremely extensive field can in no way do justice to the power and versatility of thermal analytical methods. It is hoped that the reader's appetite has been whetted to stimulate further research into new areas of applications in this rapidly growing field.

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