Thermogravimetry of Polymers

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Thermogravimetry (TG) is the study of the relationship between a sample's mass and its temperature. It can be used to study any physical (such as evaporation) or chemical process (such as thermal degradation) that causes a material to lose volatile gases. Polymers have different thermal stabilities and thus the qualitative "fingerprint" afforded by TG in terms of temperature range, extent and kinetics of decomposition provides a rapid means to distinguish one polymer from another using only milligram quantities of material. Experiments are most commonly carried out under conditions where the temperature is increased in a linear fashion with time or the sample is held isothermally at an elevated temperature, although more sophisticated temperature profiles are occasionally used for compositional and kinetic analysis. Processes which do not result in a change in sample mass are not detected by TG. Therefore simultaneous measurements by differential scanning calorimetry (DSC) are useful. Volatile decomposition products may be detected and identified (e.g. by infrared (IR) spectrometry or mass spectrometry (MS)) in order to elucidate the mechanism of mass changes. TG is used for quantitative compositional analysis of polymers, lifetime prediction and kinetic studies, making the technique invaluable in all stages of polymer development, fabrication and component testing.

1 INTRODUCTION

Mass and heat are amongst the oldest concepts known to mankind. However, only in recent times has the utility of recording mass change as a function of temperature been recognized. Many of the earliest experiments using TG were carried out by heating samples to known temperatures and removing them for weighing at regular time intervals.[1]

The concept of weighing a sample continuously while it was being heated appears to have been first used by Urbain and Boulanger in 1912,[2] who constructed an apparatus consisting of a conventional balance adapted for null-point electromagnetic compensation, with the sample hanging from the balance arm into an electrically heated furnace. The instrument was gas tight and had provision for the introduction of absorbent materials for evolved gases. Although this instrument was probably the first thermobalance, it appears not to have received further development, thus it is usually Honda who is credited with the invention of TG in 1915.[3] His equipment was reliable and allowed the heating rate to be reduced during the occurrence of mass losses (sample-controlled thermogravimetry – SCTG).

Much of the early work in this field was to use TG for inorganic chemical analysis. These efforts reached their zenith in Duval's monumental description of over 1000 gravimetric precipitates of nearly 80 elements.[4] In 1949, Jellinek[5] studied the degradation in vacuo of several important polymers including polystyrene and polyethylene. A review by Chiu[6] in 1966 still remains relevant today and covers most of the applications of TG to the study of polymers and predicts its coupling to other techniques such as IR spectrometry and MS for the study of evolved gases.

There is considerable literature dealing with TG and its applications to the characterization of polymers. Almost every scientific journal covering polymer science includes examples of the use of the technique, and two journals, the *Journal of Thermal Analysis & Calorimetry* and *Thermochimica Acta*, are devoted exclusively to thermal analysis. Together, these journals will often describe the latest advances in techniques and instrumentation. There are also a number of textbooks on thermal analysis[7–11] and a two-volume text edited by Turi[12] deals explicitly with the thermal characterization of polymeric materials. Unlike many other publications, the latter is organized by polymer type and applications rather than by techniques. This approach is useful in the context

of presenting an overview at the expense of occasional repetition.

In view of the wealth of published information regarding the applications of TG stretching back over 40 years of study this article can only hope to present an overview of the technique and its applications and the reader is referred to the numerous references and more specialist texts[13] for a fuller coverage of the subject.

2 INSTRUMENTATION AND OPERATION

Gallagher has recently reviewed the design, construction and operation of modern thermobalances.[14] A typical instrument consists of three major components:

1. a sensitive recording balance;
2. a furnace and associated controller/atmosphere management;
3. A data station, recorder, plotter and any other peripheral equipment.

Null-point balances are now used in almost all commercially available thermobalances. Many instruments used the electromagnetic compensation design described by Cahn and Shulz.[15] A beam carrying the sample and counterweight is suspended from the coil of a galvanometer. As the mass of the sample changes, the beam turns on a pivot, causing a variation in the current from a photodetector–shutter–lamp arrangement. This is used in a servoloop to apply a restoring force through to the coil. The change in current (or voltage) required to maintain equilibrium is proportional to the mass change in the sample. This analog signal is amplified and digitized to send to the data station. Typical sample masses range between 1 and 100 mg, although obtaining a truly representative sample of the material under investigation may be difficult as the sample mass decreases. Specialized thermobalances designed to accommodate larger mass ranges have been described.[14]

The furnace is the heart of the thermobalance. Whereas most instruments use a balance mechanism of a standard design, the furnace is often designed for a specific temperature range or response time. Subambient operation is of limited utility for most applications (with the exception of instruments designed for simultaneous thermogravimetry/differential scanning calorimetry (TG/DSC)), although many furnaces have the facility for air or water cooling (by means of a jacket) so that they may be cooled rapidly at the end of an experiment in order to increase sample throughput. Furnaces generally employ noninductively wound electrical resistance elements, although IR and microwave heating have been described. Low thermal mass furnaces are preferred for variable heating rate techniques such as SCTG or modulated-temperature thermogravimetry (mt-TG) where rapid changes in heating rate are required. Typical heating rates range from $50\,^{\circ}\text{C}\,\text{min}^{-1}$ to isothermal operation.

Provision must be made for some means of purging the furnace with a controlled atmosphere. Air or nitrogen are the most common purge gases employed. Operation under an inert atmosphere (such as nitrogen) may not always be possible since the furnace may not be completely airtight and may also retain trapped oxygen. Even high-purity nitrogen may not be completely oxygen-free. This is not, however, a major concern for polymers since they are generally less sensitive to oxidation than other materials commonly examined by TG. Helium may be used for good heat transfer between the furnace and sample particularly for mt-TG. Flow rates are controlled by rotameters or mass flow controllers and there is often some provision for switching between gases for compositional investigations. High-pressure and vacuum thermobalances are sometimes used.[14]

Several different arrangements of the balance and furnace are possible. The sample may hang down from the balance into the furnace, or a top-loading design may be used. Horizontal configurations may also be used in order to reduce the gas flow affecting the apparent weight of the sample during heating by impinging on the sample and thus acting as a piston. Alternatively, the inlet and outlet lines for the purge gas maybe arranged to direct the flow of gas across the sample rather than up or down a vertical furnace. The density of the gas also decreases with increasing temperature; this reduces the upthrust on the sample (Archimedes' Principle) leading to an apparent increase in weight. The gas flow path may also change with temperature. Using small samples (<10 mg) or performing a blank measurement with a similar volume of inert material can reduce these effects.[16] An alternative approach is to use a symmetrical design whereby the sample holder and counterweight both hang down into the same or separate furnaces. Automatic sample changers are available for several commercial thermobalances, thus permitting unattended operation and increased productivity.

Samples are usually contained within small crucibles made of refractory materials, such as quartz or platinum, which are chemically unreactive towards most materials. Less expensive, disposable aluminum holders may be used for polymers since the latter usually decompose below the melting temperature of aluminum ($660\,^{\circ}\text{C}$). In all cases, it is important to allow good interaction between the sample and purge gas so that the build-up of decomposition products in the immediate vicinity of the sample is avoided. Purge gas flow rates should be

sufficient to sweep volatiles from the furnace, but not so fast as to cool the sample.

The temperature of the sample is usually measured by a thermocouple placed nearby. It is unreliable to use the furnace temperature as a measure of sample temperature since this will inevitably be in advance of the sample's true temperature owing to heat transfer considerations. In the event of a chemical reaction occurring, the sample temperature will be affected by the heat of reaction and may be above the furnace temperature for exothermic decompositions. For simultaneous TG/DSC and in some conventional thermobalances, the sample holder sits directly upon a temperature sensor. In other cases it is important to locate the thermocouple as close as possible to the sample without interfering with the operation of the balance. Temperature calibration should be carried out regularly, according to a recommended procedure, and always under the same conditions (e.g. heating rate, purge gas, thermocouple location) as that used for measurements. Calibration of the mass scale of the furnace is less frequently required, but easily checked using standard masses.

Modern thermobalances typically use a personal microcomputer for data acquisition. This allows results to be stored for future reference and subsequent data analysis. It is usual to be able to plot the sample's mass (directly or as a percentage of its initial mass) as a function of time or temperature.[13] Calculation and display of the first derivative of sample mass as a function of time or temperature (dm/dt or $-dm/dT$) is a useful facility in identifying regions of interest.[6] It is common to plot $-dm/dt$ or $-dm/dT$ so that maxima in rate of mass loss appear as peaks. Analysis of such data ranges from simply determining the magnitude and the extrapolated onset of mass changes to sophisticated kinetic modelling of processes although it is essential to have a thorough understanding of any mathematical treatment of data before any reliance is placed on the results. Many computer data stations can often be used to control several thermal analyzers at one time and co-plot the results from different experiments and/or techniques.

Finally, it is important to report all results with sufficient experimental detail (e.g. sample history, measurement conditions, equipment and data treatment) so as to enable their repetition and, if necessary, reconcile any observed differences in outcome with changes in operational procedure.

3 APPLICATIONS

The information provided by TG is confined to the detection of changes in mass of the sample as its temperature is altered. Thus the technique is largely limited to the study of decomposition and oxidation reactions and to such physical processes as vaporization, sublimation and desorption.

3.1 Thermal Stability Assessment and Compositional Analysis

The assessment of thermal stability is one of the most important applications of TG to the study of polymers. Thermogravimetric curves provide information about the decomposition mechanisms for various materials.[17] In addition, the decomposition profiles may be characteristic for each type of polymer and in some cases can be used for identification purposes. The onset of mass loss often defines the upper limit of thermal stability for the material, though it must be appreciated that extensive degradation of the polymer structure by, for example, cross-linking, may have already taken place before the point at which detectable changes in mass occur.

The routes by which polymers degrade can be categorized according to six main mechanisms:[18]

1. main-chain scission
2. side group scission
3. elimination
4. depolymerization
5. cyclization
6. cross-linking.

Cyclization and cross-linking rarely result in any change of sample mass unless they occur in conjunction with 1–4. and are not detected by TG.[17] Routes 1–4 usually result in the evolution of volatile products with an accompanying mass change. In an inert atmosphere, some polymers give an almost quantitative yield of their parent monomers.[19] In air, complete oxidation of the sample to oxides of its constituent elements commonly occurs. Nitrogen-containing polymers usually generate some ammonia or hydrogen cyanide. Halogen-containing polymers yield the respective hydrogen halides.[19]

Figure 1 shows a series of thermogravimetric curves for a number of common polymers in nitrogen. When comparing the thermal stability of polymers it must be noted that such curves are purely procedural. For meaningful correlation of thermal stability with polymer structure it is essential that the experiments are carried out under similar experimental conditions. It is usual to assign a temperature at which degradation begins to occur (e.g. the extrapolated onset of the lowest temperature weight loss) or quote the temperature at which (for example) 5% weight loss has taken place. Often, significant deterioration in polymer properties has occurred below these values.
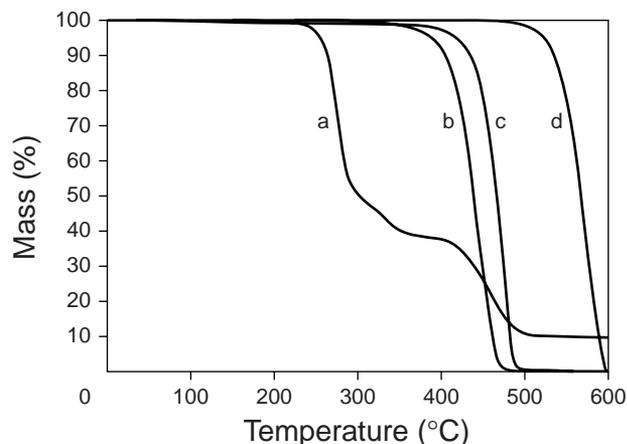
Figure 1 TG curves for several common polymers in nitrogen heated at $5\,^{\circ}\text{C}\,\text{min}^{-1}$ (a = poly(vinyl chloride), b = nylon-6, c = low-density polyethylene, d = polytetrafluoroethylene).

The information provided by TG is inherently quantitative. Provided that the temperature scale is accurately calibrated and the balance provides an output proportional to the mass of the sample across its operating range, then the mass loss profile of a mixture of materials is usually the sum of the individual profiles of each of its components.[13] This affords a means of compositional analysis of materials such as polymer blends and composites.[13] An example of this is shown in Figure 2 for carbon fiber/epoxy composite. In this case, the sample was heated to 825 °C in an inert atmosphere so that degradation of the epoxy resin took place. Then the furnace was purged with air so that oxidation of the carbon fiber took place. The percentage composition of each component in the specimen can be determined after due allowance has been made for any carbonaceous residue arising from degradation of the epoxy resin.
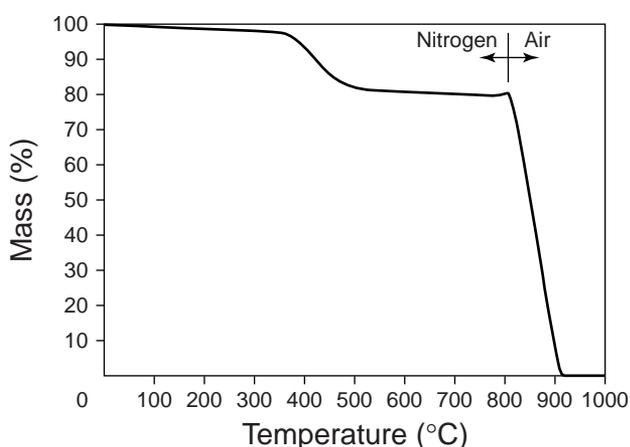
The degradation of block and graft copolymers rarely corresponds to the sum of their parent homopolymers.[12] Copolymerization may result in a material which is thermally less stable than either of the parent homopolymers since the addition of a heterogeneity in the polymer backbone may incorporate a "weak link" into the macromolecular chain. Alternatively, there are a number of co-monomers (such as alkyl acrylates or acrylonitrile) which have been used to stabilize polymers sensitive to depolymerization during processing (such as poly(methyl methacrylate)).[19]

An example of increasing vinyl acetate content on the thermal degradation of poly(ethylene-co-vinyl acetate) is shown in Figure 3. The vinyl acetate component shows a characteristic mass loss associated with elimination of acetic acid before the main chain degradation occurs. In this case TG can be used as a quantitative means of estimating copolymer composition.

Another quantitative use of TG is to study the loss of solvents from polymer dispersions.[20] Such measurements are often performed under isothermal operation and the initial stages of the process often show a linear mass loss profile with time as the solvent evaporates since this is a zero order process. During later stages of drying the rate of mass loss may decrease as the residual solvent becomes trapped in the matrix and its diffusion out of the sample is constrained. For many plasticized polymers, there may be a sudden mass loss as the material is heated through the sample's glass–rubber transition temperature, and the molecular mobility of the polymer increases so allowing the plasticizer to escape. In any drying study, the operator should be aware that the sample may be significantly cooler than the furnace temperature owing to the latent heat of evaporation of the solvent. A study by Mrklić and Kovačić[21] describes

Figure 2 TG curve of carbon fiber/epoxy resin composite heated in nitrogen to 825 °C, then exposed to air.
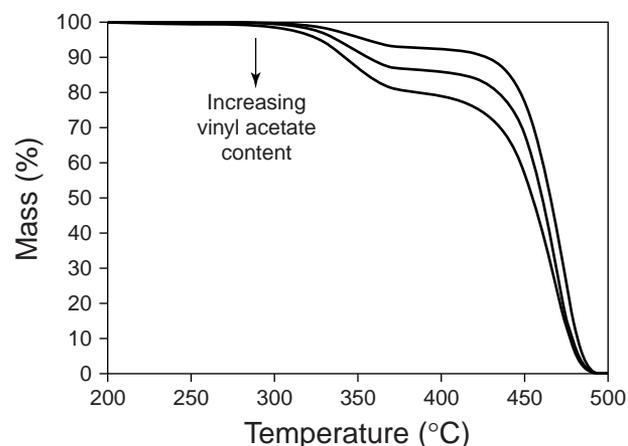

Figure 3 TG curves of poly(ethylene-co-vinyl acetate) copolymers of different vinyl acetate content (top to bottom = 9, 18 and 28 mol.% vinyl acetate).

the use of TG to investigate the volatilization of dioctyl phthalate from plasticized poly(vinyl chloride). Such work is useful in predicting the loss of additives from polymer systems, which has important implications in the lifetime of the formulated product.

3.2 Sample-controlled Thermogravimetry

In many cases the mass loss profiles of polymers are complex and consist of several overlapping steps. One way of overcoming this is to decrease the heating rate so as to achieve more complete separation of each stage of the decomposition process. Such an approach naturally increases the time for the experiment to be carried out. An alternative approach can be used whereby instead of the usual linear temperature ramp a strategy is adopted whereby the rate of rise of temperature is slowed or even suspended as soon as some predetermined rate of mass loss is detected.[22] Once this has occurred, heating is recommenced until a further mass change is detected. This technique is known as sample-controlled TG.

In its simplest implementation, the temperature program can be arranged to alternate between linear heating at a constant rate of temperature rise interspersed by isothermal segments when mass loss is occurring. Sørensen[23] has termed this "step-wise isothermal" heating. The advantage with this approach is that the temperature profile can be recorded and used to specify conditions for future experiments on similar samples (for use in quality control). Another approach is to use a dynamic heating rate[24,25] whereby the rate of temperature change is gradually reduced from an initial rate (possibly even resulting in the sample being cooled) as the rate of mass loss increases. This approach has been commercialised as "high resolution TG". A review by Reading[26] uses the term "constrained rate TG" for this approach.

Figures 4 and 5 show the mass fraction and derivative mass loss curves for a bilayer low density polyethylene/nylon-6 film. Figure 4 was obtained at a constant linear rising temperature profile of 5 °C/min whereas Figure 5 was obtained using the variable heating rate method described by Gill et al.[24] Although there is still incomplete separation of the degradation of the two components in Figure 5, measurement of the mass change between the plateaux either side of the saddle in the derivative mass loss curves allows quantitative analysis of each of the components, which agrees well with theoretical calculations based upon the thickness of each layer. The penalty of this particular approach is the extended experimental time needed to obtain such data indicated by the curves shown in Figure 6.

A final method of temperature control is to dispense with any preconceptions as to the initial choice of temperature alteration, but to arrange a feedback directly
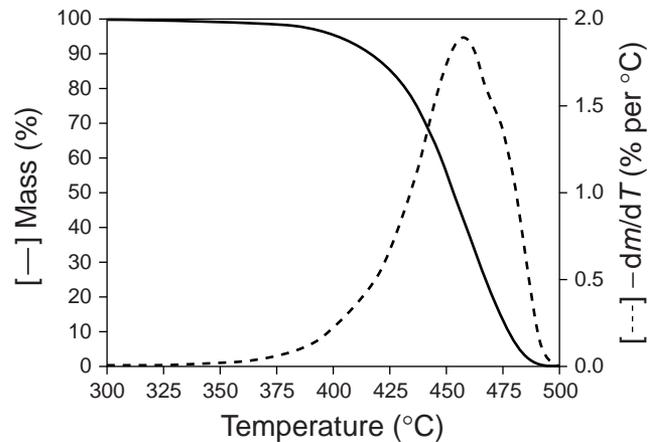

Figure 4 TG curve of low density polyethylene/nylon-6 laminate obtained at a constant heating rate ($5\,°C\,min^{-1}$).
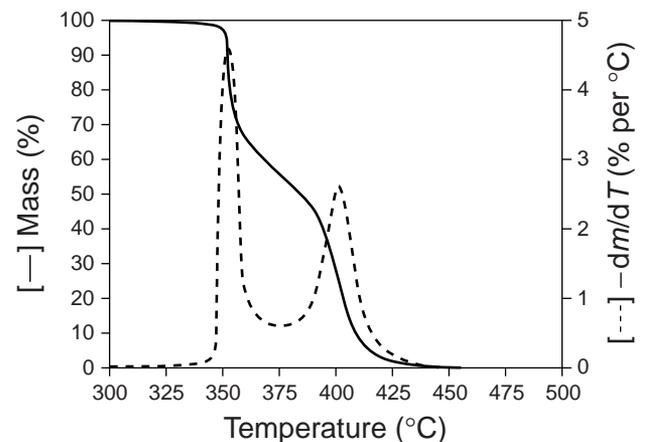

Figure 5 TG curve of low-density polyethylene/nylon-6 laminate obtained at a dynamic heating rate.
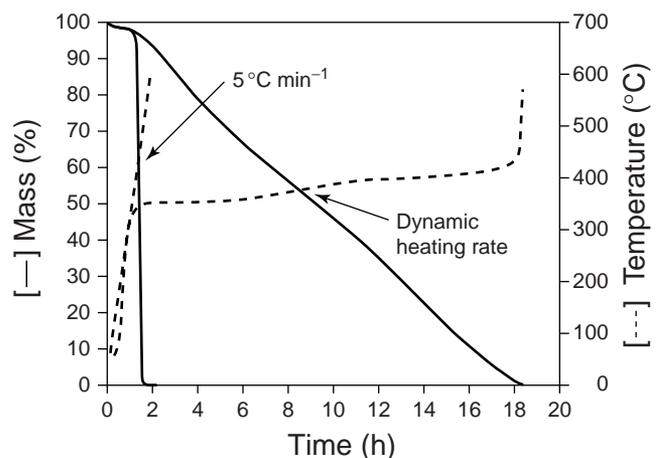

Figure 6 Comparison of Figures 4 and 5 plotted against time.

from the rate of change of sample mass so as to maintain a constant rate of mass change (or indirectly, by detecting

the rate of evolution of gaseous decomposition products). This area of study has been independently pioneered by Rouquerol[27] and Paulik and Paulik[28] and such approaches are applicable to other thermal methods.

3.3 Lifetime Prediction and Degradation Kinetics

The most obvious use of TG beyond that of thermal stability assessment and compositional analysis is to use the technique to predict the lifetime of polymers under actual service conditions. The simplest approach is to perform isothermal measurements at elevated temperatures and measure the time taken for a certain extent of mass loss to occur. Several experiments may be carried out at different temperatures so as to obtain a table of lifetime versus temperature. Whilst such data are readily obtained, it rarely spans the temperature range of interest (indeed to do so may require inordinately long experiments at lower temperatures), therefore some means of extrapolation is required.

The temperature dependence of chemical processes may be readily expressed in terms of Equation (1), the Arrhenius equation:[29]

$$k = A \exp\left(\frac{-E_a}{RT}\right) \tag{1}$$

where k is the rate constant, R the gas constant and T the thermodynamic (Kelvin) temperature. Values of the Arrhenius parameters (E_a and A) provide measures of the magnitude of the energy barrier to reaction (the activation energy, E_a) and the frequency of the occurrence of a condition that may lead to reaction (the frequency factor, A). The rate constant k is defined by the relationship between the rate of reaction ($d\alpha/dt$) and the extent of conversion or fraction reacted (α). Polymer decompositions are generally heterogeneous reactions since the sample is solid (or molten) and the products are gases. A general relation to describe the relationship between ($d\alpha/dt$) and α is Equation (2), the Ng equation:[30]

$$\frac{d\alpha}{dt} = k\alpha^m (1-\alpha)^n \tag{2}$$

Starting from this basic form, it is possible to derive various subclasses of rate equation such as first-order decay, nucleation and growth, etc. by changing the values of m and n. Isothermal experiments provide the means of determining the form of the kinetic equation though discrimination between different models is not straightforward.[31] A simpler approach is to substitute the reciprocal of the isothermal lifetime for the rate constant in Equation (1) and extrapolate the data to the region of interest. Caution should be placed on the interpretation of such data, especially at lower temperatures where

the degradation mechanism may have changed. This is especially important if the original measurements were made above a phase transition e.g. the polymer's melting point or its glass transition temperature.[32]

Isothermal measurements suffer from the drawback of being rather time-consuming. There are also difficulties in bringing the sample and apparatus to the required temperature without some decomposition of the sample having already taken place. One way of avoiding this problem is to change a rate-controlling variable during the course of the measurement. A useful method is temperature jump TG.[33] The rate of decomposition can then be measured either side of the change in temperature and the activation energy determined from Equation (3)

$$E_a = R \ln \left[\frac{(dm/dt)_{T_1}}{(dm/dt)_{T_2}} \right] \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \tag{3}$$

where $(dm/dt)_{T_1}$ and $(dm/dt)_{T_2}$ are the rates of mass loss at T_1 and T_2 either side of the temperature jump. SCTG has also been employed to investigate the kinetics of thermal decomposition of polyesters and it is claimed that the technique offers significant advantages when dealing with polymers.[34]

Another approach is to studying degradation kinetics using data from conventional linear rising temperature TG. Many such methods have been proposed, but the most popular strategy is that described by Ozawa,[35] and Flynn and Wall[36] which has been incorporated into an American Society for Testing and Materials standard method.[37] Essentially, separate measurements are carried out at different linear heating rates and the temperatures at which a set percentage mass loss occurs noted (Figure 7). These are then plotted as a function of heating rate (dT/dt) and the activation energy determined by an iterative process (Figure 8). These algorithms have been
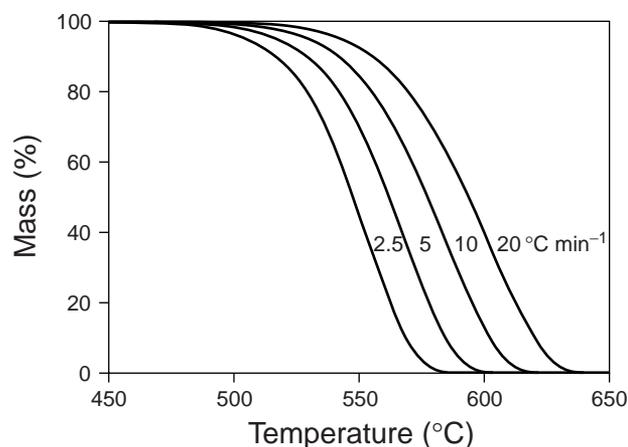

Figure 7 TG curves of poly(tetrafluoroethylene) at different heating rates.
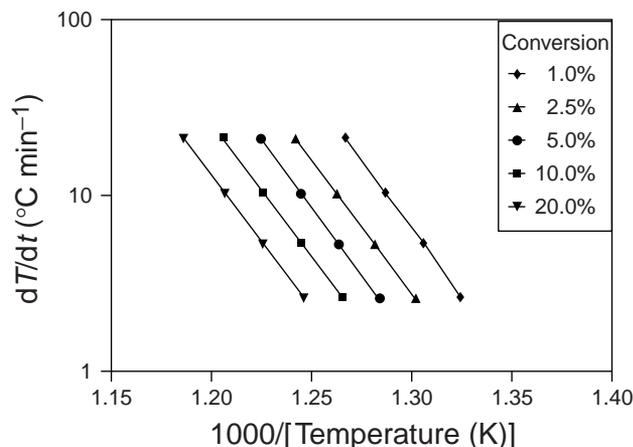
Figure 8 Kinetic analysis of results from Figure 7 to determine E_a.

Figure 10 mt-TG curve of poly(ethylene-co-vinyl acetate).

incorporated into a number of commercially available software packages,[38] although the user should always question the predictions of such "black box" methods especially since they often assume, without appropriate justification, that the polymer decomposition reactions are "first-order" processes, as in Equation (4):

$$\frac{d\alpha}{dt} = k(1 - \alpha) \tag{4}$$

Thus, it is possible to predict the lifetime for (say 10% mass loss) as a function of temperature (Figure 9).

A final method for studying polymer degradation kinetics is known as modulated temperature TG. This uses a temperature profile in which a sinusoidal temperature fluctuation is superimposed upon a conventional linear rising temperature program.[39] The raw data from such
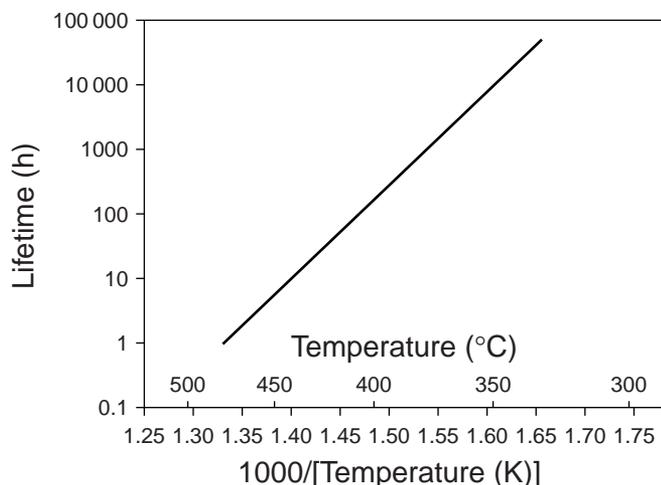
an experiment are shown in Figure 10 for an ethylene-co-vinyl acetate copolymer. The curves showing the heating rate (dT/dt) and rate of mass loss $(-dm/dt)$ make the effect of the temperature modulations apparent. E_a for the chemical decomposition is then calculated according to Equation 5:

$$E_a = \frac{R[T_{av}^2 - (0.5T_{amp})^2]L}{T_{amp}} \tag{5}$$

where T_{av} is the average thermodynamic temperature, T_{amp} is the amplitude of the temperature modulation and L is the logarithm of the amplitude of the rate of mass loss over one modulation. Plots of mass and E_a as a function of temperature from the data is shown in Figure 11. Although based on the temperature jump method described above, mt-TG is a relatively new technique which promises to simplify the acquisition of kinetic data.
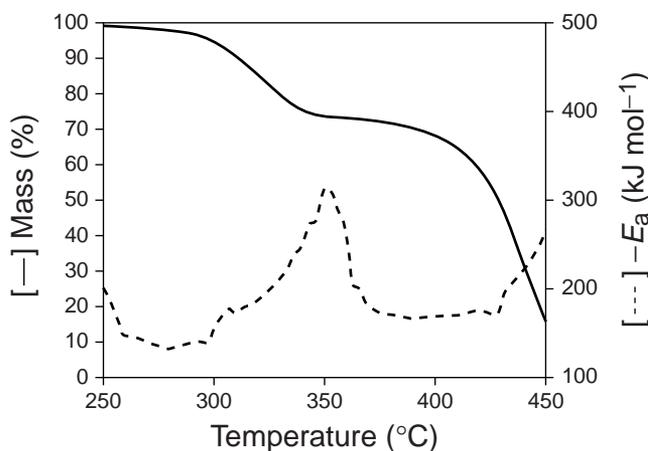

Figure 9 Predicted lifetime (10% weight loss) of poly(tetrafluoroethylene) vs temperature.

Figure 11 Plot of mass and E_a versus temperature for data from Figure 10.

The kinetic analysis of thermogravimetric data is a veritable "minefield"[40] and the reader is referred to the excellent review of this area by Galwey and Brown[41] for a more in-depth discussion.

3.4 Combined Techniques

3.4.1 Thermogravimetry/Differential Scanning Calorimetry

DSC is another thermal analysis technique whereby the difference in heat flow between a sample and inert reference substance is measured during a temperature program. Any changes in heat capacity of the sample (such as accompanies the glass–rubber transition in polymers) or processes which consume (endothermic) or liberate (exothermic) heat can be studied. The sample is usually placed in an aluminum pan, with an empty pan used as a reference. Various methods are used to measure the heat flux, but a common arrangement is to place the pans on a metal or ceramic plate containing thermocouples which serve to detect the difference in temperature between the pans and convert this to a thermal energy difference. Several instruments have been designed which incorporate the heat flux plate design into a thermobalance this affording a means of performing simultaneous DSC and TG.[42] There are several advantages to this approach over conventional DSC and TG notwithstanding the saving in experimental time needed to acquire two sets of data. It is useful to be able to determine energy changes associated with thermal decomposition reactions. Because many chemical reactions in polymer systems, such as curing of thermosets, are condensation reactions, water or ammonia may be liberated during the course of the reaction. This will cause a change in mass of the sample in addition to the heat of reaction which can be measured by DSC.[42] TG cannot normally detect physical changes in polymer structure such as those that accompany the glass transition, crystallization or melting so the additional information provided by DSC is useful. Another example of TG/DSC is shown in Figure 12 for a natural polymer (cellulose) containing an excess of water. The total moisture content of the polymer can be found from the mass loss on drying whereas the amount of free water can be determined from its enthalpy of fusion given by the area under the DSC peak around 0 °C. The difference between the two values is the amount of water chemically bound to the polymer. This will vary for cellulose obtained from different sources and will influence its reactivity towards acids and alkalis. This can be important in the preparation of cellulose derivatives such as cellulose acetate.

Differential thermal analysis (DTA) is another variant of DSC whereby the temperature difference between a
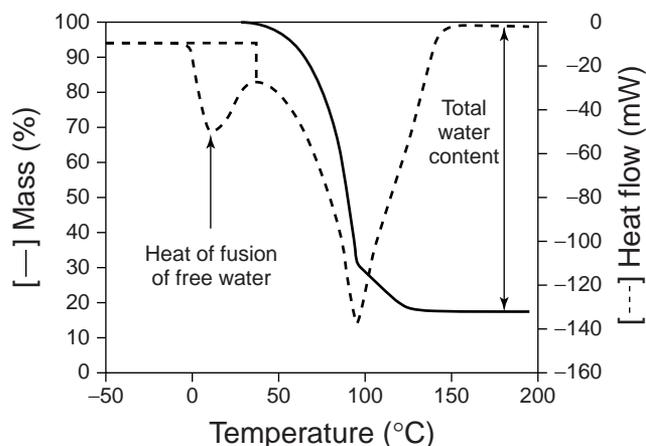

Figure 12 TG/DSC curves for cellulose containing an excess of water.

sample and reference is monitored during the temperature program. This technique is not quantitative in terms of determining energy changes although it is capable of detecting the occurrence and energetic nature of physical and chemical transformations in the same way as DSC. Kettrup et al.[43] have described a simultaneous DTA–thermobalance capable of handling up to 500 g of material for the study of waste products for environmental purposes. Such an instrument has obvious applications for the recycling of plastics and is also capable of being interfaced to a mass spectrometer for analysis of evolved gases.

3.4.2 Thermogravimetry/Evolved Gas Analysis

The capability of TG for materials characterization is greatly increased if other techniques are coupled to the thermobalance in order to identify either the residue or the products evolved during the experiment. Although Wiedemann and Bayer[44] have described an instrument for simultaneous TG with the X-ray diffraction analysis of the residue, it is more common to identify the gaseous degradation products from TG. Nonspecific methods such as coupled TG–photometry[17] afford a means of measuring smoke generation during the degradation of polymers, whereas online titration of evolved gases (e.g. by absorption in dilute alkali solution) is more selective for acidic evolved gases such as hydrogen chloride from the thermal degradation of poly(vinyl chloride)[17] or acetic acid from the thermolysis of vinyl acetate copolymers.[45]

The most usual means of identification of evolved gases employs either IR or MS.[46] In both cases, some form of interface is required to take the evolved gases from the thermobalance into the spectrometer. For thermogravimetry/infrared evolved gas analysis (TG/IR) this comprises a heated transfer line (to prevent the

condensation of less volatile products) and a flow cell through which the beam from the spectrometer is passed. Materazzi[47] has published a review of publications up to 1997 which describes the apparatus and applications of TG/IR. An example of this is shown in Figure 13 which shows the mass loss and derivative mass loss profiles for plasticized cellulose acetate.[48] The total signal from the IR detector is shown in Figure 14 along with a signal derived from the IR absorbance of the plasticizer. Thus, IR evolved gas analysis is a useful means of assigning multiple mass losses to specific degradation mechanisms.

MS is an alternative to IR analysis although the interface design is complicated by the requirement to operate the mass spectrometer under high vacuum. Various splitter designs[49] have been developed in order to reduce the transfer line pressure down to a level suitable for injection into the mass spectrometer. Again,
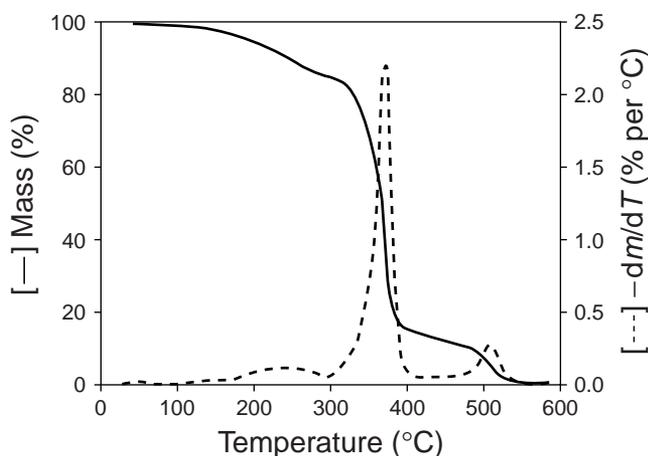

Figure 15 TG/MS curves of poly(vinyl chloride) showing the effect of 4% added MoO_3 on the release of benzene ($m/z = 78$) (a = pure polymer, b = polymer + additive).

these units are heated so as to prevent condensation of less volatile products. Materazzi[50] has also reviewed this area of research to 1998, and Jansen[51] provides an overview of both evolved gas analysis techniques with particular reference to polymers. A simple example of the application of thermogravimetry/mass spectrometry evolved gas analysis (TG/MS) to polymers is given in Figure 15 which shows the effect of adding molybdenum trioxide to poly(vinyl chloride). The reduction in the emission of benzene ($m/z = 78$) brought about by the incorporation of the additive is clearly evident.

Although both IR and MS are valuable techniques for the identification of evolved gases, in many cases a mixture of decomposition products are evolved simultaneously. Several workers have added the capability to perform online[52] or offline[53] gas chromatography to separate the effluent into individual components which can then be identified by MS. Such approaches essentially attach an analytical laboratory to the end of the humble thermobalance and make this an appropriate point at which to conclude this review of the applications of TG of polymers.
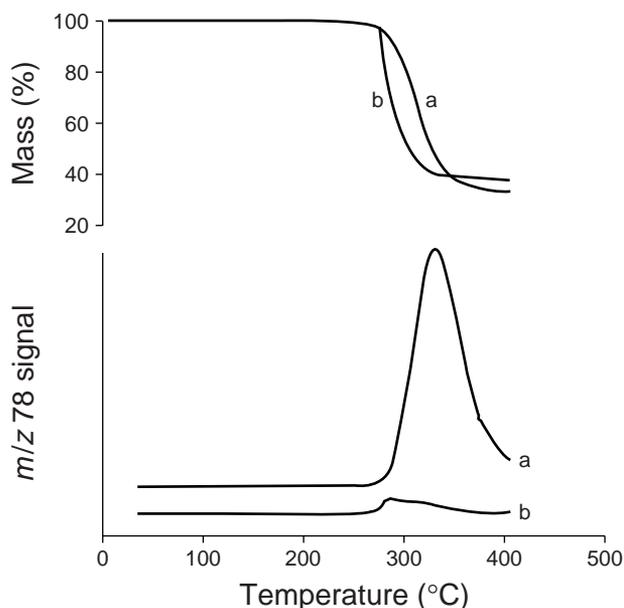

Figure 13 TG/IR curves of cellulose acetate plasticized with dioctyl phthalate.
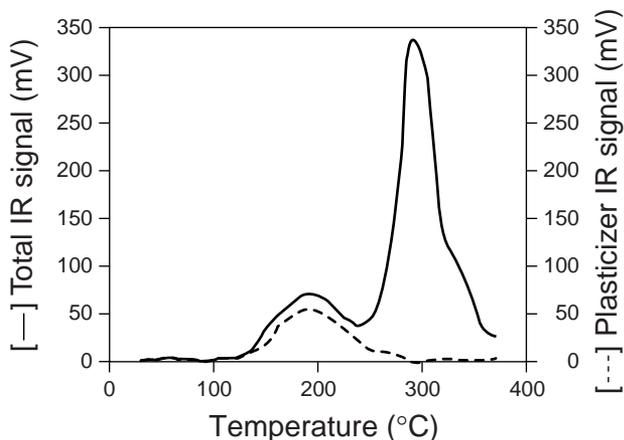
Figure 14 Total IR detector signal and signal due to dioctyl phthalate of plasticized cellulose acetate.

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article to the memory of Dr C.J. Keattch (1928–1999), author of Reference 1 and the first secretary of the Royal Society of Chemistry Thermal Methods Group (1965–1999).

LIST OF SYMBOLS

α	extent of conversion or fraction reacted
A	frequency factor
$d\alpha/dt$	rate of reaction
dm/dt	first derivative of mass change with time
dm/dT	first derivative of mass change with temperature
dT/dt	first derivative of temperature with time (i.e. heating rate)
E_a	activation energy
k	rate constant
L	logarithm of the amplitude of the rate of mass loss over one modulation (mt-TG)
m/z	mass to charge ratio
R	ideal gas constant
T	thermodynamic (Kelvin) temperature
T_{av}	average thermodynamic temperature (mt-TG)
T_{amp}	amplitude of temperature modulation (mt-TG)

ABBREVIATIONS AND ACRONYMS

DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
IR	Infrared
MS	Mass Spectrometry
mt-TG	Modulated-temperature Thermogravimetry
SCTG	Sample-controlled Thermogravimetry
TG	Thermogravimetry
TG/DSC	Thermogravimetry/Differential Scanning Calorimetry
TG/IR	Thermogravimetry/Infrared Evolved Gas Analysis
TG/MS	Thermogravimetry/Mass Spectrometry Evolved Gas Analysis

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