

Thermal Analysis of Polymers

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M. P. Sepe

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M. P. Sepe

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1 INTRODUCTION

The term thermal analysis refers to a collection of analytical techniques designed to provide information about materials by observing structure and property changes that occur with changes in temperature. Just as spectroscopy is an umbrella term for a variety of complementary methods such as infrared, ultraviolet and nuclear magnetic resonance, which are designed to study different aspects of a material's chemical makeup, so thermal analysis is inclusive of several methods which have unique capabilities but which also overlap in their ability to provide a complete picture of a material's properties. This report will review the use of these techniques as they are used in the analysis of polymeric materials.

Thermal analysis techniques are used for a wide variety of materials, but they seem uniquely suited to the study of polymers because these methods are sensitive to structural changes which are unique to substances composed of large, extended chain molecules. Whereas classical materials possess structural uniformity at the molecular level, and present relatively simple phase transitions such as melting points and boiling points, polymers are capable of a wide variety of structural arrangements owing to the complexity and non-uniformity of the individual molecular units. The molecular weight of classical compounds becomes a molecular weight distribution in polymers. Crystalline and amorphous regions coexist within the same matrix and vary in concentration as a function of processing and environmental treatment. Additionally the distinction between solid and liquid blurs in the phenomenon of viscoelasticity; polymers are a constantly changing balance of elastic solid and viscous fluid that makes considerations of time or frequency as important as those of temperature. Thermal analysis in polymers owes its success to the ability to measure events which reveal important aspects of these unique structures.

Historically, thermal analysis has developed along with the modern commercial polymer industry, providing an invaluable array of tools that assisted in the drive to create and perfect new polymeric materials. At the same time, the need for increasingly detailed information about polymers spurred the development of new techniques which were capable of measuring properties that were the unique province of polymer behaviour. As the computer has been used increasingly to model and predict the behaviour of polymers in manufacturing and in end use, the data produced by thermal analysis techniques has proved indispensable.

This report will provide an overview of the thermal analysis techniques that currently receive the greatest attention in polymer analysis. Each section will be devoted to a single technique, although the complementary nature of these techniques will make some overlap necessary in providing a review of recent original work. If a technique is not discussed in this review, such as in the case of differential thermal analysis (DTA), it is because another more widely used technique provides the same information, and is more suited to the specific study of polymers.

2 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) are related techniques that measure the same thermal events with different methods. DSC monitors the difference in heat flow between a sample and a reference as the material is heated or cooled while DTA measures a difference in temperature. There are two types of DSC instruments in commercial use today. One is known as a "heat flux" design while the other is referred to as a "power compensation" instrument. While each type has its adherents, the essential information extracted by this technique is not influenced significantly by the two approaches. An excellent review of the principles for each instrument can be found in supplier literature and a recent overview has been provided by Hatakeyama and Quinn (a.1). The information and examples provided in this review come from a heat flux design instrument.

In essence, both heat flux and power-compensated DSC's use a temperature difference between a sample and a reference as the raw data and in that sense they operate very much like a DTA. Both types of DSC instruments convert temperature difference into a measurement of the energy per unit mass associated with the phase change that caused the temperature difference to arise. Any transition in a material that involves a change in the heat content of the material can be detected and measured by DSC.

Figure 1 shows a cross section diagram of a DSC cell which operates by the heat flux method. The cell uses a constantan disc as the means of transferring heat to the sample and the reference positions. The sample is contained in a metal pan and the reference is an empty pan of the same material as the sample pan. The most

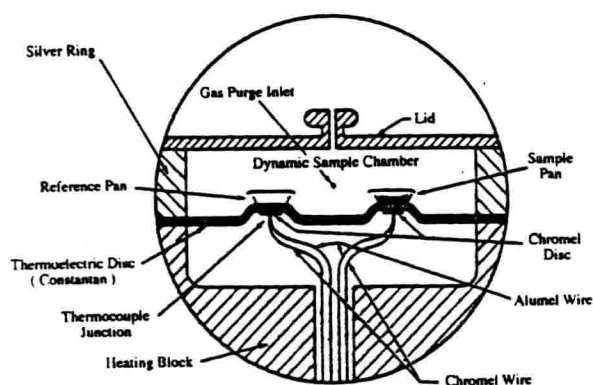


Figure 1

Cross-section of heat flux DSC cell

Source: TA Instruments

common material used in sample pans is aluminum. Most DSC cells have an upper operating temperature of 700-725°C, and aluminum, which has a melting point of 660°C, can accommodate most test regimens. For more demanding heating routines, or for materials where the aluminum might interact with the test material, copper, gold, or graphite may be used or samples may be encapsulated in glass ampoules. The sample and reference pans sit on raised platforms formed in the constantan disc. As heat is transferred through the thermoelectric disc, the differential heat flow to the sample and the reference is measured by thermocouples formed by the junction of the constantan disc and chromel wafers which cover the underside of the platforms. Chromel and alumel wires attached to the chromel wafers form thermocouples which measure the sample temperature directly. Purge gas is introduced to the sample chamber through an orifice in the heating block wall. The purge gas is typically nitrogen but may

also be argon or helium. Oxidizing gases such as air or oxygen can be introduced to observe specific chemical reactions.

Figure 2 shows a generalized plot illustrating the physical and chemical changes measurable by DSC. The x-axis is usually temperature but may also be time, while the y-axis is usually heat flow in energy units or energy per unit mass. Reactions may be endothermic or exothermic, and different instruments employ different conventions for displaying the graphical data. Some instruments show exothermic transitions as downward trends and endothermic transitions moving upward. Others use the opposite notation. The results shown in this review will use the latter convention which is shown in Figure 2.

2.1 Crystallinity (43,54,91,153,164,167)

A primary use of DSC in polymer analysis is the detection and quantification of the crystalline melting process. Since the crystalline state in a polymer is influenced by inherent properties such as molecular weight distribution and the stereoregularity of the chain as well as by processing and subsequent environmental treatment, this property is of considerable importance. Often when a new polymer is first produced, DSC is the technique of choice for identifying the presence of a crystalline component. Figure 3 shows melting endotherms for several well known semi-crystalline polymers. The melting point is typically taken as the peak of the melting endotherm. The latent heat of fusion for the event is the area under the curve from beginning to ending baseline. This number is often used to calculate the degree of crystallinity for a polymer by

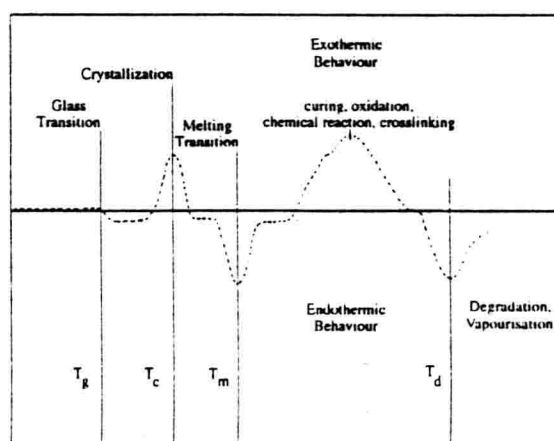


Figure 2

Generalized DSC curve

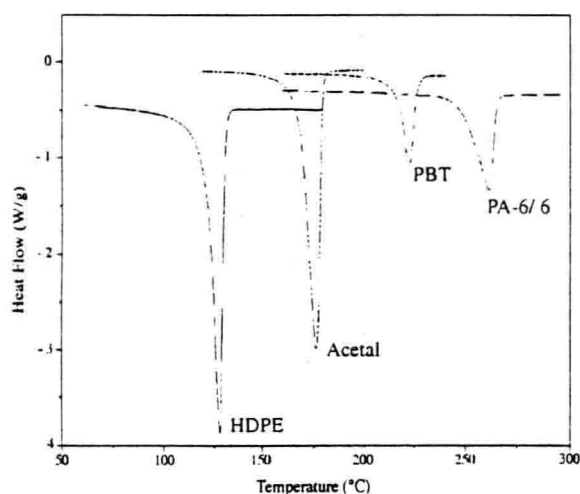


Figure 3

Melting endotherms of unfilled semi-crystalline polymers

dividing the heat of fusion for the polymer sample by the heat of fusion for a 100% crystalline analogue.

Recrystallization appears as an exothermic process and may be detected during cooling from the melt. Typically the heat of recrystallization from the melt will be very close to the heat of fusion, but the temperature will be offset to a lower value as shown in **Figure 4**. Some polymers are slow to crystallize due to a highly aromatic backbone structure. Rapid cooling of these materials will produce a structure which is amorphous but capable of solid state crystallization. In these cases, the recrystallization exotherm can be observed when the quenched material is reheated. The energy

associated with the exotherm will be strongly dependent upon the original cooling rate from the melt. Commercially significant polymers in this slow-crystallizing family are poly(ethylene terephthalate) (PET), poly(phenylene sulphide) (PPS), and poly(phthalamide) (PPA).

DSC can be used to study the formation of multiple crystal types that arise due to different thermal histories. Nylon 6/6 and poly(butylene terephthalate) (PBT) are notable members of this group. **Figure 5** shows this effect for PBT. The relationship between melting point and crystal thickness can be used to evaluate polymer microstructure using appropriate thermal treatments to

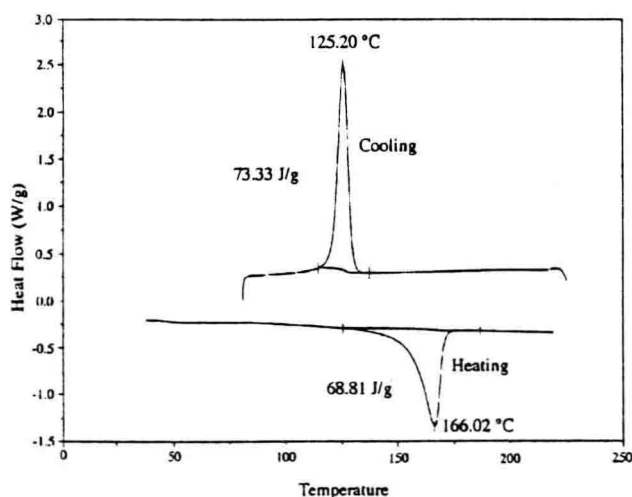


Figure 4

Melting and recrystallization of polypropylene homopolymer, heating and cooling rate of 10°C/minute

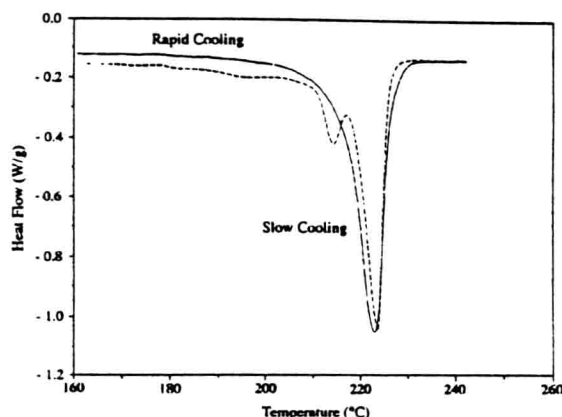


Figure 5

Melting endotherm of PBT polyester cooled from the melt at different rates

fractionate the different crystal types. Recent work on linear low-density polyethylene (LLDPE) utilizes a procedure which rapidly cools material from the melt to successively lower temperatures. At each isothermal step, the material is held for a period of time to allow for complete crystallization. The material is then reheated in a conventional manner and the different melting endotherms are quantified. Quantitative determinations of the chemical composition compare very favourably with the more sophisticated and time-consuming techniques of thermal rising elution fractionation (TREF) and ^{13}C nuclear magnetic resonance (NMR) (54,140). In general, interpretations of complex melting processes observed by DSC require elucidation by supplemental methods such as Fourier transform infra-red (FTIR) spectroscopy, size exclusion chromatography (SEC), and small-angle X-ray scattering (SAXS).

2.2 The Glass Transition (86,98,180,187,201,202,247)

Many polymers do not crystallize under normal conditions and even semi-crystalline polymers contain a significant amount of material that remains in the amorphous state. Without crystals there can be no melting point, however the amorphous regions do undergo an important phase change known as the glass transition. The glass transition is defined as the onset of conjugated main chain motion, a phenomenon where extended sections of individual chains become capable of independent motion. In amorphous polymers the

glass transition signifies a softening of the polymer; the modulus of the material will decline by two to four orders of magnitude and the material is no longer useful as a load-bearing entity. In semi-crystalline and crosslinked polymers the glass transition represents the onset of significant changes in a wide variety of mechanical, thermal, and even electrical properties. As an example, modulus may decline 75-85% for a neat polymer. Addition of glass fibre may reduce this loss to 40-50% but will not change the transition temperature. DSC detects the glass transition as a step change in the heat capacity of the polymer. **Figure 6** shows the identification of the glass transition for polycarbonate. The inflection point of 148.12°C is considered to be the glass transition temperature and the associated value in watts/gram is the magnitude of the step transition. While polymer scientists are accustomed to referring to a glass transition temperature, the graph shows that the event spans nearly 5.5°C , with the onset occurring near 144°C and the end of the transition positioned at 149.41°C .

Several thermal analysis techniques are used to measure the glass transition temperature (T_g) and there is considerable discussion in the literature about the best method for identifying T_g . Because the glass transition is a relaxation phenomenon, the measurement is dependent, in part, upon the heating rate employed in the experiment. Other factors affecting the glass transition are molecular weight, molecular weight distribution, degree of crystallinity, orientation in fibres, and stereoregularity. DSC can be used to evaluate the effects of these factors on this very important property. While the changes in heat content associated with the

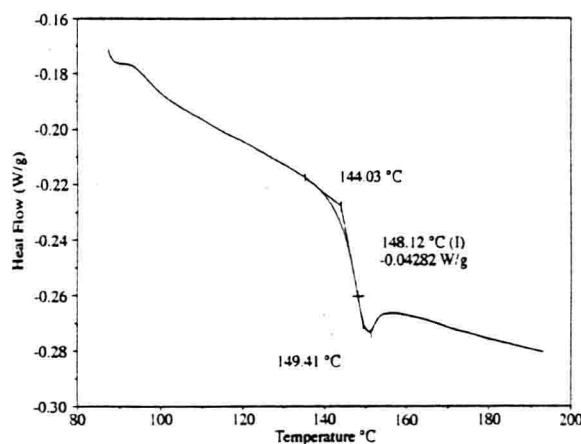


Figure 6

DSC scan for polycarbonate showing the glass transition

glass transition are easily detected in amorphous polymers, highly crystalline and crosslinked systems can be more difficult to work with. **Figure 7** shows the glass transition for a quenched and a properly crystallized sample of PPS. The quenched sample is primarily amorphous and exhibits a strong and easily detected glass transition. The properly crystallized material has a much smaller amorphous fraction and without prior knowledge of the value for T_g it is difficult to locate. This problem is aggravated by the fact that the other transitions such as recrystallization and melting take place on a much larger scale and serve to obscure the glass transition. In addition, DSC sample sizes are relatively small, typically about ten milligrams. When taken from a moulded part, significant differences may be detected between the outer layers and the interior of a moulded part due to

differences in orientation and cooling rates. Thus it can be dangerous to draw too many conclusions about the bulk properties of material from a single sample. Nevertheless, DSC is widely used because of its convenience and its ability to accommodate small samples in a variety of forms, including powders and liquids.

2.3 Characterization of Blends and Copolymers (92,102,104,108,121,122,181)

Blends and copolymers exhibit changes in the glass transition temperatures and the melting points of the component polymers. Miscible blends, which typically involve two amorphous polymers, are identified by the formation of a single T_g which is dependent upon the

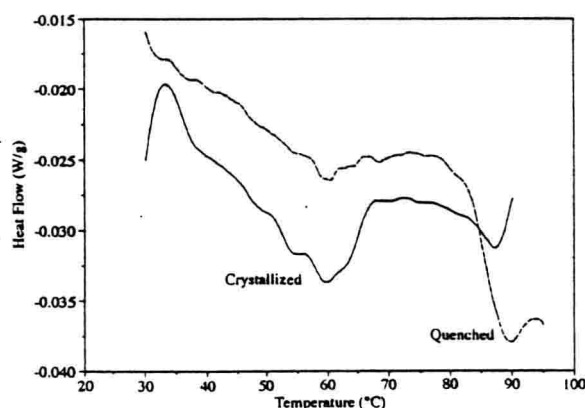


Figure 7

The effect of cooling rate on the strength of the glass transition in reinforced PPS