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SOME APPLICATIONS OF DIFFERENTIAL SCANNING CALORIMETRY FOR THE ANALYSIS OF POLYMERS*

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ABSTRACT

Applications of differential scanning calorimetry (DSC) have continued to grow in many diverse areas. It is the purpose of this paper to discuss some of the newer applications of DSC for the analysis of polymers. Applications include: heat-sealing characteristics of polyethylene, determination of additives, the cross-linking of polyethylene by peroxides and the analysis of impact polystyrene.

INTRODUCTION

Differential scanning calorimetry (DSC) has gained wide acceptance for the analysis of polymers. Some of the applications are so well accepted that they have become routine in many analytical laboratories. These include the determination of glass transition temperatures, melting points, percent crystallinity, crystallization and polymerization kinetics, and the evaluation of thermal stability among many others. DSC has been applied to both thermoplastics and thermosets. It is the purpose of the following discussion to demonstrate some of the newer applications of differential scanning calorimetry.

EXPERIMENTAL

A Perkin-Elmer Model DSC-2 differential scanning calorimeter was used for all measurements. With an instrument of this type, both transition temperature and transition energy are obtained simultaneously. The DSC-2 was calibrated for temperature using materials with known temperatures of fusion. The improved temperature linearity of the Model DSC-2, as compared with the Model DSC-1B, requires only two such materials. Calibration for energy was made by measurements on accurately weighed samples of high purity indium (indium is supplied with the instrument along with other calibration standards) taken to have a heat of fusion of 6.79 cal g^{-1}.

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Since, like the DSC-1B, the calorimetric response of the DSC-2 has been shown to be independent of all instrumental or experimental variables, a single point calibration is sufficient. All samples were precisely weighed with a Perkin-Elmer autobalance, Model AD-2.

RESULTS AND DISCUSSION

The following is intended to illustrate some of the broad range of applications of DSC for the analysis of polymers and some typical experimental conditions such as sample weight, scan speed and sensitivity.

Heat-seal polyethylene

The heat-sealing properties of polyethylene are very sensitive to melting range and crystallinity. This is illustrated in Fig. 1 where three different types of polyethylene, low-, medium-, and high-density, were scanned over their melting region.

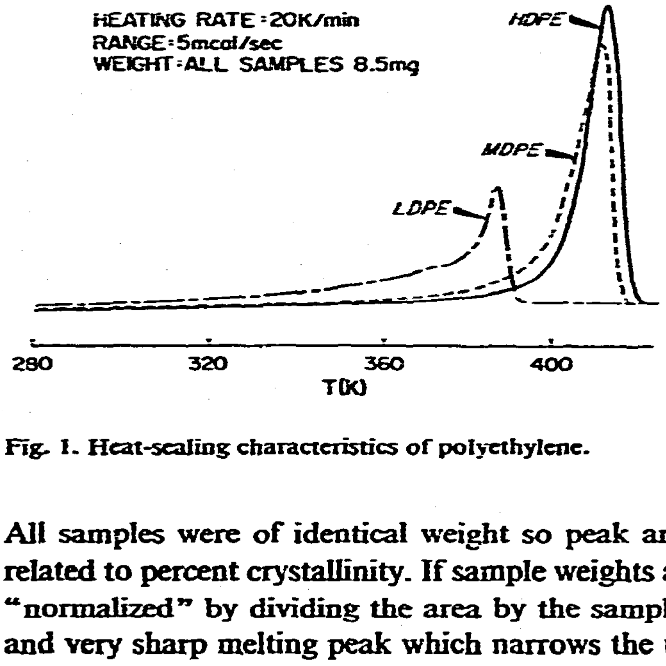

Fig. 1. Heat-sealing characteristics of polyethylene.

All samples were of identical weight so peak areas may be compared directly and related to percent crystallinity. If sample weights are not the same, peak areas may be "normalized" by dividing the area by the sample weight. HDPE melts with a high and very sharp melting peak which narrows the useful range of heat-sealing temperatures. This particular sample melts over a temperature range of about 380 to 410 K, thus the heat-sealing range is rather narrow. MDPE has a wider melting range but is still high in crystallinity and has a melting point, as indicated by the temperature of the peak of the curve, almost as high as HDPE. Both conspire to reduce the usefulness of MDPE for heat-sealing applications.

In contrast, LDPE melts over a very wide temperature range and produces a melting peak which is very broad, small in area (indicating low crystallinity) and peaking at a much lower temperature than either HDPE or MDPE. These features make LDPE ideal as a heating-sealing material. On a routine basis then we can test polyethylene to insure it has the proper melting characteristics before a large batch of material has been used, or conversely to determine the heat-sealing range of a polyethylene, or any other similar material for that matter, for the proper setting of sealing temperatures.

Poly (ethylene terephthalate) film

One of the most important forms of polymer materials is film. Film can be made by a wide variety of techniques from an ever expanding variety of polymers. Typical of the polymers used in film applications is poly (ethylene terephthalate). The high crystallinity and melting point of poly (ethylene terephthalate) produces a useful high strength film which enjoys numerous applications. The procedure for drawing a heat crystallizable polymer, such as poly (ethylene terephthalate), involves at least two steps generally carried out at two different temperature levels. First, the drawing or stretching of the amorphous polymer is carried out at a temperature higher than the glass transition temperature, T_g; and, second, the polymer is subsequently heated to a higher temperature to induce crystallization and heat setting which also freezes in the oriented structure.

Using DSC it is possible to determine these processing temperatures. For example, Fig. 2 shows a wide range temperature scan on a poly (ethylene terephthalate) sample which had previously been quench cooled from the melt by cooling at the maximum rate in the DSC. In Fig. 2, three thermal events are evident. The first of these is the glass transition temperature at 354 K (81 °C), the second is an exothermic peak due to the cold crystallization of the sample centered at about 410 K (137 °C), and finally the high temperature melting peak. From this single curve we can determine typical processing temperatures for the film. First, the drawing of the film

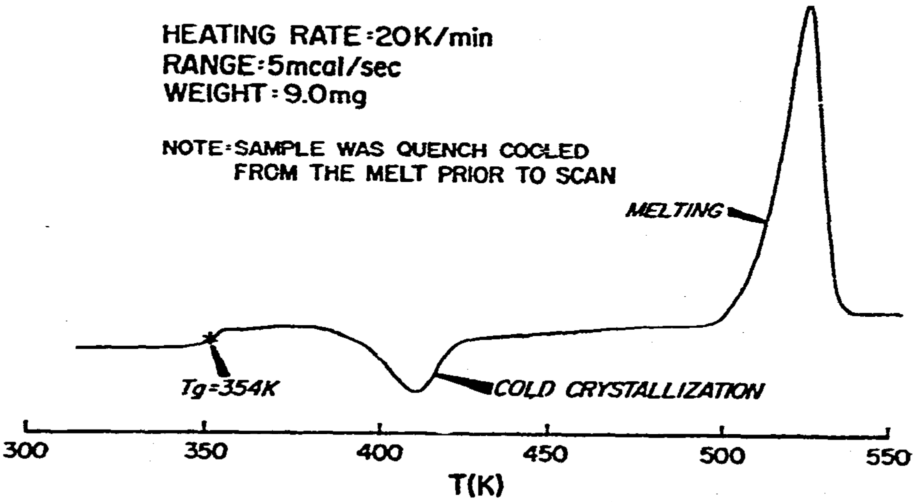

Fig. 2. Establishing processing conditions for polyester film.

must take place above $T_g = 354$ K but at a temperature below about 390 K where cold crystallization begins. Second, heat setting to induce crystallization must occur above about 425 K where cold crystallization is complete but below the onset of melting at about 500 K. Heat setting at too high a temperature would permit rapid motion of the polymer and reduce, or even completely negate, any orientation that had been achieved. A similar procedure could, of course, be employed to analyze other polymers used for film.

Determination of polymer additives

Polymers, in general, are essentially electrical insulators or non-conductors. Because of this, polymers may build up large charges of static electricity on their surface attracting dust particles and making the processing of these materials difficult either by the discharge of the static charge on handling or by attraction of or adherence to other materials. To alleviate or at least reduce some of these problems, anti-stat substances are frequently employed. These anti-stat materials work by providing a conductive path for bleeding off any static charge which may have accumulated.

In some instances, DSC may be used to quantitatively determine the amount of anti-stat which had been blended into a polymers. An example of this determination is shown in Fig. 3. Two runs are initially required. The first of these is shown at the top of Fig. 3 and is the melting curve for the pure anti-stat to determine its heat of fusion, in this case, 10.1 mcal mg^{-1}. Knowing this value we can then proceed to measure the amount of anti-stat which had been blended with a polymer. The run at

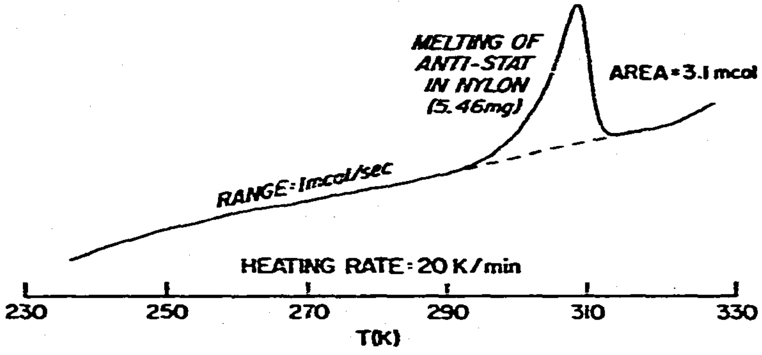

Fig. 3. Determination of anti-stat in nylon.

the bottom of Fig. 3 shows the melting of an unknown amount of anti-stat which had been blended into a sample of nylon. The area under this curve is the energy required to melt any anti-stat material which is present in the nylon. A summary of the calculation procedure is presented in Fig. 3 and involves two steps, first the amount of anti-stat in nylon is determined by dividing the energy necessary to melt the anti-stat in nylon by the heat of fusion of the pure anti-stat, and, second, the determination of percent anti-stat in nylon.

A similar procedure could be used to determine quantitatively the presence of other additives. Another example is shown in Fig. 4 where the amount of an anti-soil in nylon is determined. The procedure exactly parallels that of the previous example. First, the heat of fusion of the pure material is determined in the run at the top of the figure; and, second, the energy necessary to melt the unknown amount of anti-soil in a polymer (again, in this case nylon) is determined in the run at the bottom of Fig. 4. The calculation procedure is identical to that of the previous example.

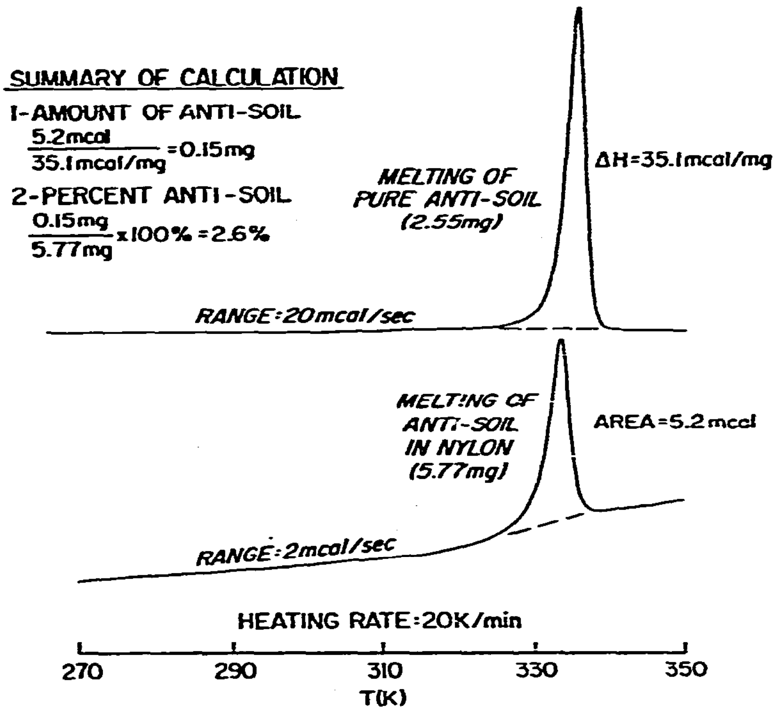

Fig. 4. Determination of anti-soil in nylon.

Cross-linked polyethylene

While there are a great number of exceptions to be noted, it is in general observed that the processing of a polymer to form a final product is easiest at low molecular weight while the properties of the finished product are better at high molecular weight. The processing of polymers is generally carried out at a constant molecular weight which represents the best compromise between processability and properties. For example, low-molecular-weight polyethylene is readily processed at moderate temperature but lacks some of the important properties of high-molecular-weight polyethylene which is relatively more difficult to process.

This situation can be improved upon by processing low-molecular-weight polyethylene while simultaneously cross-linking the material to achieve a higher molecular weight. An example of the DSC analysis of the cross-linking reaction and its effects is shown in Fig. 5. The dotted line is a scan of a LDPE sample which contains dicumyl peroxide, a cross-linking agent. As the sample is heated from 260 K, we see the expected melting endotherm peaking at 380 K. Upon further heating the cross-linking reaction occurs in the region 440 to 480 K. Cooling this sample and re-running over the same temperature range shows the results of the cross-linking, illustrated as the solid line in Fig. 5. As expected, the melting point, as indicated by the peak of the curve, has been lowered and; in addition, the crystallinity of the sample has been reduced as indicated by the smaller area under the curve. Finally, as we continue to heat the sample to 500 K, the cross-linking exotherm is no longer observed.

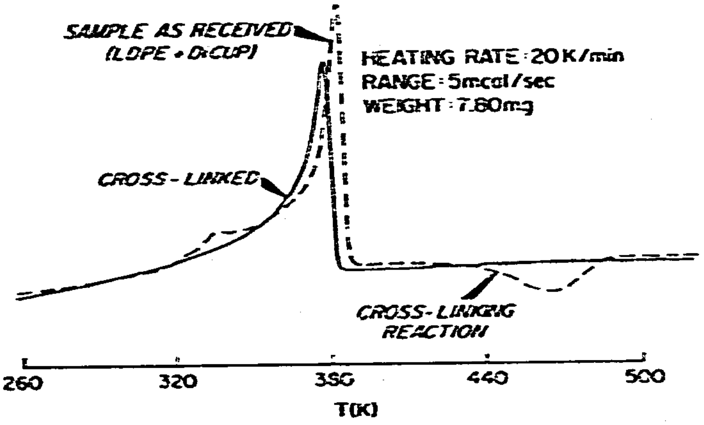

Fig. 5. Cross-linking of polyethylene by dicumyl peroxide.

A further example of this type of analysis is shown in Fig. 6. In this example, we observe the effect of cure time on a sample of polyethylene/ethylene vinyl acetate copolymer again containing the cross-linking agent, dicumyl peroxide. In this example, the sample was heated to an elevated temperature (450 K) in the DSC and held at that temperature for various periods of time. In each case the sample was subsequently cooled well below its melting point and re-heated in the DSC to observe the decrease in melting point with cure time. Even after a ten-minute cure time the melting point of the sample is still decreasing indicating that the optimum cure time at this temperature is greater than ten minutes. This procedure could, of course, be

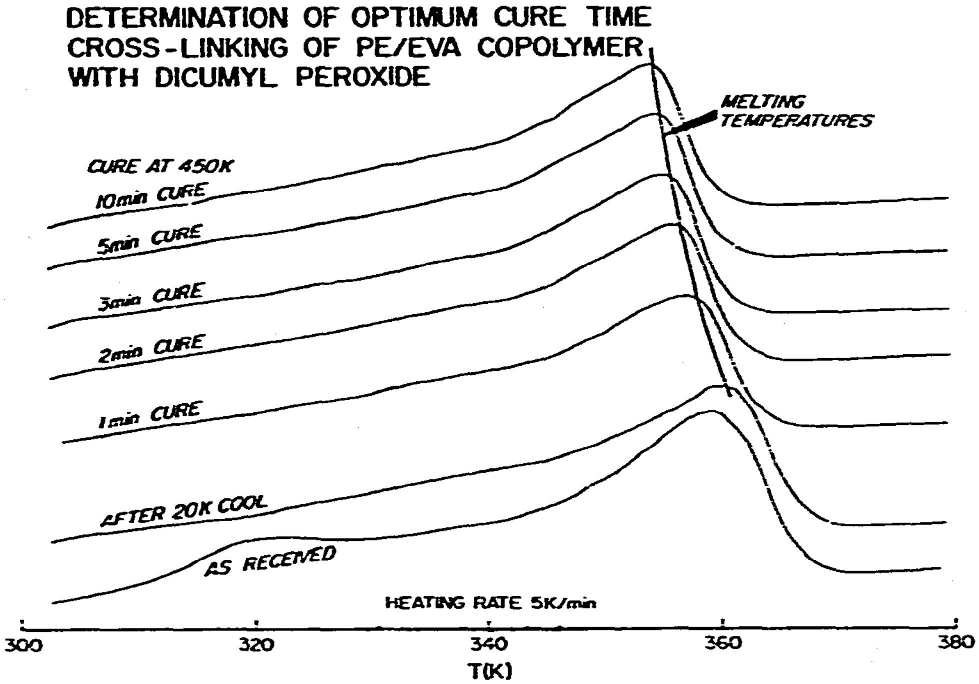

Fig. 6. Determination of optimum cure time. Cross-linking of PE/EVA copolymer with dicumyl peroxide.

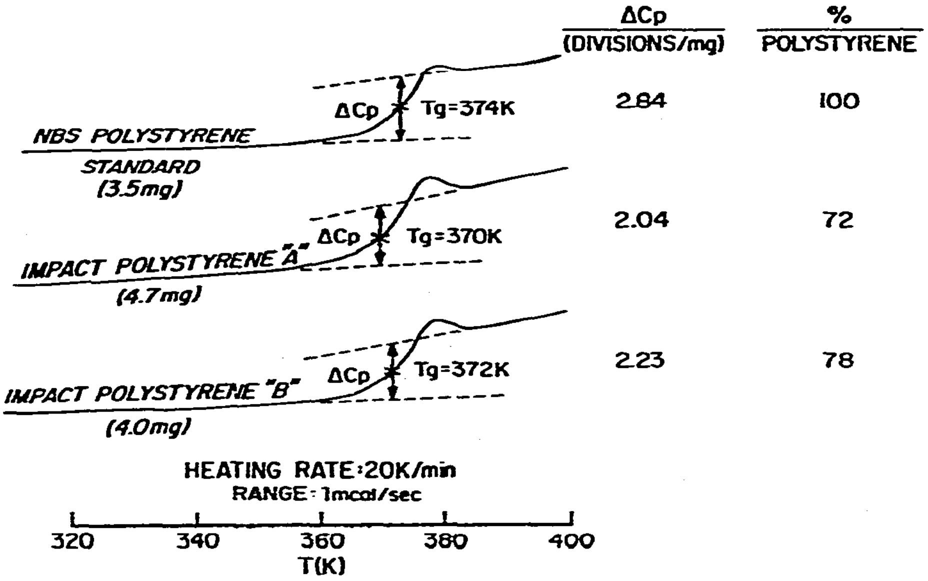

Fig. 7. Analysis of impact polystyrene blends.

continued for even longer cure times and also at different temperatures for the determination of the optimum time–temperature relationship.

Impact polystyrene

Polystyrene is a very useful engineering thermoplastic material but in some applications it lacks the necessary impact strength. To improve its impact strength, polystyrene is frequently blended with another polymer such as butadiene. The dispersed soft or rubbery phase provided by butadiene contributes to certain critical properties, for example, processability and most importantly, resistance to high-speed impact. In such two phase polyblends each phase retains its individual properties and each phase will exhibit its separate glass transition temperature. This last observation permits us to determine the styrene/butadiene ratio in this impact polyblend by the application of a DSC technique.

Figure 7 shows this determination for two different impact blends, "A" and "B". The first step in the procedure is the determination of the ΔC_p of polystyrene as the sample is heated through its glass transition. This value is recorded as chart divisions per milligram. This is followed by heating the impact blend through the glass transition region of styrene. Since only styrene contributes to the increase in specific heat in this region, it becomes a routine calculation to determine percent styrene in the impact blend by dividing the ΔC_p for the impact material by that of the styrene standard.

Polyester resin-isothermal cure

Low-molecular-weight polyesters are viscous liquids or brittle solids which are soluble in an appropriate solvent. Upon the application of heat and perhaps after the addition of catalysts or accelerators, polyesters are cured to form a highly cross-linked structure providing rigidity, impact strength and chemical resistance. Polyesters of this type are frequently used for the impregnation and lamination of glass fabrics. Polyesters are also frequently used as a protective coating.

The cross-linking or curing reaction is generally carried out isothermally, and we can follow the progression of the curing reaction by DSC. A typical example is ˙ ..rated in Fig. 8, where the curing of a polyester resin was carried out at 380 K. ..itially, the components are mixed and placed into the DSC cell at room temperature (about 300 K) where the reaction occurs either not at all or so slowly as to be unobservable. The sample is then rapidly heated at 320 K min^{-1} to the desired curing temperature, in this case, 380 K. To carry out this type of experiment successfully, the instrument must be capable of very fast heating rates and very fast equilibration times so that essentially all of the curing reaction occurs during the time the sample is at the curing temperature and not in the time period it takes to reach the desired curing temperature. The exothermic release of heat continues for the duration of the curing reaction. Here the reaction went to completion in 28 min. The area under this curve is equal to the total heat of curing. In addition, we can determine the percentage of cure for various cure times. For example, the percentage completion of the cure in

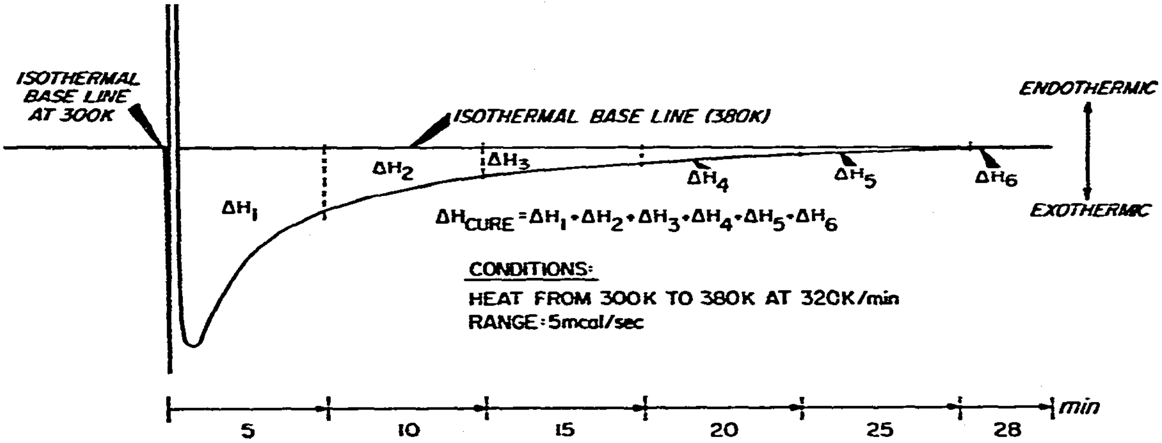

Fig. 8. Isothermal cure of a polyester resin at 380 K (225 °F).

5 min is equal to $\Delta H_1/\Delta H_{\mathrm{cure}}$. A similar procedure could, of course, be employed to determine the extent of cure for other time intervals. In addition, all of the necessary information to perform a kinetic analysis of the curing cycle is contained in this single experiment.

CONCLUSIONS

Differential scanning calorimetry is a useful, if not indispensable, technique for the analysis and quality control of polymers. With only a few milligrams of sample, DSC readily provides a wide variety of information on polymers which is difficult or impossible to obtain by other analytical techniques. Analysis time is short, the methods are relatively simple and straight-forward making DSC an ideal technique for either basic research or routine quality control.