

Transition Measurements Using Differential Thermal Analysis Techniques

MARK L. DANNIS, *B. F. Goodrich Research Center, Brecksville, Ohio*

Introduction

Differential thermal analysis (DTA) techniques have been well known in the metallurgical and ceramic fields for many years, but they have only recently been adapted to the study of polymer structure and properties. Reviews discussing both older techniques and some applications to polymer studies appeared recently.¹⁻⁴ In most polymer applications discussed so far, the changes in heat balance have been measured against an inert reference body, preferably having thermal diffusivity characteristics which closely match those of the polymer. The technique presented in this paper differs from conventional procedure in that the inert reference body is eliminated. The differential measurement is obtained from a thermal delay within the sample itself. Other changes in procedure arising from the low thermal conductivity of organic polymers compared to metallic alloys have resulted in a DTA system particularly adapted to studying the first- and second-order transitions of rubbers and plastics in the temperature range from about 90 to 500°K.

Transition temperatures, representing changes in state of a polymer, are important in defining the limits of rubbery or glassy behavior and in understanding peculiar physical properties which may change with temperature. While a useful system for measuring transition temperatures using a thermal expansion technique evolved in this laboratory has already been described,⁵ the DTA technique provides another tool for investigating the same phenomena, giving a better description of events which take place in the transition regions.

Apparatus and Theoretical Background

Differential thermal analysis techniques are based upon the measurement of a heat flux and/or a heat capacity effect. These measurements are usually conducted in a system that is being warmed or cooled at a programmed (or constant) rate, in order to establish a steady state condition of heat transfer, resulting in a fairly constant rate of temperature rise in the sample. The properties of polymers are such, however, that constant heat flux inputs (or losses) do not result in fixed rates of temperature change, inasmuch as the heat capacity of polymeric materials changes with tem-

perature. Hence, deviations in the rate of rise indicate changes in the phase structure of the material.

While curves showing changes in heat capacity with temperature have been published by many authors, the data on the heat capacity of natural rubber⁶ reproduced as Figure 1 can be regarded as typical. The abrupt change in heat capacity at 200°K., without measurable endothermic or exothermic changes, has led to the definition of this change as a second-order transition, taking place at the glass temperature T_g . This definition, from the thermodynamic variables of heat capacity C_p and enthalpy H , corresponds exactly to the definition of T_g from specific volume and thermal expansion relationships. From an experimental point of view, it is obvious that a calorimeter experiment using natural rubber conducted below about 200°K. will show a larger temperature rise for the same energy input than a similar experiment conducted just above 200°K. While T_g can be detected by measuring the decreased rate of rise of temperature at steady rates of

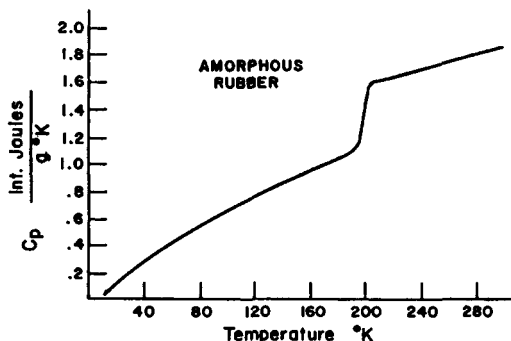


Fig. 1. Heat capacity of natural rubber (Bekkedahl and Matheson, ref. 6).

heat input to a calorimeter, the small difference in C_p can be lost in the usual type of experiment if conducted with fairly large temperature steps.

However, the change in heat capacity can be easily detected in steady heat-rate experiments by directly measuring the temperature drop across the sample. Obviously, as the heat capacity of the sample increases, a larger heat sink becomes available, and *at fixed energy input* the thermal head across the sample must increase. This concept is easily visualized in the illustration of a rubber sample confined in a rectangular slab calorimeter, heated at a fixed energy input rate as shown in Figure 2. A differential thermocouple probe can be used to plot the temperature differential profile within the calorimeter. Typical curves are illustrated for two temperatures above and below T_g showing the similarity of shape but different magnitudes. The corresponding experiment, in which the differential thermocouple is maintained in a fixed position, showing a rise in temperature drop (sic) as a polymer warms through the second-order transition region, is illustrated in Figure 2c.

This line of reasoning has been applied to a calorimetry system, evolving

into the DTA calorimeter illustrated in Figure 3 and an experimental arrangement shown in Figure 4. A cylindrical calorimeter confines a polymer sample in which are imbedded two thermocouple junctions. One is connected to an automatic millinolt recorder through a reference ice junction in the usual procedure for measuring temperature. The other junction is part of a differential thermocouple measuring the temperature

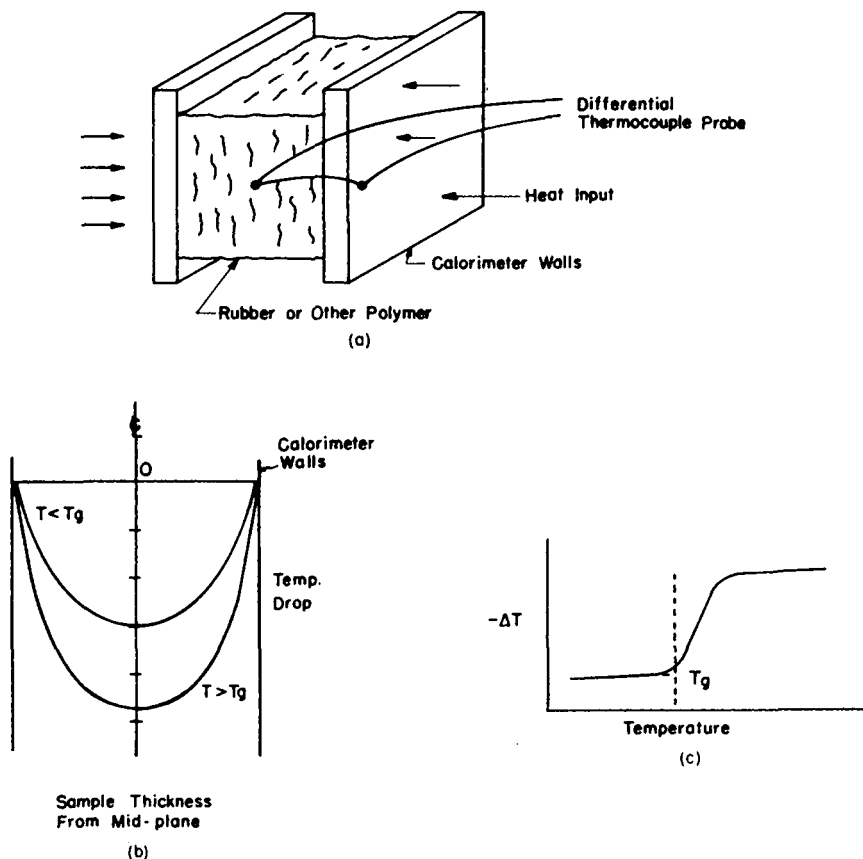


Fig. 2. Concepts in heat flow calorimetry. (a) simple heat flow experiment, (b) temperature profiles in cylindrical calorimeters, and (c) temperature changes near the midpoint of a cylindrical sample.

drop across the sample, i.e., from the center to the surface. Since the copper case has a very high thermal conductivity compared to the sample, the differential junction at the surface of the sample can be conveniently located on the calorimeter shell itself, under a screwhead. The thermojunctions within the rubber are stabbed into place close to center using a hypodermic needle. The thermocouples, made of No. 38 gauge (later No. 40) wire, are threaded through the needle lengthwise and remain in the rubber

after the needle is withdrawn from the sample. Fine slots in the calorimeter rim provide clearance for the wires.

The e.m.f. from the differential thermocouple is too small to register on the 10-mv. Minneapolis-Honeywell recorder normally used. A very stable d.c. amplifier, Minneapolis-Honeywell type 2HA7, was used to boost the differential e.m.f. to a significant recording level. The record of the experiment then consists of two curves, the temperature of the sample and the temperature drop across (or within) the sample, both plotted as a function of time. These are called the "thermal record" and "differential curve," respectively. Two separate experiments are usually run simultaneously, utilizing the full capacity of the four-point recorder.

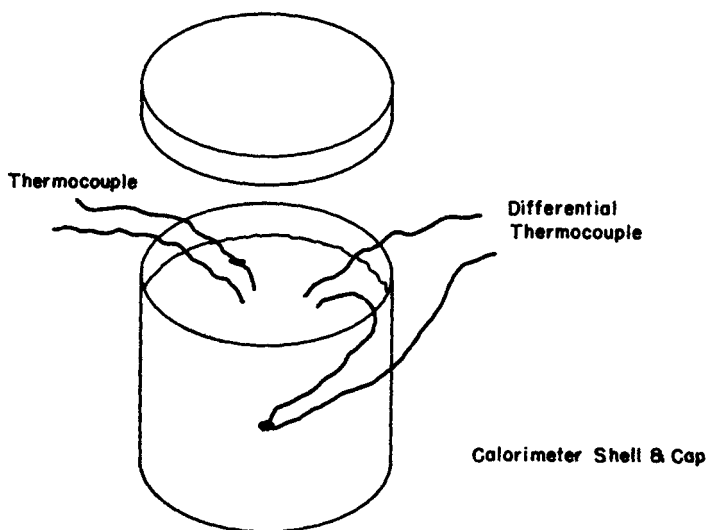


Fig. 3. Schematic arrangement of polymer in cylindrical calorimeter, with one probe and one differential thermocouple.

Roughly constant heat input can be obtained using three separate units of apparatus, each best fitted to a particular temperature range. Above room temperature, a small electrically heated oven is used, controlled by a clock-driven variable transformer. Below room temperature but above liquid air conditions, a small narrow-necked Dewar flask is used, sitting out on the laboratory workbench. While heat input to the sample is not constant, no confusing, abrupt breaks in the input curve are found. Practical heating rates impose a useful upper temperature limit about 0°C . upon this type of run. In the range from slightly below 0°C . to above about 40°C ., a "double Dewar" technique is used. The small Dewar is placed inside a larger one together with a heating jacket. Heat input is adjusted to give a satisfactory set of curves. All the heating rates are relatively low, usually less than $0.5^{\circ}\text{C}/\text{min}$.

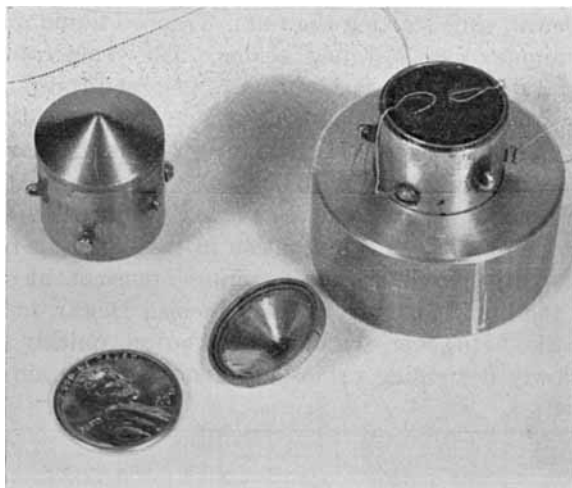


Fig. 4. Loaded calorimeter, showing terminals for securing thermocouples.

Experimental Results

A typical set of data is shown in Figure 5 obtained from a low temperature run on a sample of styrene butadiene rubber (SBR). For convenience of presentation, all these curves are displayed in the same manner as plotted by the machine with appropriate coordinates labeled. However, rather than the series of closely spaced points actually printed by the machine, smooth curves are shown.

Cooling of the sample by liquid air in its calorimeter prior to time zero is shown by the increasing negative value of the thermal record, until a steady state is achieved. The chilled calorimeter is then transferred to

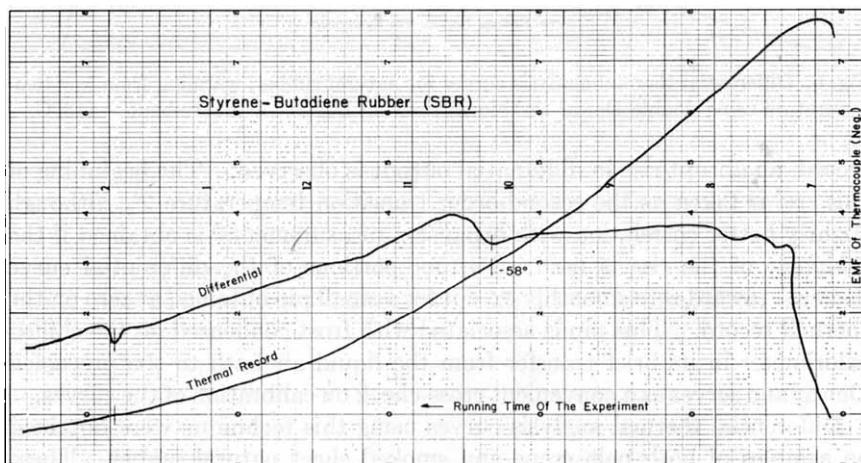


Fig. 5. Differential thermal analysis curves for SBR rubber, warming from low temperature in a Dewar flask.

a precooled Dewar, thus starting the run. Trapped liquid air evaporates after a few minutes and warming begins. The temperature increases steadily but at a decreasing rate as shown. A normal run takes about six hours to warm from about -180 to 0°C . The rate of rise at first is about $1\frac{1}{2}^{\circ}\text{C./min.}$, but decreases to less than $\frac{1}{4}^{\circ}\text{C./min.}$ near 0°C . The amplified differential output, the differential curve, associated with the temperature record, starts off-scale in the negative sense as the sample cools prior to time zero. As equilibration in the liquid air bath is established, the differential curve approaches zero. Transients at zero time and transfer from the liquid air bath to the precooled Dewar, make the start of the run erratic. However, the differential output quickly settles into a constant or slowly decreasing value. At about -3 mv. on the thermal

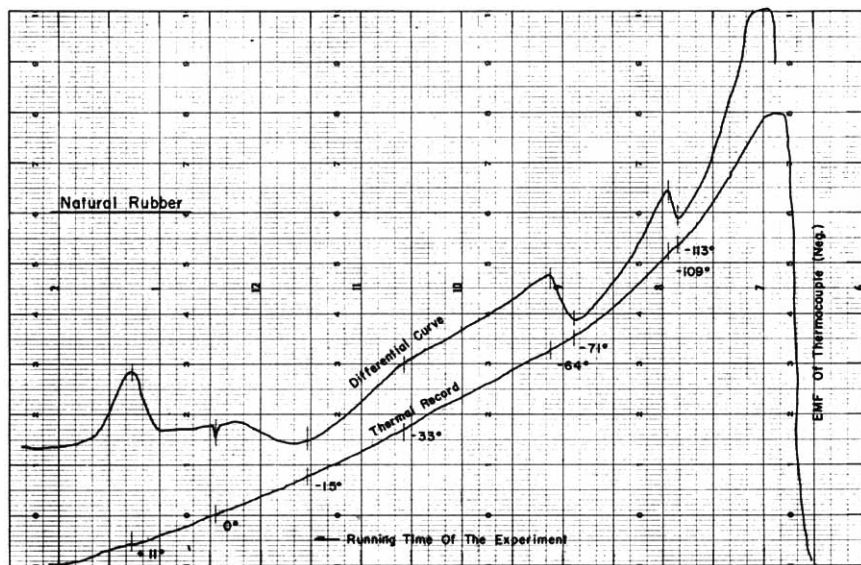


Fig. 6. Differential thermal analysis curves for natural rubber, warming from low temperature using double Dewar technique, showing Dry Ice artifact about -113°C .

record, an abrupt rise in differential output is observed. The beginning of this rise is taken as the second-order transition temperature T_0 , although slightly better correlation with expansion measurements⁵ is obtained if the midpoint of the rise is used. Further portions of the differential curve decrease toward zero smoothly except for a small pip obtained at zero on the thermal record. This pip is associated with frost condensed on the chilled calorimeter in its brief transfer from the liquid air bath to the precooled Dewar and serves as a convenient cross-check on calibration of the curves.

Differential thermal analysis curves using this technique were obtained on samples of both pale crepe and smoked sheet natural rubber. These were experimentally identical in their pertinent features, as shown in Figure 6.

Cooling prior to zero time and the subsequent warming curve are similar to that shown in Figure 5. In addition to the second-order transition identified by the prominent rise in the differential curve at about -71°C ., several other phenomena are displayed. A similar stepbreak in the differential curve at about -113°C . seems to be an additional second-order transition not previously reported. Above the well-known transition region about -70°C ., the differential curve starts to decrease slowly in the same manner as described before until about -33°C . on thermal record a more rapid decrease is noted. Pronounced curvature, not always repeatable, is found in the region between about -20 and -40°C ., after which the differential curve returns to a continuation of the smooth curve obtained before. This curvature, or "sag" in curve, represents a heat gain at a rate faster than expected. This additional heat is believed to have come from latent heat of crystallization liberated by the rubber.

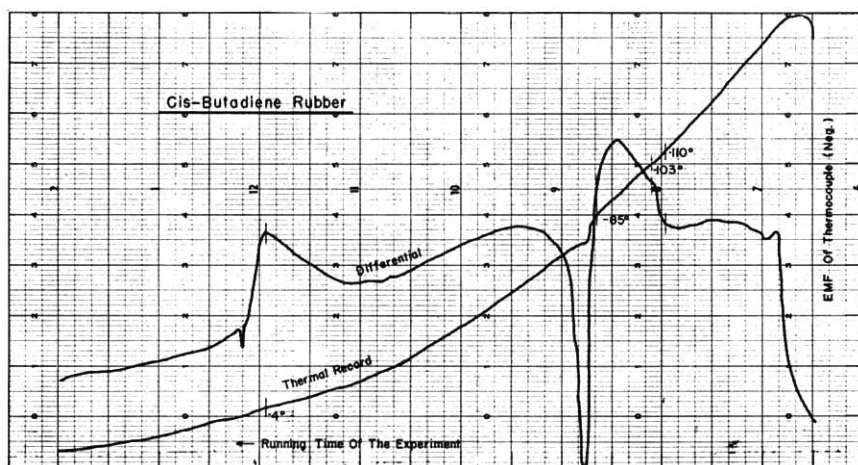


Fig. 7. Differential thermal analysis *cis*-1,4-polybutadiene rubber.

The thermal record is continued into the positive voltage region as warming is continued longer than usual. The differential curve shows a hump about 11°C ., as though the rubber had excess heat capacity near this temperature, but suffered no change in C_p above or below this region. This "hump" is not exactly repeatable in size or shape but does repeat within a narrow range of temperature, dependent upon the thermal history of the sample, suggesting that this is a melting point peak. The "excess heat capacity," then, is only the latent heat of crystallization which has to be supplied to melt the sample. The drop in the differential curve as the latent heat demand is satisfied represents the disappearance of last traces of crystallites and defines the melting point of the polymer under these experimental conditions.

Differential thermal analysis curves using this technique were obtained on a sample of *cis*-1,4-polybutadiene believed to have a *cis* content about

98% and are shown as Figure 7. This is the same material for which a differential expansion curve has been published.⁵

Cooling prior to zero time and the early part of the warming record are again similar to those shown before. However, about -85°C . an abrupt jump in warming curve is noted. Another change, a decrease in slope is also noted just below 0°C . The differential record starts off in a normal manner, decreasing slightly as the sample warms up. A rapid increase in value at -110°C . marks the second-order transition. An abrupt decrease in the differential curve resulting in an off-scale peak is associated with the break in the heating record. Subsequent return to the normal warming condition is followed by departure from this steady state condition beginning about -20°C . The differential curve rises to a

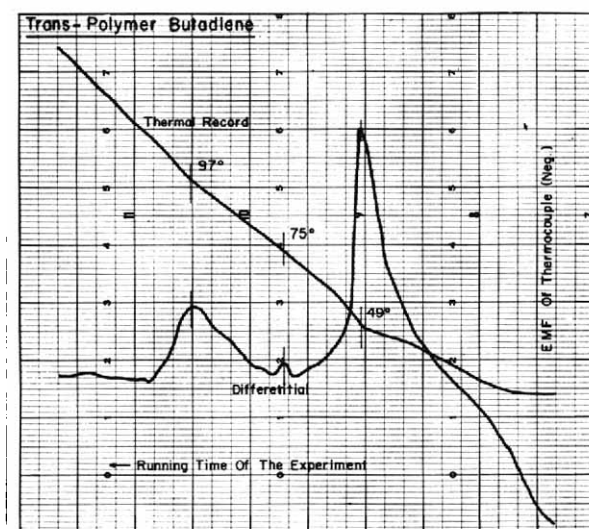


Fig. 8. Differential thermal analysis for *trans*-1,4-polybutadiene crystalline material.

peak about -4°C ., then falls to a low value as equilibrium is approached. The "frost peak" clearly identifies 0°C .

These curves show that high *cis*-polybutadiene rubbers are crystallizable materials that can be shock chilled to the amorphous glassy state by liquid air cooling. Subsequent warming first identifies the second-order transition region. Continued warming confers enough mobility on the polymer chains that some of the material can crystallize. Crystallization liberates heat of fusion, raising the temperature, further increasing the rate of heating accelerating the process to exhaustion. The liberated heat is sufficient to make a break in the thermal record and drive the differential curve off-scale in the negative sense. The crystallized rubber settles back into a steady state of warming until about -20°C . where melting begins. A heat deficit now exists such that heat of fusion must be supplied. Hence, the differential curve rises to a peak at -4°C ., at which the last traces of

crystallites have disappeared. Further warming to higher temperatures gives an uneventful record indicating no further phase transitions.

The crystallization peak of *cis*-polybutadiene at low temperatures can be reduced by cooling slowly enough that the material is fully crystallized in this treatment. The melting peak of the high *cis*-polybutadiene materials cannot be suppressed however, since the thermal treatment carries the material through the region of maximum crystallization rate slowly enough to fully develop a high crystalline content. The ultimate melting point of the high *cis*-polybutadienes is related to the *cis* content, a topic to be discussed in a subsequent paper.

Differential thermal analysis curves of this type were also obtained on a sample of polybutadiene having a *trans*-1,4 content believed to be about 90%, and are shown in Figure 8. This polymer is a hard, somewhat waxy material at room temperature which softens to a sticky rubber above 100°C.

The thermal record starts in equilibrium with room temperature then changes to a steady state warming curve shortly after the oven is turned on. A distinct break is noted about 49°C. Further warming gives relatively featureless thermal record up to the limit of the run. The differential curve rises from zero to a steady state, then abruptly traces a large peak matching the discontinuity in the heating curve. A second, much smaller peak, is encountered about 80°C., followed by a third endothermic peak at 97°C. This latter peak defines the melting point of the material; the other two represent crystalline phase transitions of a kind not often encountered in polymers. The α -, β -, γ -transitions of balata⁷ are the only comparable example known to this author. Natta and Corradini⁸ have described a strong crystalline transition occurring about 69°C. in a polybutadiene having a high *trans* content, prepared in their laboratory. Since melting points, identified by the disappearance of x-ray diffraction patterns, have been reported up to about 135°C., it is believed that the lower melting and phase transition temperatures of this particular sample merely reflect a lower *trans* content.

Differential thermal analysis curves have been presented showing typical behavior of amorphous and crystalline polymers. The technique is more general in its application to phase studies than indicated so far. Rubbers and plastics are rarely used in their pure condition but are compounded and cured to develop and enhance particular properties. While compounded rubbers can be studied easily by this technique to determine the effect of pigments and oils on the transition behavior, studies on the oils themselves have usually been restricted to determining chemical structure, i.e., aliphatic and aromatic contents or ester structure. This DTA technique offers an opportunity to determine the same transition properties on oils as are found for polymers. Two equivalent techniques differing only slightly are used. The calorimeter may be loaded with a thin cup which both holds the oil and locates the thermocouples. Alternately the calorimeter may be filled directly with the oil and the thermo-

couples held in place by an ordinary cellulose-type cement. This latter technique is preferred for polymeric liquids of high viscosity not likely to ooze out through the threaded screw holes in the calorimeter. Differential thermal analysis curves for a sample of paraffinic oil obtained using the cup technique are presented in Figure 9.

The thermal record appears similar to the curves discussed before. The differential curve again starts in a familiar manner. A rise in the differential record about -90°C . defines T_g for the oil. A slight dip in the differential record indicates crystallization at low temperatures, followed by warming in an uneventful manner to room temperature. The crystallization peak has been checked by running DTA curves up in temperature to the minimum of the dip, then rechilling in liquid air to start over. Any crystallization that took place in the first portion of the run is "frozen in" such that the second portion of the run no longer shows this exothermic

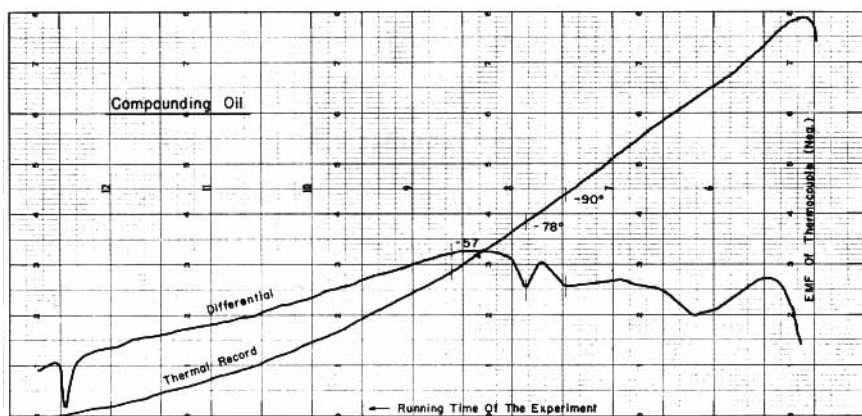


Fig. 9. Differential thermal analysis for a paraffinic compounding oil.

dip. An unambiguous melting point is not obtained, since the amount of crystalline phase is apparently small and seems to melt over a broad range of temperatures.

The analysis and technique presented has considered only "continuous" materials (i.e., rubbers, plastics, and liquids which have low void contents or are bubble-free). The system will work well on porous or powder charges, if due allowance is made for their inherently lower thermal conductivity. This factor increases the thermal head across the sample and spreads out peaks or rises at transitions to a level where some difficulty in recognition is encountered. Thus, while powders and crystalline preparations have been studied, locating the thermocouples by simple burial, an effort is made to compact powders to a dense plug. Artifacts from partial fusion or sintering are thus reduced to a minimum, and in the case of fluffy powders, dense packing results in a higher charge to the calorimeter raising the ratio of active to passive material.

Discussion

The DTA curve for natural rubber shows most of the phenomena encountered in this kind of measurement technique. The second-order transition at -70°C . is clearly shown, along with both weak crystallization and melting behavior. In addition, this curve shows a rarely found artifact directly relatable to the double Dewar technique used at that time. Because it was thought that this additional "break" at about -113°C . represented an additional second-order transition in *cis*-polyisoprene, a great deal of experimental time was devoted to either proving the existence of this additional second-order transition or trying to find its origin if an artifact. This break in the differential curve is directly related to the precooling procedure which uses Dry Ice as a refrigerant between the outer and inner Dewar flasks. The ambient temperature for the first portions of warming is roughly the sublimation temperature of Dry Ice, about -78°C . As the last portions of the Dry Ice evaporate, the heat flux from the outside is no longer shielded by this heat sink, and the differential curve for the rubber settles into a new higher steady state value. If the outer Dewar is chilled with liquid air rather than Dry Ice, both containers warm up smoothly, without producing artificial discontinuities in the differential curve.

Several materials have been found which do show several low-temperature second-order transitions. These are usually materials which have several kinds of subgroups within their structure, i.e., di-2-ethylhexyl sebacate which shows a glass transition at -93°C ., and an additional transition at -107°C . Incidentally, these phenomena are not third-order transitions, which theoretically cannot exist.

The second-order transition temperature of a polymer is a unique characteristic of a polymer, identifying it clearly.^{9,10} The T_g is not affected by simple mixture with an inert diluent, even when that "diluent" is another polymer.¹¹ Hence this DTA technique offers a way of distinguishing between true solutions involving polymers and finely dispersed but simple mixtures thereof. Mixtures show their own transition phenomena, both first and second order, entirely unaffected in temperature by other constituents, while solutions show large changes in T_g and small changes in T_m .⁹ While differential expansion techniques have been used to show that polychloroprene and natural rubber exhibit their own T_g in a mixture,¹¹ DTA curves seem to offer a more sensitive technique. Blends of natural rubber and SBR polymers show two separate T_g 's, indicating again the fundamentally insoluble nature of these two high polymers. While it must be admitted that certain polymers, such as this latter pair, can be dispersed in one another to make a smooth mechanical blend, it must be emphasized that these data show the blend to be no more than that. The polymers are truly insoluble in one another. Similar data on the insoluble nature of other pairs of high polymers lend support to the hypothesis that all high polymers are insoluble in one another. While one can visualize dispersions

down almost to a molecular scale, *true* insolubility must mean that the boundary surface of a polymer random coil volume is not penetrated by another polymer species. The obvious argument involving the solubility of two random copolymers having only slightly different proportions of constituents is recognized but not discussed herein.

The present DTA technique is being used only to determine the temperatures at which the thermal behavior of a polymer changes. Quantitative capacity data might be obtainable if the energy input to the sample could be measured or computed, but the heat transfer conditions inside the Dewar flask seem too complex to analyze easily. One bit of calorimetric data is obtained, however, on those materials which crystallize rapidly during the heating cycle. The thermal record, Figure 7, for example shows a thermal discontinuity from the liberated latent heat of crystallization. This thermal record can be extrapolated from both above and below to a mid-temperature to define an equivalent instantaneous temperature rise, 6.1°C. The heat capacity of the copper calorimeter has been computed from its weight and published data. The C_p of the polybutadiene rubber should be similar to that of other known rubbers, making its total heat capacity small compared to that of the metal calorimeter. The known weight of rubber is 2.3 g., yielding a heat evolution pulse 8.3 cal./g.

This value can be combined with an estimate of the extent of crystallinity, 0.22, derived from the thermal expansion data⁵ and the published density of the unit cell of crystalline *cis*-polybutadiene.⁸ A value of 2.1 kcal./mole is so derived.

The DTA system described in this paper has been developed particularly to study polymeric materials by a fairly routine procedure. While some limitations on size, range, and function of equipment have been encountered the technique seems general enough to be useful over a wider set of conditions than described. Cooling below liquid air temperatures is possible although it has not been tried. The calorimeters used require about 2½ cc. of sample to fill them adequately. Smaller calorimeters have been used, but they require fairly critical centering of the differential thermocouple. A wide variety of thermocouples is available for use at various temperature ranges. The -1 to +10 mv., four-point recorder has been used to run two different samples simultaneously. With a six- or eight-point recorder, more samples could be run at the same time, but the effort of preparing samples and identifying curves properly would become a full-time task. The high stability microvolt amplifier has adequate gain for the differential voltages generated, but an adjustable gain range would offer some advantage. (An amplifier of this type with gain adjustable in large steps has become available recently.) Relatively low heating rates are not essential but do offer confidence in an approach to equilibrium conditions convenient for phase-structure studies. Heating at high rates (greater than 2°C./min.) provides a convenient procedure for studying reactions at higher temperatures, i.e., decompositions, oxidation, or crosslinking.

References

1. Smothers, W. J., and Y. Chaing, *Differential Thermal Analysis, Theory and Practice*, Chemical Publishing Co., New York, 1958.
2. Murphy, C. B., *Modern Plastics*, **37**, 12, 125 (1960).
3. Murphy, C. B., *Anal. Chem.*, **32**, 168R (1960).
4. Ke, B., *J. Polymer Sci.*, **42**, 15 (1960).
5. Dannis, M. L., *J. Appl. Polymer Sci.*, **1**, 121 (1959); *J. Appl. Polymer Sci.*, **4**, 249 (1960).
6. Bekkedahl, N., and H. Matheson, *J. Research Natl. Bur. Standards*, **15**, 503 (1935).
7. Bunn, C. W., *Proc. Roy. Soc., (London)*, **A180**, 40 (1942).
8. Natta, G., and P. Corradini, *Rubber Chem. Technol.*, **33**, 703 (1960); reprinted from *Nuovo cimento*, Suppl. 1-V, **15**, Ser. X, 9-39 (1960).
9. Mandelkern, L., *Rubber Chem. Technol.*, **32**, 1392 (1959).
10. Wood, L. A., *J. Polymer Sci.*, **28**, 319 (1958).
11. Floyd, K. L., *Brit. J. Appl. Phys.*, **3**, 373 (1952).

Synopsis

A system for the study of polymer structure by differential thermal analysis (DTA) techniques is presented. The need for an inert reference body has been eliminated by the use of a thermal delay within the sample itself. Typical data showing both first- and second-order transition behavior for appropriate polymers are presented. The applicability of the technique to liquids is also shown. Three first-order transitions have been found in *trans*-1,4-polybutadiene. The insoluble nature of high polymers in one another is again confirmed, even in those systems which disperse well. The latent heat of crystallization of *cis*-1,4-polybutadiene is about 2.1 kcal./mole.

Résumé

On présente un système pour étudier la structure des polymères par les techniques de l'analyse thermique différentielle (DTA). On a écarté la nécessité d'un corps de référence inerte en utilisant un retard thermique à l'intérieur même de l'échantillon. On présente des résultats typiques montrant la transition de premier et de second ordre pour des polymères appropriés. On montre également que cette technique peut s'appliquer aux liquides. On a trouvé trois transitions de premier ordre dans le *trans*-1,4-polybutadiène. La nature insoluble des hauts polymères dans un autre polymère est de nouveau confirmée même dans les systèmes qui dispersent bien. La chaleur latente de cristallisation du poly-1,4-*cis*-butadiène est d'environ 2,1 kcal/mol.

Zusammenfassung

Ein System für die Untersuchung der Struktur von Polymeren durch Differentialthermoanalyse (DTA) wird angegeben. Die Notwendigkeit eines inerten Bezugskörpers wurde durch die Verwendung einer thermischen Verzögerung in der Probe selbst ausgeschaltet. Typische Daten für das Verhalten sowohl bei Umwandlungen erster als auch zweiter Art von geeigneten Polymeren werden mitgeteilt. Auch die Anwendungsmöglichkeit dieser Technik auf Flüssigkeiten wird gezeigt. Drei Umwandlungen erster Art wurden bei *trans*-1,4-Polybutadien gefunden. Wieder wird die gegenseitige Unlöslichkeit von Hochpolymeren bestätigt, sogar in gut dispergierenden Systemen. Die latente Kristallisationswärme von *cis*-1,4-Polybutadien beträgt ungefähr 2,1 kcal/mol.

Received October 17, 1961