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THE USE OF HEAT FLOW APPARATUS TO FIND POLYMER TRANSITION POINTS

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As changes that occur at transition points, e.g. the glass temperature of polymers, involve factors such as thermal conductivity rather than exothermic or endothermic reactions it was considered that heat flow would be the most suitable technique to study the occurrence of these transitions. A simple heat flow apparatus is described and examples are given of its application to polymer films and to co-polymers.

When amorphous thermoplastic polymers are heated, a temperature is reached at which the molecular chains have sufficient energy to overcome the barriers to movement relative one to another. At this point the polymer changes from a relatively brittle glassy material to a plastic solid. The temperature at which this transition occurs has a considerable influence on processing conditions as well as being indicative of the structure of the material.

This transition is known as the glass transition (T_g) or the brittle point and is generally regarded as a second order transition. At a first order transition such as a melting point the rate of change with increasing temperature of primary thermodynamic variables (e.g. volume, enthalpy) shows a sharp discontinuity or kink. At a second order transition the discontinuity occurs in the first derivative with respect to temperature of the primary thermodynamic variable (e.g. coefficient of expansion, specific heat).

Differential thermal analysis (DTA) has become established as a technique for finding glass transition temperatures [1].

DTA, however, is not the best technique for the detection of these transitions since it is designed to detect the much more energetic transitions associated with chemical reactions or first-order transitions.

Glass transitions are characterized by changes in thermal conductivity so that DTA equipment used to detect these changes must be very sensitive and accurately balanced – and, in consequence, costly.

Equipment has been described [2] that enables changes in the T_g of polymer discs to be readily identified but this involved the use of a heating fluid that did not affect the polymer. The present apparatus may be used with discs of varied hiickness and is particularly suitable for use with polymer films and hence is of interest in both packaging and surface coating applications. The specimen does not

come into contact with the heating fluid thus enabling the fluid to be chosen solely on the basis of thermal characteristics.

The equipment may be used to compare the thermal conductivity of the specimen with that of a reference material of similar conductivity (usually another polymer, e.g. a polycarbonate) that does not undergo a transition in the temperature range under investigation. In this case a single copper heater is used. The specimen is placed on one side of the heater and the reference on the other. Opposed thermocouples are located on the surfaces of the films away from the heater. These give the differences in temperature between the specimen and the reference whilst a normal thermocouple gives the temperature of the heater.

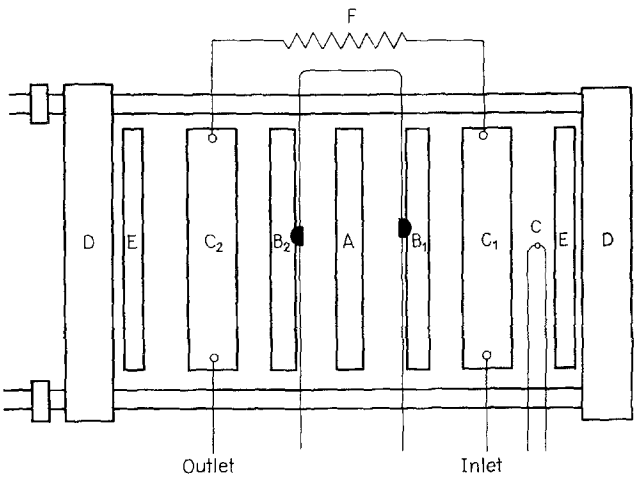

Fig. 1. Sketch of apparatus (Exploded view)

The preferred form of the apparatus, however, has two heaters between which a temperature difference is maintained, thus obviating the need for a reference. An exploded diagram of this arrangement is shown in Fig. 1. The specimen of film, A, approx. 0.01 inch is mounted between thermocouple discs, B_1 and B_2 and two heaters, C_1 and C_2. The whole arrangement is held in a brass clamp, D to ensure good and reproducible contact between the surface of the thermocouples and the polymer film. The brass clamp is thermally insulated, E, alternatively the brass may be replaced by insulating material such as nylon or phenolic laminate.

A heat transfer fluid is pumped into the top heater C_1 and then through an air-cooler, F, into the lower heater C_2 thus maintaining the bottom disc at a temperature slightly below that of the upper disc. The fluid then returns to the reservoir which is heated at the required rate by means of a cam driven programme con-

troller (Ether 'Transistrol). A motor driven variable auto transformer (Variac) is less suitable but may be satisfactory in certain cases. The thermocouple, G measures the temperature of C_1.

Experimental

1. *Temperature indicators.* The thermocouples on either side of the specimen are 28 s.w.g. and are mounted on discs that serve both to locate the thermocouple leads and to insulate them from the rest of the apparatus. These discs were made from four layers of Kraft paper which were impregnated with a phenolic resin and laminated by pressing for five minutes at 150°. The wires were on the top of the impregnated layers and at the end of the process were firmly embedded in the discs with the junctions just proud of the discs. It is likely that other thermosetting resins e.g polyesters could be used if these are more readily available.

Holes are punched for the bolts of the brass clamp to serve to locate the thermocouples. To increase the signal to noise ratio a four junction thermopile is used and the cold junctions are maintained at 0°. Each cold junction is kept in a test tube of aqueous glycerol and the tubes are held in an ice bath to avoid electrical contact through the water produced on melting.

If unsupported thermocouples are used there is considerable noise due to short term wander (ca. 0.25 to 0.1 Hz) and after the T_g the thermocouples move into the plastic sample.

In some experiments a copper disc with copper and constantan leads was used as the temperature sensor. This, however, gave a noisy trace and was not employed further. These poor results may in part have been due to the disc being too large. Much less noise was noticed with a smaller disc that was less subject to variations at the edge of the heater. Copper-constantan thermocouples are convenient as they have a strong signal and there is no problem of contact with dissimilar metals where the thermocouples are attached to the measuring equipment.

Thermistors would appear to be a better way of detecting temperature differences in this application but it has not been possible so far to obtain completely flat thermistor discs; the soldered connection interferes both with the packing of the sample and the balance of the heat flow through the apparatus.

2. *Heaters.* Each heater consists of a hollow copper cylinder, 1½ in. dia. × 3/8 in. deep, wall thickness approx. 0.05 in. Into the centres of the side of this cylinder, diametrically opposite to each other, are soldered two copper pipes 1 in. long × 1/4 in. dia. to which the pipes carrying the heating fluid are connected.

3. *Cooler.* This is a glass tube 12 in. × 1/4 in. bent so that the inlet and outlet are parallel and 1/2 in. apart.

4. *Clamp.* This is two solid brass discs 2 in. dia, 1/2 in. thick. The lower disc has holes drilled through 1¾ in. apart. The upper disc is tapped similarly to take two, 2 BA rods, 2 in. long. The whole assembly is held with thumbscrews on these rods.

5. *Insulant.* (E) Discs of phenolic laminate, 1½ in. dia., previously heated at 140° for 12 hours.

6. *Heat transfer fluids.* Water is a convenient heating fluid for the range of 0–95°. For higher temperatures glycerol is suitable but is too viscous below 60°. Water-glycerol mixtures may be used at temperatures about 100° but the temperature rise is small unless a high proportion of glycerol is used and on the whole, these mixtures are more bother than they are worth. It is preferable to use hydrocarbon oils (e.g. Shell Turbo 37) and the high cost of silicone fluids may be justified where a very large temperature range is needed.

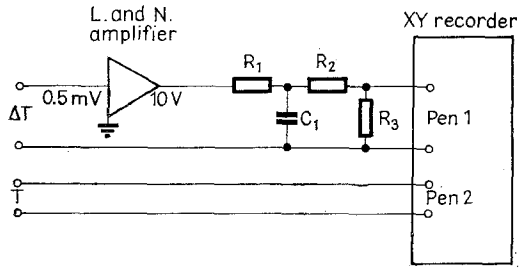

Fig. 2. Circuit diagram

A certain amount of long term drift is inevitable with the simple cooling system used and *ceteris paribus* it is advantageous to have a fluid that has a regular drop in viscosity with temperature. In this instance the increased flow rate tends to counteract the increasing cooling effect of 'F' as it rises above ambient temperature.

At low temperatures methanol or acetone have been found to be satisfactory.

7. *Circuit.* The electrical circuit used for both forms of heating is shown in Fig. 2. The voltage generated by the opposed thermocouple is amplified by a factor of 2×10^4 (Leeds and Northrup 9835–B) and then fed to an X–Y recorder (Houston HR 93. 1 mv per inch).

Short term noise is reduced by means of a capacitor resistor smoothing to provide electrical damping. The capacitor is 100 micro farad, 35 volts. To provide a lag of 40 seconds the charge limiting resistor R_1 and the discharge resistor R_2 should both be 150 Kohm; for a delay of four minutes R_1 and R_2 should be 1 Mohm. In the former case, for this recorder, R_3 should be 1 Kohm, in the latter R_3 is 6.8 Kohm to provide an equivalent output.

Results

The apparatus may be used to detect glass transitions in low molecular weight compounds such as β-D-glucose penta acetate as may be seen in Fig. 3, where the trace obtained is compared with one from a DuPont 900 apparatus using a

DSC head. Both instruments show a glass transition near 34° and crystallization commencing around 56°. As the latter is exothermic it shows more readily in the conventional equipment on which the peak is an order of magnitude greater. The endotherm commencing at 48° in the trace from the heat flow apparatus is caused by the penta acetate flowing under the pressure of the clamp.

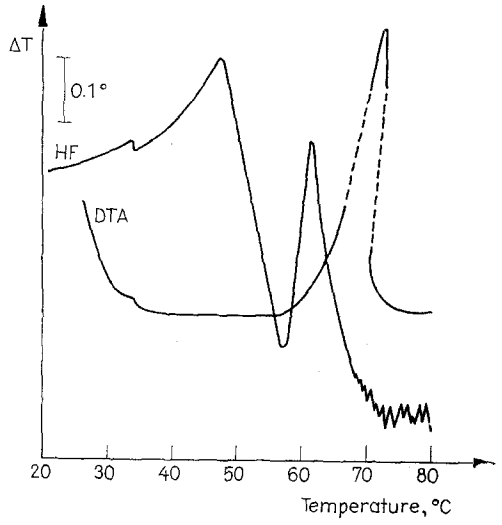

Fig. 3. Glass transition and crystallization of β-D-glucose penta acetate

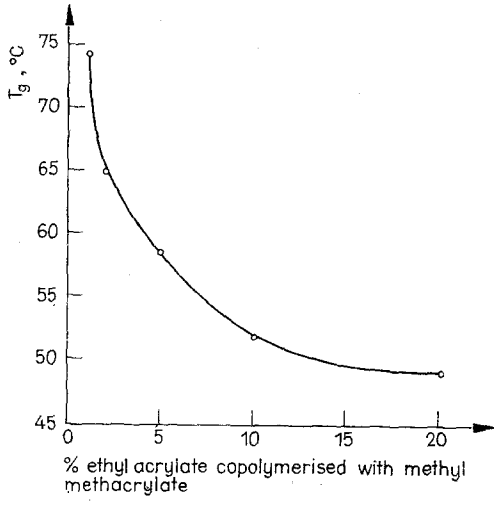

Fig. 4. T_g of copolymers of methyl methacrylate and ethyl acrylate (single heater)

Ethyl acrylate is often copolymerized with methyl methacrylate in order to produce a material of lower T_g. The decrease in the T_g of methyl methacrylate with various amounts of copolymer is shown in Fig. 4.

The heat flow apparatus is, however, particularly aposite for the study of polymer films and Fig. 5 illustrates the T_g of Melinex (polyethylene terephthalate film) 0.008 in. thick showing an initial T_g at 71° for amorphous film. After one experiment the film was cooled by circulating cold water through the heaters and then the experiment was repeated. In this case the T_g now is at 96° illustrating the use of heat flow apparatus to check on the thermal history of a film. The traces of Melinex in the DSC head of a DuPont 900 apparatus are shown in the lower half of Fig. 5.

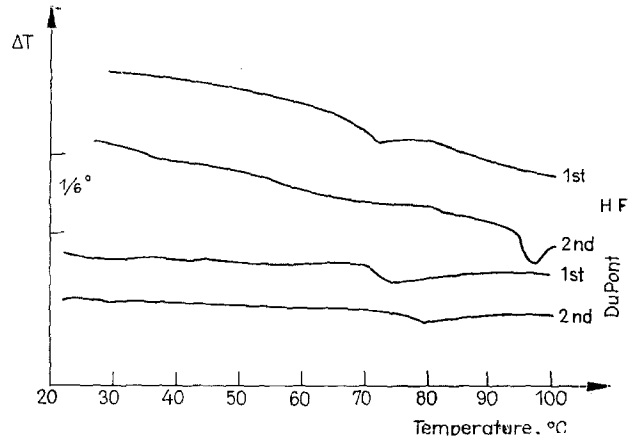

Fig. 5. T_g of polyethylene terephthalate (Melinex). Upper traces: heat flow apparatus; Lower traces: DuPont 900

Reasonable agreement between the two instruments is obtained for the amorphous material but not for the partially crystallized specimens. It is not possible to provide the same crystallization conditions in the two instruments.

The trace obtained varies with the thickness of the film, between 0.005 and 0.01 in. was satisfactory.

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References

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RÉSUMÉ — Les changements qui se produisent aux points de transition, par exemple la transition vitreuse des polymères, mettent en jeu des facteurs tels que la conductivité thermique plutôt que des réactions exo ou endothermiques. C'est pourquoi le flux thermique peut représenter la technique la mieux adaptée à l'étude de ces transitions. On décrit un appareil à flux thermique de conception simple et l'on donne des exemples d'application aux films de polymères et aux copolymères.

ZUSAMMENFASSUNG — Änderungen in den Umwandlungspunkten wie z. B. Glasbildungstemperatur von Polymeren beeinflussen Faktoren wie thermische Konduktivität mehr als endo- und exothermische Reaktionen. Deshalb ist der Wärmefluß zur Untersuchung derartiger Umwandlungen geeignet. Es wurde ein einfacher Wärmeflußapparat beschrieben und Beispiele zur Anwendung bei Polymerfilmen und Copolymeren gegeben.

Резюме — Для описания процессов, происходящих при переходных состояниях, например, стеклование полимеров, можно использовать такие факторы как теплопроводность еще более экзотермических и эндотермических реакций. Как наиболее подходящий метод для изучения этих превращений предложено измерение потока тепла. Описан простой прибор и приведены примеры и их применение для полимерных пленок и сополимеров.