Notes and Communications

The Detection of Transition Points of Polymers by Comparative Thermal Diffusivity Measurements

THE thermal conductivity of a polymer provides information on the structure of the material that is useful in studies of the interrelation of the structure and physical properties of polymers. Several techniques are available for the measurement of the thermal conductivity of polymers but these usually require a good deal of time and special equipment in order to obtain the required results. Thermal conductivity is also important in the polymer processing industries and it was felt that equipment to give values of thermal conductivity quickly and easily would be of use in industry.

Again one of the major points of interest with respect to thermal conductivity measurements is that being related to the internal structure of the polymer they are sensitive to any transitions that may occur. These are most marked at first order transitions (melting points) but are readily seen at transitions such as the glass–brittle temperature (T_g) and may also be detected at the temperatures at which side chains become mobile with respect to the polymer main chain.

Thus if the introduction of a copolymer in place of a previously used homopolymer led to a fall in the temperature of the glass–brittle transition (T_g) by 5 deg. C when measured under comparable conditions this would enable a fabricator to make the necessary adjustments in processing.

In practice what is of interest is not thermal conductivity, which is needed to predict rates of heat flow and temperature distributions for steady state conditions, but thermal diffusivity which determines the time-dependent conditions for non-steady states. These parameters are related as follows

$$\alpha = k/\rho C$$

where α is thermal diffusivity, k is thermal conductivity, ρ is density, and C is specific heat.

Changes in the thermal diffusivity of polymers are readily observed by the simple method of heating a specimen with a standard or reference material and measuring the difference in temperature between them by means of an opposed thermocouple. The standard material should be one that undergoes no transitions in the temperature range under investigation and should have a thermal conductivity very close to that of the material under test. The latter requirement is often difficult to meet and the present arrangement permits the use of the same material as both specimen and reference. In this case, of course, two changes in baseline will be observed.

EXPERIMENTAL

Specimens were made from polyvinylchoride (PVC) (Geon 121) and dibutylphthalate by solvation blending, in tetrahydrofuran. No other materials were added. Thin films of the polymer were cast and the thermocouples were sandwiched between two equal thicknesses of the film. These were then mounted between standard injection moulded discs of polyethylene (Rigidex 35) as shown in *Figure 1.* The whole arrangement was clamped and the polyethylene edges heat-sealed to prevent ingress of fluid from the heating bath and also to avoid dislocation of the thermocouples.

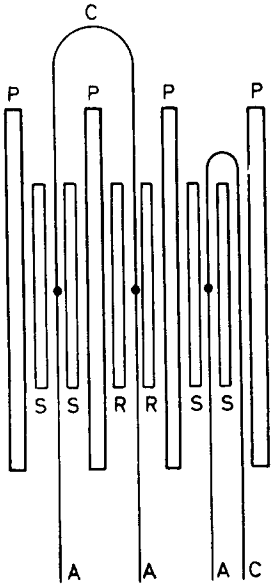

Figure 1—Sketch of apparatus: A alumel thermocouple wire; C chromel thermocouple wire; P polyethylene discs; S specimen of PVC; R reference material

The two outermost samples are of the material under test, and the inner is the reference material.

The opposed thermocouple measures the difference in temperature between the specimen and the reference material. The ordinary thermocouple gives the temperature of the second specimen which, as both are assembled in an identical manner, is taken as the same for both specimens. The differential signal is amplified and then both temperatures recorded on a 10 mV X/Y recorder. If necessary a second opposed thermocouple may be mounted between this specimen and the reference material in order to strengthen the signal for the differential temperature. *Figure 2* shows that the transition temperature is clearly defined.

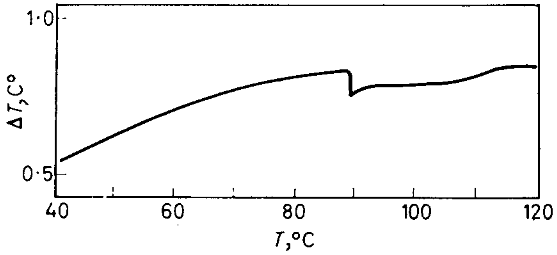

Figure 2—Typical recording (8 per cent plasticizer) (Plot of Δt versus T°C)

It was originally intended to use the greater sensitivity afforded by thermistors to detect these transitions but this plan was abandoned when it was seen that the much simpler thermocouple arrangement gives adequate sensitivity.

The whole assembly is immersed in a heating bath and gradually raised in temperature (Ether proportional controller); 1 deg. C per minute is a convenient heating rate. Glycerin and water form a convenient heating fluid; a fluidized bed may be used but the control problems are much more difficult in this case and can lead to excessive drift.

The difference in temperature between the specimen and the reference is approximately constant until the transition temperature is reached when the change in thermal diffusivity manifests itself as a break in the heating curve, or as a definite peak. After the transition a new baseline is obtained as the temperature difference between the sample and the reference materials once more becomes approximately constant.

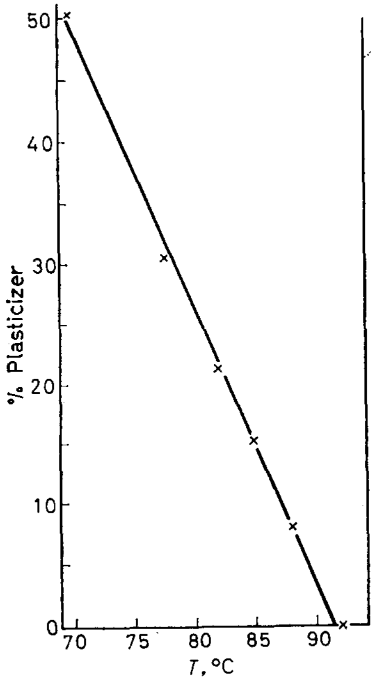

Figure 3—Variation of transition temperature with amount of plasticizer (Plot of percentage plasticizer versus T°C)

Figure 2 illustrates a typical trace obtained with this equipment and *Figure 3* shows the relationship between the transition points and the proportion of plasticizer (HAMPSON, F. W. and MANLEY, T. R. Unpublished).

The thermal insulation of the outer polyethylene discs causes these apparent transition temperatures to be too high; if required this lag could be reduced by replacing the polyethylene with metal discs.

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Dependence of Polymer Glass Transition Temperatures on Heating Rate

TECHNIQUES such as Differential Scanning Calorimetry and Differential Thermal Analysis allow the measurement of the glass transition temperatures (T_G) of polymers on small samples (10 to 20 mg) provided that fairly high heating rates are used (8 to 64 deg./min). The T_G so measured is usually considerably higher (~ 10 to 30 deg. K) than that found by dilatometry at a low heating rate (~0·06 deg./min), so that a method of relating T_G to experimental heating rate would be very useful for providing comparative data.

The molecular processes that occur in a polymer at the T_G are undoubtedly complex[1–4], but it has been found that the time dependence of the glass to liquid transformation can be treated to a good approximation as a simple first-order kinetic process with a single relaxation time[5,6], and the following treatment is based on this approach.

If the glass transition is considered to be a first-order kinetic process, the rate of transformation of 'glass' to 'liquid' molecules on heating through the T_G, is given by

$$-\mathrm{d}n/\mathrm{d}t = kn \tag{1}$$

where n is the mole fraction of 'glass' at any given instant, and k is the rate constant. This equation can be written in the form

$$-\mathrm{d}n/n = (k/\phi)\,\mathrm{d}T \tag{2}$$

where $\phi = \mathrm{d}T/\mathrm{d}t$, the linear heating rate.

Integration of equation (2) gives

$$\ln(n_0/n_t) = (1/\phi)\int_{T_0}^{T_t} k\,\mathrm{d}T \tag{3}$$

where the subscripts 0 and t refer to the state of the system at time zero and time t. If T_G is defined as the temperature corresponding to the half-life of the process, so that $n_0/n_t = 2$, then

$$\ln 2 = (1/\phi)\int_{T_0}^{T_G} k\,\mathrm{d}T \tag{4}$$

For two different heating rates ϕ_A and ϕ_B, equation (4) gives

$$\phi_B/\phi_A = \int_{T_0}^{T_B} k\,\mathrm{d}T \Big/ \int_{T_0}^{T_A} k\,\mathrm{d}T \tag{5}$$