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A Modified Density Balance for Studying Phase Transitions in Polymers

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Synopsis

The design and operation of an automated density balance are outlined. Diverse uses for this equipment are discussed.

INTRODUCTION

A density balance[1–5] has been used frequently for studying material behavior. Such equipment utilizes Archimedes' principle to determine the change in sample density with time and temperature, etc. In the polymer or plastics field, such a balance finds many applications. Specifically, it can be used to determine (a) kinetics of isothermal crystallization, (b) rates of phase transitions (solid → solid type), (c) density or density changes, (d) kinetics of melting, and (e) influence of additives (nucleating agents, fillers, plasticizers, etc.) on (a) through (d).

The apparatus can be used as a routine laboratory technique for the classroom experiment or industrial sample control. In the past, the technique has been employed mostly for (c) and (e), particularly because conventional density balances have not been automated. The device reported on here is automated to the extent that it circumvents the tedious weighing and transfer procedures normally encountered.[4,5] All operations such as weighing, melting and crystallization are conducted in situ. As a result, operations can be hastened so that faster changes in properties can be monitored than with conventional apparatus. Furthermore, the density balance described here can be used for a student laboratory experiment or as a research tool, depending on the degree of elegance and expenditure in its construction.

The alternative basic equipment is described below, especially for studying kinetics of crystallization, but the utility of the technique is also referred to for the other purposes outlined in (b) through (e).

APPARATUS AND OPERATION FOR STUDYING KINETICS OF CRYSTALLIZATION

The apparatus (Fig. 1) consists of a calibrated quartz spring, S, which replaces the conventional pan balance. The spring may be placed and

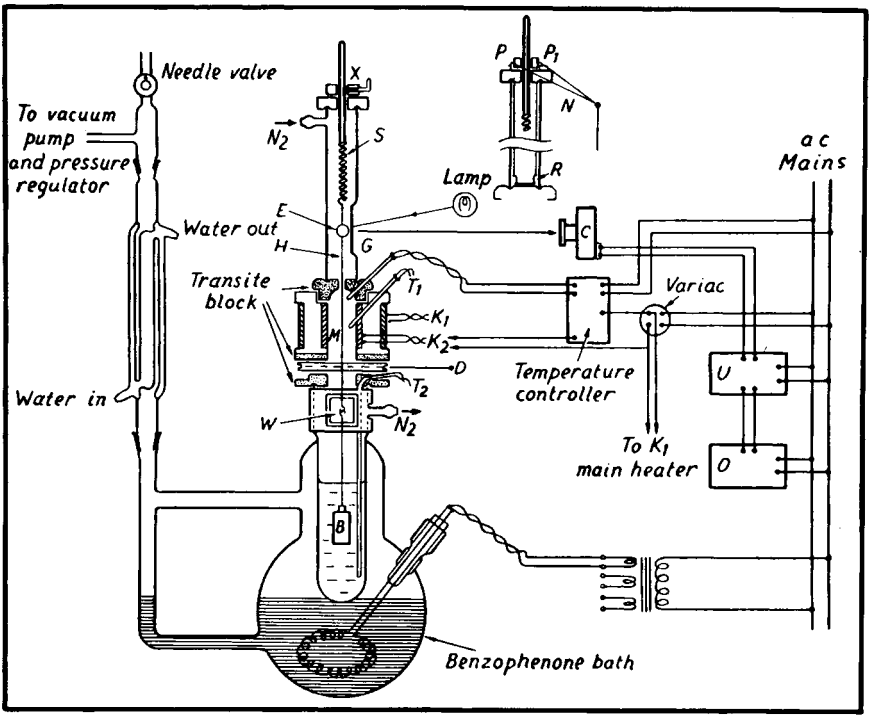

Fig. 1. Schematic outline of the density balance assembly. The parts designated are described in the text.

clamped at any desired position by moving the rod in the vertical direction. For further convenience, the rod may be rotated through a 360° angle. A glass cylinder with a cut-away front and plane glass insert comprises the upper section. This cylinder rests in a round grove cut in a circular transite block. The oven is made of the same material. The lower part of this furnace assembly consists of a movable diaphragm, D, which can enclose the polymer and basket during melting. This diaphragm D may be a metal camera iris that can be stopped down to an opening comparable in size with the suspension wire diameter. Alternatively, a sliding plate with a slit and centered hole may be used for this purpose. A stop (crosswire), may be placed on the wire itself just below the ball bearing for lifting purposes.

Melting and crystallization, or other experiments (a) through (e), are carried out in situ in an atmosphere of nitrogen or other inert gas to minimize sample degradation. The temperatures in the melting oven, M,. and the crystallization bath are measured by thermocouples T_1 and T_2, respectively. (Silicone oil (DC 702) is particularly good as a bath fluid because of its good thermal and chemical stability over long periods of time.)

The weighed polymeric material is placed in the basket, B, and then transferred into the apparatus via a rotatable window, W, just above

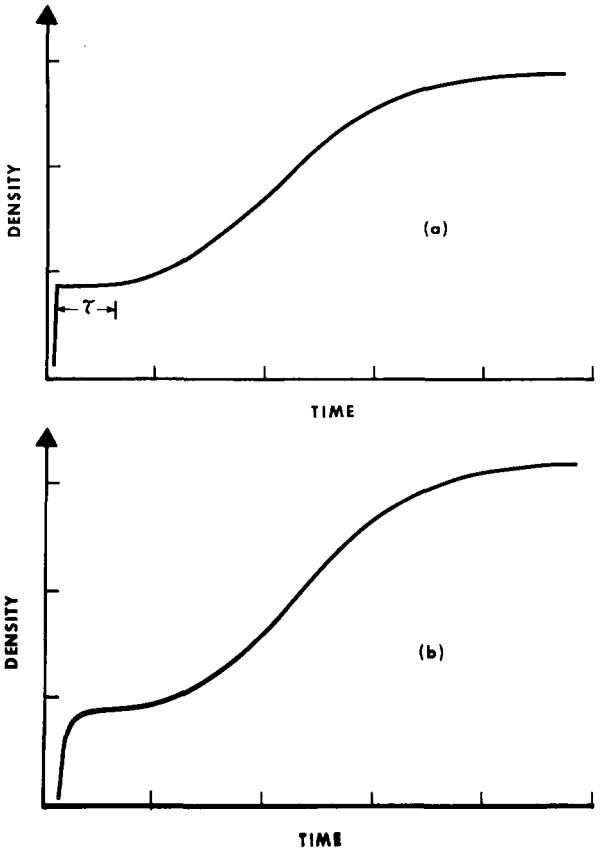

Fig. 2. (a) Ideal plot of the change in sample density with time at a given temperature. (b) Change observed in practice.

the bath zone. Here, the sample is attached (or hooked) to a fine suspension wire, H. The dried, outgassed sample may be introduced in the form of pellets or it can be preformed in the shape of a plug, depending on the design of the containing basket. The latter normally consists of concentric cylinders with a bottom spacer and top lid to maximize heat transfer between the polymer sample and crystallization bath. The inner cylinder is usually about 0.5 cm in diameter, and the outer one may be about 1 cm in diameter. A 200 stainless steel mesh is adequate for constructing the basket.

The window, W, is then closed and the sample is equilibrated to the bath temperature before raising into the melt zone, M, by means of the nylon threads, NN. The outer bath contains benzophenone (bp 304° at S.T.P.) or an alkyl phthalate which is also a stable high boiling material. By reducing the pressure over this fluid, its boiling point and hence the temperature of the inner silicone oil bath may be adjusted at will to the desired temperature. The vacuum line may be a laboratory supply or vacuum pump usually connected to a ballast tank and pressure regulator. A finely

adjustable air leak enables final adjustment to be made during the equilibration process preceding the measurements.

The nylon threads pass over the two pulleys, PP′, connected to a suspension ring, R, that is smaller than the ball bearing or mirror diameter. In this way, the entire weight of the basket/sample assembly is supported when it leaves the silicone bath and lifted into the furnace. The diaphragm is now closed for a predetermined time until fusion is completed. Then the diaphragm is opened and the basket and molten sample are dropped rapidly into the crystallization bath by releasing the nylon threads. At the same time the camera, C, its control unit, U, and intervalometer, O, are started. The position of the illuminated ball bearing, E, is photographed through the plane glass window, G, at predetermined intervals. The position of the ball bearing is also recorded photographically or otherwise recorded in the equilibration stage of the experiment prior to melting. During the initial experimental adjustments the light source (laser tungsten or mercury arc) is placed roughly in line with E and the light detector (movie camera, light sensitive recorder, or photopen recorder suitably positioned to follow the vertical movement of the reflected beam). The sensitivity of the light lever can be improved by increasing the distance between the ball bearing and detector. The latter may simply be a ground glass screen with a fiducial scale attached to it, if a more sophisticated recording system is not available. Time may also be measured with a stop watch.

The course of the crystallization can be mapped out afterward from the projected film. An ideal curve is illustrated in Figure 2a. Figure 2b depicts the practical result.

Theory

It can be readily shown from the schematic outline (Fig. 3) that the displacement b_1b_2 of the ball bearing (or other reflecting source) at distance d_1 from the illuminating device is directly proportional to the vertical displacement d_1d_2 at any other distance d_2 from the reflecting object. Summarily,

$$\frac{b_1b_2}{d_1d_2} = \frac{d_1/\tan\varphi_2 - d_1/\tan\varphi_1}{d_2/\tan\varphi_2 - d_2/\tan\varphi_1}$$

$$= \left[\frac{d_1}{d_2}\right]\frac{\tan\varphi_1 - \tan\varphi_2}{\tan\varphi_1 - \tan\varphi_2}$$

$$= k \text{ (constant)}$$

Hence, $b_1b_2 = k(d_1d_2)$, and the sensitivity (or magnification) of the assembly can be enhanced by changing the ratio d_1/d_2.

The displacement, as a function of time, can be correlated via Archimedes' principle with the changes in sample density at a given temperature. The polymer density ρ_p,

$$\rho_p = W_p\rho_L/(W_p + W_b - W_{bp})$$

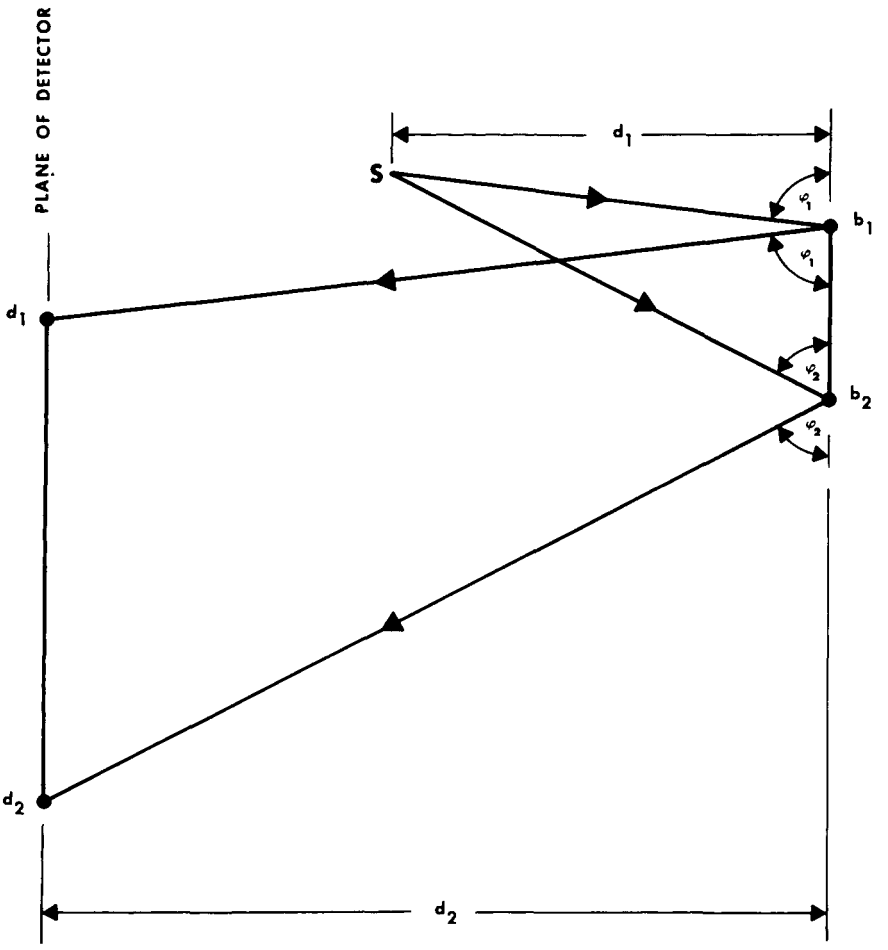

Fig. 3. Schematic outline pertinent to the balance light lever and detection system. Distances are described in the text. The angles ϕ_1 and ϕ_2 correspond to the displacements for the incident and reflected light.

where W_p is the polymer weight in vacuo based on its dry weight, W_b is the weight of the empty basket plus suspension in silicone fluid, and W_{bp} is the overall weight of the basket, suspension, and polymer in the fluid. This relationship follows from the hydrostatic weighing procedures outlined in the literature.[1] A conversion factor may be obtained for the weight of the basket in the fluid over the temperature range of experimental interest.

The data may be analyzed according to the Avrami[6] equation

$$\theta = e^{-kt^n}$$

which is frequently used to describe the crystallization behavior. In this equation, θ is the amount of untransformed material at some time t. The

rate constant is k, and the mode of nucleation (growth) is determined by the parameter n.

Other applications of the apparatus are outlined below.

RATES OF PHASE TRANSITIONS

Where a polymer or plastic undergoes a solid–solid transition, with a concomitant change in material density, this technique can be employed to follow the rate of the transformation process at different temperatures.

DENSITY AND DENSITY CHANGE

With a calibrated quartz spring, the sample weight can be determined at any point during the experimental measurement, and the density of the sample can be deduced if the temperature dependence of the density of the silicone fluid is known, or has been previously determined. A single pan balance may also be used instead of the spring.

KINETICS OF MELTING

The kinetics of melting can also be followed by this technique. The sample temperature can be raised stepwise or gradually through careful control of the refluxed solution in A. The position of the basket, and hence any change in the density of its contents, can be monitored with time.

INFLUENCE OF ADDITIVES

The experiment may also be conducted using polymer which contains additives, such as nucleants, which normally accelerate the rate of crystallization. The efficiency of these additives may be readily determined by the density balance method.

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