On the use of a density gradient column to monitor the physical ageing of polystyrene

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A modification to the standard procedure for the use of the density gradient column is described. Silicone oils are used as column liquids to provide an inert environment for the polymer samples, and the column is operated at 53°C. This system is used successfully to monitor the volume relaxation during ageing of polystyrene following a quench.

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Introduction

Over the past 50 years or so, the density gradient column has become an established tool in polymer science, materials science and the life sciences for the determination of the densities of small specimens. Two particular advantages are noteworthy. First, once the column has been prepared it is an extremely quick and easy procedure to make measurements of density, and second, comparative measurements can be of very high precision.

In polymer science, it is commonly used for the determination of crystallinity, which can be obtained directly from the density. Most often, it is the instantaneous density of the specimen at the time of the experiment that is measured. This overcomes one of the drawbacks of the use of the density gradient column, which is that the column liquids can interact with the polymer samples (for example, polyamides in aqueous solutions), which would render meaningless the floating height of the specimen after a period of immersion.

Nevertheless, the column can be used to monitor density changes as a function of time provided that there is no interaction of specimen and solution, and provided also that the density changes occur more slowly than the time required for the specimen to assume its changed height in the column. An example of this kind of application is a study over several days of the density changes of fish eggs[1] between fertilization and hatching; here the column was made from sea-waters of different densities.

The purpose of the present paper is to describe a procedure for using the density gradient column to monitor the changes in density of amorphous polymers, and in particular here of polystyrene, during volume recovery following a quench from above the glass transition temperature (T_g) to below the T_g. These changes in volume or density are believed to be closely related to the physical ageing process[2], which involves changes in mechanical properties, such as creep compliance and toughness, as a function of elapsed time following the quench.

Two problems are immediately apparent. First, the volume changes to be measured are small, typically a maximum of ~0.5%. Furthermore, they are of similar order of magnitude as changes due to temperature, and it is therefore desirable to measure the density at the ageing temperature of interest, and not necessarily at room temperature. In the past, volume recovery has usually been monitored by volume and length dilatometry[2].

Second, the density changes during ageing occur rather slowly as the polymer glass approaches an equilibrium state. Thus long immersion periods are required in order to follow the evolution of the density; it is clearly therefore imperative that the column liquids do not in any way interact with the glassy sample. Both of these problems are addressed in this paper.

Density gradient column

The procedure for constructing and operating a density gradient column is detailed in the appropriate British Standard[3]. The equipment consists of a glass column which is filled with two miscible liquids of different densities in such a way that there is a smooth density gradient from a maximum at the bottom of the column to a minimum at the top. The less dense liquid is fed from a conical flask through a capillary tube to the bottom of the column. During the filling process, its density is continuously increased by stirring in the denser liquid from a second conical flask. The liquids in the two flasks must be in hydrostatic equilibrium at all times; only in this way can a uniform density gradient be achieved. Glass beads of calibrated density float in the column to indicate the absolute value of the density at their floating height. Thus the density of any specimen floating in the column can be determined from its position within the column.

The liquids most commonly used and recommended are either aqueous solutions or organic liquids; these are clearly inappropriate for the present study of polystyrene, as it is intended that specimens should remain within the column for long periods of time (weeks or months), and a slow swelling would result in significant errors.

To overcome this problem, two different silicone oils

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were used as column liquids. These oils were the only liquids which could be found which were truly inert for polystyrene[4], and which had the right densities at the temperature of interest (53°C, see below). At room temperature, the densities and viscosities of these silicone oils were, as quoted by the supplier (Dow Corning), respectively, 1.11 g cm^{-3} and 500 cS for the denser oil and 1.07 g cm^{-3} and 115 cS for the less dense oil. They are both exceptionally viscous for column liquids, particularly the denser one, and it takes much longer than usual (or desirable) for the specimen to settle at its column height.

Because of the high viscosity of the denser oil, the column liquids only mix sufficiently if they are very well stirred. A magnetic stirrer as used in the standard method[3] is certainly inadequate for this purpose. A more powerful stirrer was used here, with an adjustable speed, taking care not to entrain any air bubbles into the liquid.

Also, because of the high viscosity, it is more difficult to maintain hydrostatic equilibrium between the conical flasks containing the two silicone oils when the column is being filled. In particular, the less dense and less viscous oil tends to flow through the capillary too quickly for the denser and more viscous oil to follow. Under these circumstances, the resulting density gradient would not be uniform. In order to overcome this problem, the connection between the two conical flasks was heated, which reduced noticeably the viscosity of the denser oil during its passage, and in addition a very slow filling rate was used (20 cm^3 h^{-1}). This slow filling rate was achieved by opening only partly the valve between conical flask and capillary.

Temperature

The density gradient in the column is built up at the temperature at which it is to be used. One aspect of our work is a study of the temperature dependence of physical ageing, and since the ageing range is considered[2] to lie between T_g and the β-relaxation, which for polystyrene are ~100°C and ~50°C, respectively, the initial temperature selected for the gradient column was 53°C. The column therefore needed to be set up and maintained at this temperature, since any major temperature changes, such as would be introduced by setting up the column at room temperature and then heating it to 53°C, would destroy the gradient.

To ensure that the liquid has the correct temperature when it reaches the end of the capillary, the capillary itself is heated. This is achieved by heating the water in the jacket to the required temperature (53°C) and filling the glass tube with a liquid compatible with the column liquids, but lighter (here, another grade of silicone oil was used). The growing density gradient pushes the auxiliary liquid up, where it can be siphoned off. Because of the step change in density between the auxiliary liquid and the gradient, it is easy to establish where the gradient begins. A further advantage of having the auxiliary liquid is that it helps to weigh down the glass tube and keep it fully immersed in the water jacket.

The water jacket is maintained at 53°C, and the water level is frequently and regularly topped up by only small amounts to counter evaporation and to avoid any major temperature changes which would destroy the gradient. At 53°C, the column has a maximum temperature difference of 1°C between top and bottom; the temperature control is adjusted such that the required ageing temperature lies in that region of the column in which the specimen actually settles.

Results

The development of the density of small polystyrene specimens has been measured, using a column con-

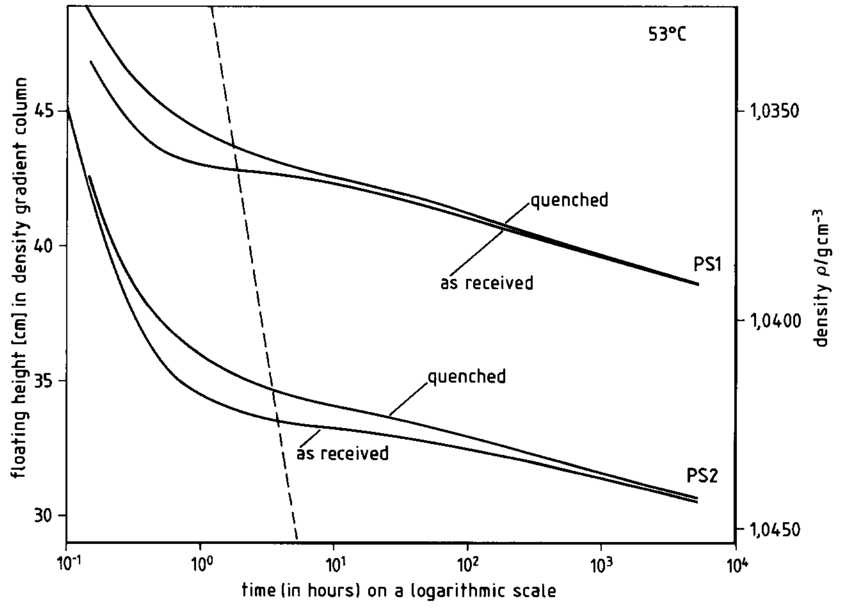

Figure 1 Typical curves showing the time dependence of the floating height or density of samples of polystyrene in the density gradient column. Two different polystyrenes were used: PS1 is a low molecular weight grade from Hüls (T_g~85°C); PS2 was polymerized in our own laboratory (T_g~100°C). Results are shown for samples both as-received and quenched from above the T_g. Data to the left of the broken line (approximately) represent the sinking of the samples to reach their hydrostatic equilibrium. Data to the right of the broken line represent changes due to ageing

structed in the above manner, at 53°C following a quench from equilibrium above the T_g. The specimens are simply placed into the top of the column, whereupon they begin to settle towards their floating heights; the high viscosity of the column liquids here ensures that the specimens fall sufficiently slowly not to disturb the density gradient. A graph showing the typical variation of floating height as a function of time for several specimens is shown in *Figure 1*.

Two grades of polystyrene (PS1 and PS2) are compared, and results for each are shown for both quenched and as-received samples. It is clear from this graph that the initial density of the quenched specimens is less than that of the as-received specimens. The precise thermal histories for the latter were not known, but for both PS1 and PS2 the material had been stored at room temperature for several weeks prior to the experiment.

Because of the high viscosities of the silicone oils used in the column, a significant length of time (typically of the order of 3 or 4 h) is required for the specimens to fall to their hydrodynamic equilibrium. This is indicated approximately by the broken line in the figure. Note that slightly longer times are required at the higher densities, or lower in the column height where the viscosity is greater. Following this, further changes in the floating height, and hence density, of the specimens is indicative of the ageing process. Over the time-scale for which the column has been operating (up to 8 months) the density has increased by between 0.2% and 0.3%, typical for glassy polymers. For the quenched specimens, the increase in density occurs almost linearly with log time after ~30 h, with a slower rate of increase for shorter times. For the as-received specimens, on the other hand, there is initially very little volume relaxation; thereafter, though, they contract at a slightly slower rate than the quenched specimens, with the curves approaching and merging at long times. This behaviour is typical for glassy polymers, whereby the effects of the different thermal histories are eliminated after long annealing times.

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