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Spatial variation in viscosity in sheared polymer melts

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Measurements have been performed using a Weissenberg Rheogoniometer equipped with parallel plates in order to investigate the rheological properties of a polymer melt, namely polystyrene, at very small plate separations. An appreciable gap dependent torque was observed which is indicative of an inhomogeneous viscosity through the sample thickness. The effect is associated with the macromolecular nature of the melt, as confirmed by subsequent measurements performed with polystyrenes of different molecular weight together with a low molecular weight silicone fluid. The results are discussed in relation to models of the molecular chain conformation at a solid–melt interface.

1. Introduction

The purpose of the present note is to report some rheological observations on polymer melts which, to our knowledge, are at variance with common expectations. We arrived at these results through a particular history which is noteworthy to recall as it involves several different effects outside the sphere of rheology but which may all have a common explanation.

One type of effect relates to crystallization in sheared melts reported by Grubb and Keller [1]. This experiment consisted of shearing molten isotactic polystyrene between glass slides by the relative sliding motion of these slides. On subsequent cooling, the bulk of the still amorphous melt solidifies into an isotropic glass within which isolated birefringent crystalline regions were discernible under the polarizing microscope. These regions were rod-like, aligned along the shear direction, and were evidently products of flow induced crystallization. The unusual feature, however, was the location of these birefringent rods within the film: they were neither uniformly distributed throughout the thickness of the film, as would be expected if they formed at random in a uniform shear field, nor were they at the glass surface itself, as they might have been had these surfaces had a nucleating effect. In fact they were located within planes parallel to the glass but at a distance of 15 to 20 μm from the glass surface. This indicated to us that the shear field is not homogeneous across the film as might be expected through the macroscopic application of simple shear. The simplest explanation suggested was that a stationary layer of 15 to 20 μm was adhering to the glass. The existence of thick layers of material termed "adsorption entanglement layers" by Pennings were also inferred in another area of research. This was concerned with the production of fibres of polyethylene from dilute solutions using a Couette viscometer by Zwijnenburg and Pennings' "surface growth" method [2]. Later research [3, 4] revealed that this layer in fact consisted of gel adhering to the Couette rotor, a fact which, however, does not alter its significance as regards its potential effect on the flow field. A further indication of the formation of surface layers of thickness far exceeding the molecular dimensions along solid walls, has come to light recently in flow experiments in slit dies involving noncrystallizable polymers [5]. In both of the above cases involving solutions, the adhering layer displayed orientation.

The common feature of all these different effects appears to be departure from uniform simple shear flow. Furthermore these observations

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seem to be associated with a distinct behaviour of the polymer along the solid–liquid interface in systems where the solid and the bulk of the liquid is in relative motion. It was to test the rheological consequencies of such a situation that the present experiments were taken up choosing polystyrene melts as a follow up of the Grubb–Keller experiment.

2. Experimental details

2.1. Materials

Preliminary experiments were carried out on both isotactic and atactic polystyrene samples. The results of these tests indicated that the isotactic samples became degraded with time at the temperatures ($\simeq 295^\circ$C) at which the experiments were performed. The results presented in this paper are, therefore, confined to the atactic polystyrene samples which also have the advantage that a wide range of molecular weights $M_w = (1.5 - 970 \times 10^3)$ can be obtained. In addition, a silicone fluid was also used to serve as a control sample, having a very low molecular weight and exhibiting known Newtonian rheological properties.

2.2. Experimental procedure

The experiments were carried out with a Weissenberg Rheogoniometer using parallel plates. Since very small plate separations must be used, both the upper and lower plates had to be adjusted for maximum concentricity and alignment to a high degree of precision. In fact, a precision of better than 8 μm could be achieved. Great care was also needed in the preparation of suitable samples for the rheological measurements. In the case of the polystyrene materials, thin discs were pressed and then subsequently placed in the Rheogoniometer. It was essential that only void-free discs were used for the measurements. To ensure that only steady-state flow conditions pertained in the melt, the maximum shear rate (at the periphery of the disc) was slightly less than 1 sec^{-1}. This figure was chosen after several trials. When the plate separation was altered, a proportional change in angular velocity was made to the moving plate to maintain this shear rate constant from one experiment to another.

Apart from the silicone fluid which was sheared at room temperature, all the polystyrene samples were sheared at fixed temperatures above their softening points. The actual temperature for each sample is indicated in the caption to the figures or on the figures themselves.

When the equilibrium temperature was established, as indicated by the thermocouple inserted near the gap, the plates were brought into contact to set the scale for zero separation. Then the thermocouple was removed, and the plates separated to allow the sample disc to be introduced and the required gap separation set. This was done as rapidly as possible to minimize the temperature drop, but a further 20 min preheating was allowed with the sample in the gap to allow the temperature to recover before rotation of the lower plate. The torque exerted on the upper plate was then recorded as a function of time. The experiment was performed for a series of plate separations.

3. Experimental results

The results of the initial experiment with general purpose polystyrene (PS) ($M_w = 15 \times 10^4$) are shown in Fig. 1. Surprisingly there is a substantial change in the torque recorded with gap width for identical shear rates, which, as mentioned above, were maintained on change of plate separation. These differences are appreciable and are not obscured by the variations between runs repeated with the same plate separation, neither are they obscured by time variations within a given run. As seen, the initial torque was reached within a very short time interval and stayed more or less constant thereafter. It is clear from Fig. 1 that, instead of the increase in torque with decreasing plate separation, as expected from impinging adsorption layers, there was a substantial reduction as the gap was narrowed.

We felt it imperative to confirm that the effect was a genuine characteristic of the nature of the material. This was achieved by performing measurements using polystyrene samples of different molecular weight. Fig. 2 shows the effect of plate separation on the torque for silicone oil and for PS with a range of molecular weights (because of the increasing viscosity, the measurements were carried out at successively higher temperatures for increasing molecular weights). We see that there was no gap effect for the silicone oil and neither for the very low molecular weight PS (curve b). The gap effect first became noticeable for $M_w = 32 \times 10^3$, and became unmistakeable for $M_w = 4.70 \times 10^5$, taking an appreciable value for $M_w = 9.70 \times 10^5$. In Fig. 3 the torques are expressed as the ratio T_{25}/T_{500} (the subscripts refer to the gap widths in micrometres) as recorded during the first ten minutes of shearing. In addition to displaying

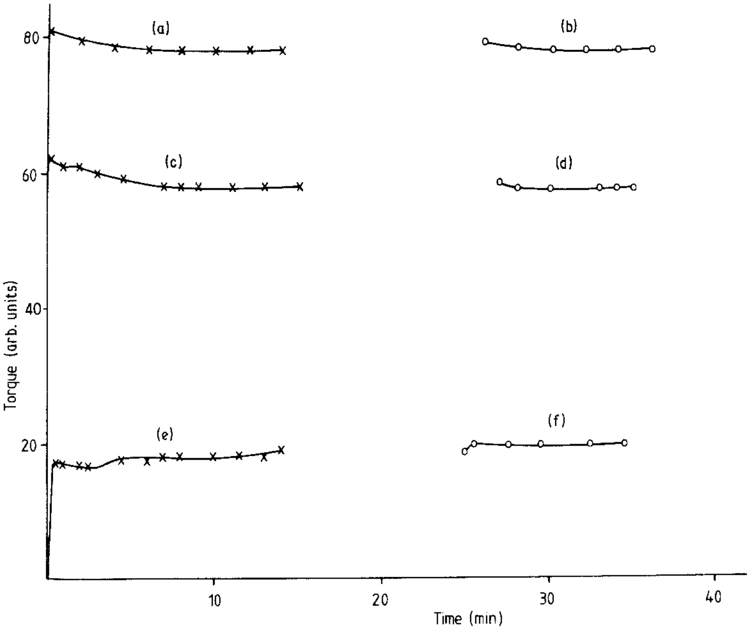

Figure 1 Parallel plate rheogoniometric measurement on a "general purpose" atactic polystyrene ($M_w = 15 \times 10^4$) melt at 195°C. Torque against shearing time. Plate separation (a) 250 μm, (c) 50 μm, (e) 25 μm; (b), (d), (f) the same after stopping and restarting 10 min later. The speed of the rotating plate was adjusted to maintain a constant shear rate of 1 sec^{-1} for all plate separations.

the effect apparent already in Fig. 2 its persistence over 8 min and the approximate constancy of the effect through 15 repeated readings adds support to the reliability of the results.

In the last context it is to be noted again that the long term time dependence of the torque is small and does not come near to overriding the gap effect. This is apparent in Fig. 1 where it is seen that the torque reverted practically to the same gap dependent value after stopping and restarting (after 10 min) the experiment. This result is similar to those reported by Galvin and Whorlow [6] using low density polytheylene and observed by Leech [7] in short glass fibre reinforced polypropylene.

4. Discussion

It is a basic tenet of rheology that when a fluid is sheared between rotating parallel plates the rate of shear will vary radially across the sample, but if these rates are kept constant at any given radius (by adjustment of the rotational speed of the moving plate) the torque would be expected to be independent of the separation of the plates. The results presented here confirm that for silicone fluid and for low molecular weight polystyrene this is truly the case. However, with the higher molecular weight polymer, the above experiments revealed an appreciable departure from this expected behaviour; there was up to a three-fold decrease in the torque on decreasing the plate

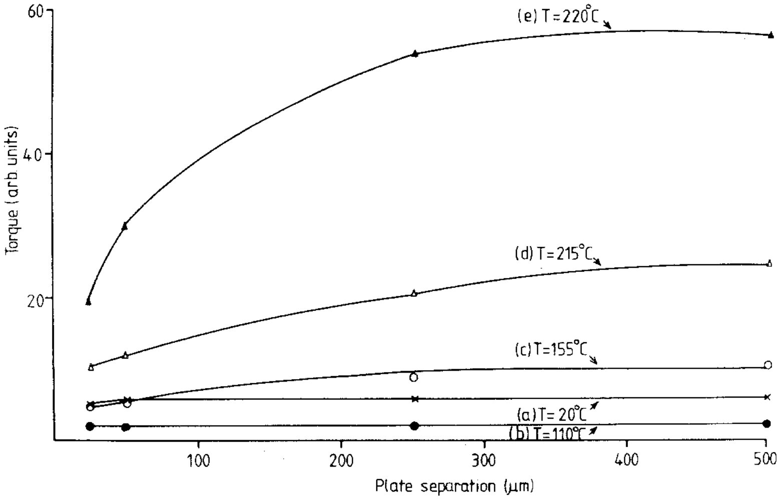

Figure 2 The gap effect on monodisperse polystyrene melts of varying molecular weights and a silicone fluid. Average torque against plate separation for ten minutes shearing. The speed of the rotating plate was adjusted to maintain a constant shear rate of 1 sec^{-1} for all plate separations. (a) silicone fluid (b) a-PS (Kristalex F100) $M_w = 1.5 \times 10^3$ (c) a-PS (monodisperse) $M_w = 32 \times 10^3$ (d) a-PS (monodisperse) $M_w = 470 \times 10^3$ (e) a-PS (monodisperse) $M_w = 970 \times 10^3$.

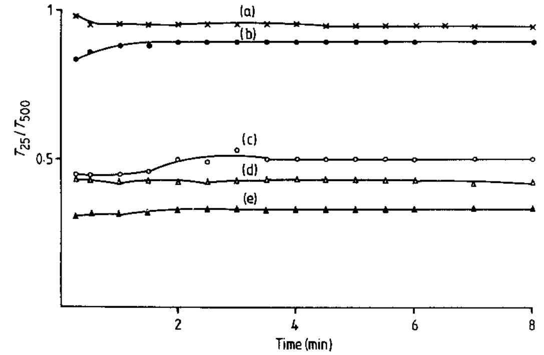

Figure 3 Same as Fig. 2. Ratio of torque at 25 μm gap width to that at 500 μm against shearing time. Shearing temperatures and all other data as indicated in Fig. 2.

separation from 500 μm to 25 μm, most of the effect occurring below 200 μm. As the behaviour within the bulk melt is not expected to be affected by the gap, it follows that the presence of the surfaces separated by the plates is the cause of the effect from which it follows further that the strain rate across the gap cannot be truly homogeneous.

The sign of the effect, i.e. reduction of the torque on reduced plate separation, clearly means that there must be a reduction in energy transfer, and hence a reduction in overall viscosity across the melt as a whole (an effect which increases with molecular weight). This implies the presence of a layer of melt having a reduced viscosity. The question which arises is the location of this layer with respect to the plates. There are clearly two possibilities. First that it is in the vicinity of the plates, the second that it is in the mid region of the gap due to the indirect influence of the surface.

Lowered viscosity along the surface may appear unexpected by any *a priori* consideration. Nevertheless it is not inconceivable that the chains become more aligned in the vicinity of the surfaces leading to shear thinning there. Such an orientation could possibly arise if the chains become anchored to the walls through adsorption and the resulting orientation spreading sufficiently deep into the gap to make its effect felt as illustrated in Figs. 4a and b which show the possible conformation of the molecules in the wide (Fig. 4a) and narrow (Fig. 4b) gaps. Indeed oriented layers near the walls as already stated in Section 1 were recently observed through birefringence in experiments on polymer solutions [5].

The second possibility is that there is a stagnant adsorption layer formed along the walls, which resists deformation, and that therefore reduction of the total gap separation between the plates is at the expense of the thickness of the centre layer. The disproportionate decrease means that its shear rate is increased and, hence, for a polymer exhibiting pseudoplasticity, a reduction in its viscosity.

Consider for example, the situation illustrated schematically in Figs. 5a and b, and a polymer exhibiting a viscosity/shear rate characteristic shown in Fig. 6. When the gap is reduced from 200 μm to 100 μm, with halving of the rotational speed to maintain the overall shear rate at the same value, the thickness of the sheared middle layer is reduced to 3/8 of its previous value. From existing data on shear thinning as shown in Fig. 6, at this higher effective shear rate the viscosity of the layer would only be reduced by 10% at the most, insufficient to account alone for our experimental results. However, here no departure from uniform shear has been suspected, the possibility to which the present communication is now draw-

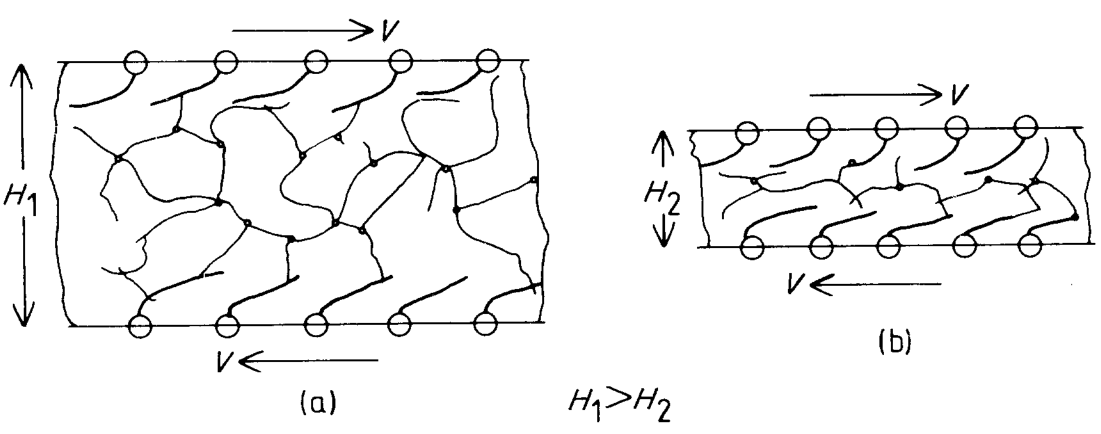

Figure 4 Schematic diagrams illustrating one class of conformation of polymer molecules in the gap between the parallel plates of the rheogoniometer producing lower viscosity near the surfaces: (a) wide gap (b) narrow gap.

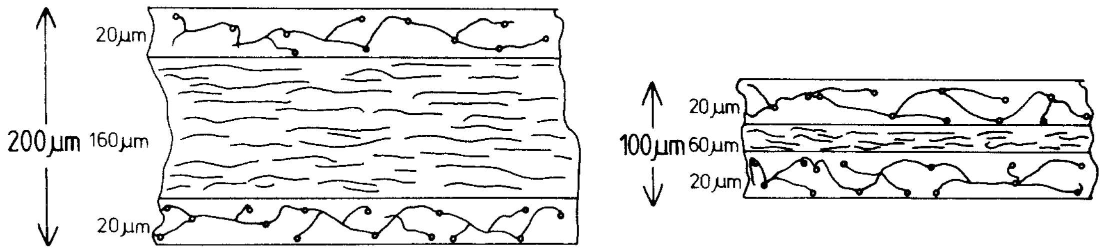

Figure 5 Schematic diagrams illustrating another alternative, namely, the possible mechanism of shear thinning i.e. lower viscosity in the central region of the gap between the plates of the rheogoniometer.

ing attention. It is to be recalled at this point that a stationary layer along surfaces in relative motion comes closest to the conception of the adsorption entanglement layer first postulated in solution and later identified as an adhering oriented gel in the relevant polymer solution system [3]. It was in the expectation of an analogous effect in the melt, as indicated by the localized crystallization observed in [1] (see Section 1) that this work was originally undertaken. It is nevertheless worth recalling however, that the orientation induced crystallization localized at specified distances from the walls as in [1], in itself merely indicates a discontinuity in the flow field at these points. That is, without other suggestions of an adsorption entanglement layer, localized orientation in the melt would arise in either case whether the layer near the wall is more or less viscous than the melt further in. The only requirement is a comparatively discontinuous change in viscosity so that the displacement of chains or entanglement of chains spanning this region are retarded at one of their extremities and pulled along at the other.

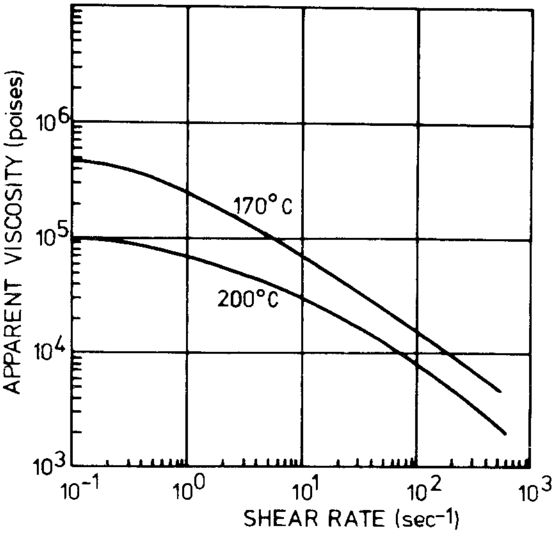

Figure 6 The effect of shear rate on apparent viscosity of a general purpose high molecular weight polystyrene melt (adapted from "The Europlastics Handbook", 1973).

Whichever model pertains it is associated with the long chain nature of the molecules as evidenced by the molecular weight dependence observed. It is tempting to relate this to the well known change in the melt viscosity with molecular weight (from $\eta \propto M^{1.0}$ to $\eta \propto M^{3.4}$) which in the case of PS is known to occur at $M_w \sim 50\,000$ and is hardly affected by the temperature over wide limits [8]. This rather abrupt change is usually attributed to the onset of entanglements. It is clear that entanglements could be effective in creating a coherent surface layer which extends more deeply in the melt than a layer due to one molecule, thus capable of giving rise to the gap effect in Fig. 5. On the other hand longer molecules are more readily oriented by flow, which in turn provides scope for an explanation by the model of Fig. 4. Thus, while both models (Figs. 4 and 5) are compatible with the observed influence of the molecular weight as such, no distinction between them can be made on the basis of present evidence involving molecular weight alone.

As a conclusion, an unconventional, pronounced rheological effect was found which is clearly associated with the long chain nature of the molecule and with its unspecified interaction with solid surfaces in relative motion. We can think of two plausible structural models to account for the effect without trying to distinguish between them at this stage. We feel that even as observed, the effect has further implications for rheological data in general and the phenomena associated with wall slip in particular, and as such deserves to be noted.

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