Extrusion and injection moulding properties of glass-filled polystyrene

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Introduction

The effect of fillers on the processing characteristics of thermoplastics has been well reported and all observers have found that the fillers studied increase the apparent viscosities of the melts, the greatest effects being observed at the lowest shear rates. Some studies have been made on the effect of fillers on the onset of extrudate distortion in polymer melts and it has been found that the effect of the additive depends on the particular type of filler, its concentration and particle size, its ability to from structures and on the polymer melt studied.

One of the most popular fillers in rubbers is carbon black, because of improvements in such properties as elastic modulus, tensile strength and abrasion resistance. The carbon black is comprised of spherical particles of diameters 15–50 nm. These particles tend to fuse into chain-like agglomerates, which are referred to as structure. The addition of carbon black to elastomers reduces their elasticity thereby decreasing die swell and extrudate distortion[1–7].

White and Crowder[8] studied the effect of carbon black (particle size 23 to 80 nm) on the extrudate distortion of melts of SBR and BR. The unmasticated, unfilled SBR melts gave grossly distorted extrudates at all the shear rates studied. However, when the material was masticated or compounded with carbon black, surface irregularity without gross distortion occurred at the lower shear rates. Unmasticated BR extrudates showed surface irregularities and gross distortions and these effects were accompanied by stress oscillations. Masticated samples showed only gross distortion, but when carbon black was added all three phenomena occurred again.

It has been suggested that the gross distortion is due to an entrance effect as it can be reduced by increasing the L/D ration of the die for the same shear rate. The surface irregularity was unaffected by this change, and is thought to be due to conditions at the die wall and exit.

The additive delayed the onset of extrudate distortion and reduced the severity of the distortion in the SBR melts but only reduced the distortion in the BR extrudates. White and Crowder concluded that extrudate distortion is reduced by increasing black loading, decreasing particle size and increasing structure.

Similar observations were described by Minagawa and White[9] for a filler in thermoplastic materials. They used TiO_2 as a filter in particle sizes between 180 and 250 nm in LDPE, HDPE and PS. In all these polymer melts the filler reduced distortion and delayed its onset and increases in filler loading increased the critical shear rate at which the onset occurred.

In both cases, for elastomers and thermoplastics materials, the fillers reduce the elasticity of the melts, thereby reducing die swell, the entrance pressure drop and extrudate distortion.

This communication investigates the extrusion and injection moulding characteristics of a filled general purpose polystyrene to observe the variation of the onset of extrudate distortion with filler content and to determine whether the additive seriously worsens the mould-filling qualities of the melt.

Experimental

In the experiments a filler of coated glass microspheres (Ballotini 3000) of average diameter 35 μm was used in a general purpose polystyrene of $M_w = 261\,000$ and $M_w/M_n = 4.43$ and $MI = 5$.

The materials were mixed in a 1″ single screw extruder, granulated, fed through the extruder again and then regranulated. Unfilled polystyrene was treated in the same manner and subsequent melt flow experiments showed than no measurable change in properties occurred due to the mixing process. An accurate determination of the volume percentage of the filler was made with a Soxhlet extractor.

The extrusion experiments were carried out on a Davenport Extrusion Rheometer, which consists of a vertical die connected to a heating barrel. The melt is extruded through the die by a piston, which moves at a preset rate. Temperature and pressure measurements were made at the entrance to the die.

The experimental die was of diameter 1.5 mm and of length 20 mm, and corrections for entrance loss were obtained using a die of length 2 mm and of the same diameter as the experimental die. The corrected shear stress at the wall, τ, is given by:

$$\tau = \frac{(\Delta p - \Delta p')}{4\left(\frac{L}{D}\right)}$$

where Δp is the pressure drop across the experimental die, $\Delta p'$ is that across the short die at the same flow rate, L is the difference in length between the two dies and D is their diameter.

Any pressure fluctuations that occurred were averaged, but this proved necessary only at shear rates greater than the critical shear rate for extrudate distortion, $\dot{\gamma}_c$. No corrections were considered necessary for the variation of melt viscosity with hydrostatic pressure because the maximum hydrostatic pressures at the onset of extrudate distortion in the present work were considerably lower than in the experiments of[10,11] and similar to those of ref 12, where the same procedure was adopted.

The apparent shear rate at the wall $\dot{\gamma}_a$ was obtained from the piston velocity, s, by:

$$\dot{\gamma}_a = \frac{s}{16.53\, r^3}$$

where s is in cm min^{-1} and r is the radius of the die in cm.

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Corrected values of shear rate at the wall were obtained using the Rabinowitsch correction:

$$\dot{\gamma}=\left(\frac{3n+1}{4n}\right)\dot{\gamma}_a$$

where n is the shear-thinning index.

Results were obtained for the filled and unfilled polystyrene melts in the temperature range 160° to 220°C, and for each melt at least 20 readings of τ and $\dot{\gamma}$ were taken. The value of n for each melt was obtained from these readings and values of τ_c, $\dot{\gamma}_c$ and η_c were obtained from a visual observation of the onset of extrudate distortion in the emerging melts.

The injection mould-filling characteristics of the melts were investigated using a spiral flow moulding test similar to that devised by ICI Plastics Division[13]. In the authors' test, the mould, in the shape of a spiral, has a long calibrated channel for the measurement of the moulding lengths. The melt is injected at the end of the mould under preselected conditions of barrel temperature, ram pressure, mould temperature, feed and time cycle. The spiral mould used in the present experiments had the following dimensions: channel diameter 4.8 mm, decrease in radius of the Archimedian spiral per revolution 6.6 mm, and channel length 1.2 m. The mould was used with a 1" injection moulding machine.

For a given barrel temperature, an average of ten spiral lengths was obtained for different values of ram pressure. The experiment was then repeated at a constant ram pressure for different barrel temperatures. Graphs were plotted of spiral length and ram pressure and spiral length and barrel temperature for the various melts.

Results

Figure 1 shows a scanning electron microscope picture of an extrudate. The glass microspheres are uniformly dispersed in the polymer matrix. In some cases the microsphere has been lost during sample preparation, leaving a well-defined hole.

The types of distortions observed in the extrudates, both filled and unfilled, were typical of polystyrene and were accompanied by the occurrence of pressure fluctuations. The severity of the distortion was reduced by increasing the L/D ratio of the die, and *Figures* 2 and 3 show photographs of typical extrudates obtained from the 20 and 2 mm dies. In the latter, the distortion appeared at much lower shear rates and was far more severe. These figures also show that surface irregularities occur in extrudates containing the filler. These fine irregularities are present at all shear rates and melt temperatures.

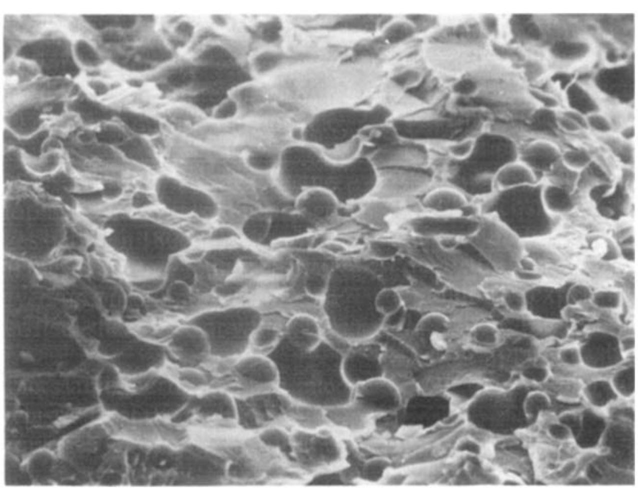

Figure 1 Extrudate fracture surface after extrusion viewed by an *SEM* at a magnification of 240 (17.1% filler)

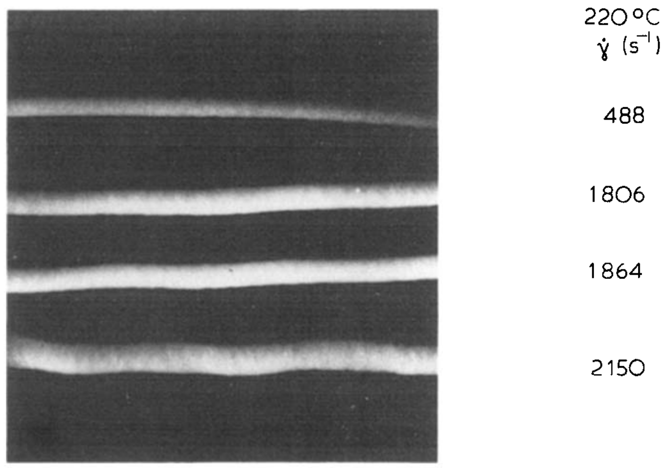

Figure 2 Typical extrudates containing 10.3% filler (20 mm die)

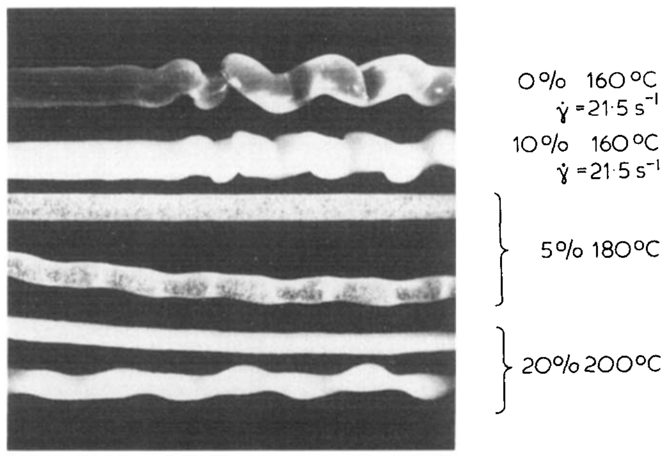

Figure 3 A selection of extrudates from the 2 mm die

Values of τ_c and $\dot{\gamma}_c$ for the different melt temperatures and melts are given in *Table* 1. In all cases there is a tendency for τ_c to increase slightly with melt temperature, but there is an indication that values of τ_c for the extrusions at 160°C may be higher than those for 180°C, in agreement with Collyer and France[12]. Values of $\dot{\gamma}_c$ were not affected by filler concentration except at the highest concentration and melt temperature, where not only was there a reduction in the severity of the distortion but a delay in its onset. Graphs of $\dot{\gamma}_c$ and $1/\eta_c$ give straight lines for all the different filler concentrations, in agreement with previous observers.

The injection moulding results show there is only a marginal reduction in mould-filling ability with increase in filler concentration. *Figure* 4 shows the variation in the spiral length as a function of the ram pressure, and *Figure* 5 shows the relationship between spiral length and barrel temperature.

Discussion

The addition of the Ballotini 3000 with the coating did not in general delay the onset of extrudate distortion,

Table 1 Values of shear stress, τ_c, and shear rate, $\dot{\gamma}_c$, at the onset of extrudate distortion as a function of filler concentration and melt temperature

% Ballotini volume	Melt temperature (°C)	Critical shear stress (kN m^{-2})	Critical shear rate (s^{-1})
0	160	68	72
	180	75	318
	200	81	950
	220	–	–
4.3	160	83	80
	180	83	197
	200	89	867
	220	84	2981
10.3	160	85	83
	180	80	287
	200	87	975
	220	94	2823
17.1	160	92	64
	180	87	368
	200	107	743
	220	96	3740

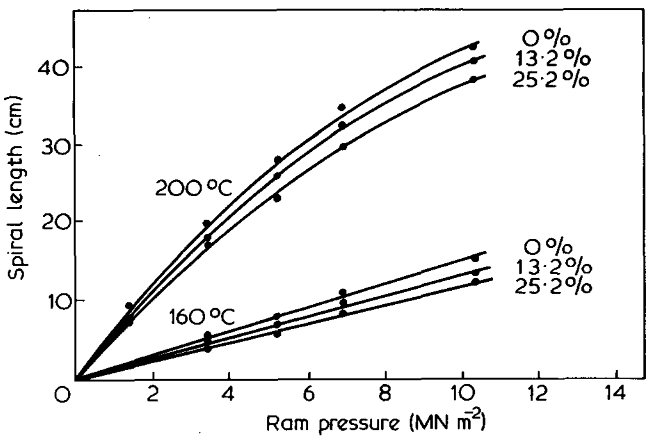

Figure 4 Spiral length *versus* ram pressure for various barrel temperatures

except for the melt of 17.1% concentration at 220°C. This is attributed to the relatively large particle size of the filler. For this reason, it may be better to obtain an improvement in extrusion properties by using fillers that are readily available in smaller particle sizes, such as carbon black and titanium dioxide. It is certainly necessary to use a smaller particle size than 35 μm, as was used in the present experiments.

Further experiments are being carried out to determine the relative importance of particle size and particle

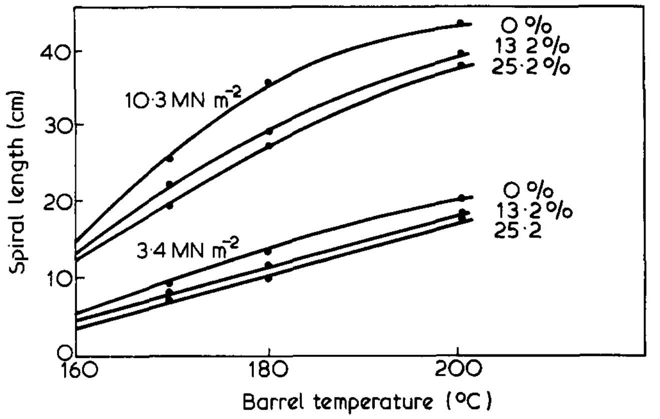

Figure 5 Spiral length *versus* barrel temperature for several ram pressures

material on the reduction in and delay of extrudate distortion.

The injection moulding results were more promising in that the enhancement of apparent viscosity at the high shear rates involved does not drastically reduce the mould-filling qualities of the melt.

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