

# A STUDY OF THE RHEOLOGY, PROCESSING AND DIE SWELL OF GLASS BEAD FILLED POLYSTYRENE

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## ABSTRACT

This paper presents some recent experimental results on the effects of the addition of glass beads (both coupled and uncoupled) on the linear and non-linear rheology, and hence processability, of a commercial polystyrene. Oscillatory, low strain, measurements showed an increase in viscosity with the addition of the glass beads, which varied depending on the testing frequency and degree of coupling. For the coupled beads, at low frequencies the increase in viscosity was well predicted by the Kreiger-Dougherty relationship, while at higher frequencies a smaller increase than this was seen, linked with a shift to lower frequencies of the lower frequency cross-over between  $G'$  and  $G''$ . For the uncoupled beads, the viscosity was found to shift vertically with no change in the position of the  $G'$ ,  $G''$  cross-over. For the non-linear shear and extension measurements, at low shear rates and low strains the increase in viscosity agreed well with the linear results, whereas at high strain rates and strains, more disparity was seen, which in non-linear extension was been linked to voiding. For non-linear shear measurements, the plateau viscosities of the pure polystyrene were found to fit the Cox-Merz rule, while the glass bead filled materials did not. The deviations in behaviour of the filled materials were found to be closely linked to the characteristic relaxation times of the polymer, particularly the reptation time  $\tau_d$  and Rouse time  $\tau_R$ . Finally, die swell measurements were carried out on both the pure and filled materials. The addition of the glass beads was found to reduce die swell and lead to voiding in the extrudate when  $\dot{\gamma} / \omega_c \geq 1$ , where  $\dot{\gamma}$  is the wall shear rate and  $\omega_c$  is lower frequency cross-over between the moduli.

## 1. INTRODUCTION

In this work, which is part of the UK government funded Microscale Polymer Processing Project ( $\mu$ PP), we have investigated the effect of the addition of glass beads on the melt processing of a commercial polystyrene. The philosophy of the  $\mu$ PP project, now in its second stage, has been to model and interpret experimental results (such as rheology and processing) via molecularly aware physics based models (for example, see reference [1]). In the first stage of the project (1997-2003) the focus had concentrated mainly on carefully synthesised, monodispersed pure polymers. In the current project ( $\mu$ PP2), which is more industrially motivated, the drive has been to apply these theoretical treatments to, amongst other things, two-phase materials based on commercial polymers.

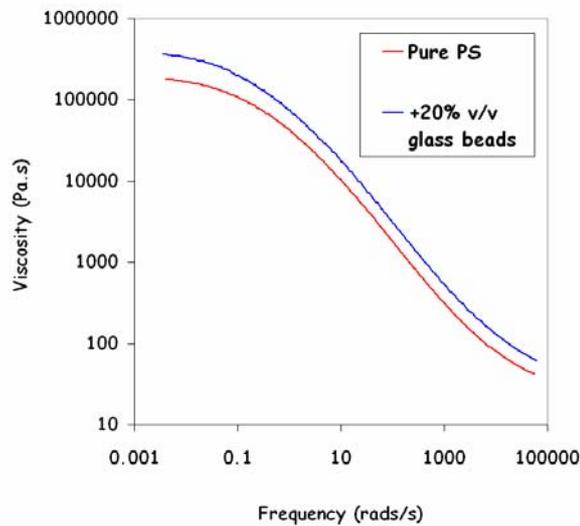
## 2. EXPERIMENTAL

The polystyrene was supplied by BASF (grade PS2,  $M_w = 274,000$ , polydispersity 2.7) and the glass beads (Spherglass 5000 CP01 and CP00 with and without a coupling agent respectively) by PQ Potters Europe. Blending was carried out using a solvent procedure (THF) with a thermal stabiliser (Irganox 7610) to limit degradation of polymer during the solvent drying process (48 hours in a vacuum oven at 140°C). Infra-red spectroscopy, carried out post blending, showed no residual solvent and GPC measurements on the pure polymer and composite blends showed very similar molecular weight distributions.

### 3. RESULTS AND DISCUSSION

#### 3.1 Linear rheology: polystyrene and coupled glass beads

First, a set of oscillatory (small strain) measurements were carried out on both the



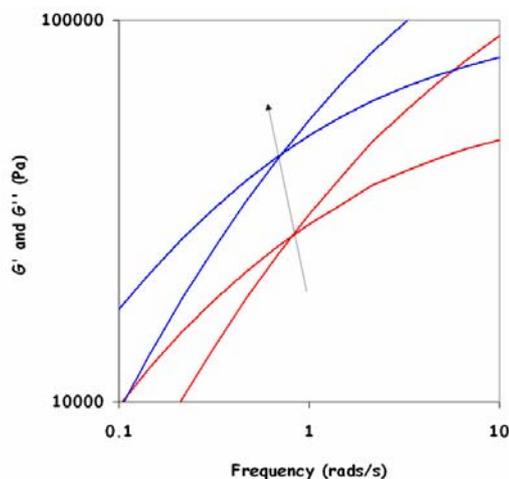
**Figure 1:** Complex viscosity vs frequency of PS (—) and filled with 20% coupled glass beads (—) at 170°C.

pure PS and a 20% v/v coupled glass bead/PS blend. The measurements were carried out using a strain controlled rheometer (Rheometrics RDA2) with 10mm diameter parallel plates. Measurements were carried out from 100 rads/s to 0.1rads/s and over a range of temperatures between 130°C and 210°C. Time-temperature superposition was used to obtain the complex viscosity behavior over a much wider range of frequencies, at a particular reference temperature. Typical results, for a temperature of 170°C are shown in Figure 1. The complex viscosity is shown both for the pure polystyrene sample and

filled with 20% by volume of coupled glass beads. In agreement with the majority of the previous works, the presence of the glass particles raised the viscosity over all frequencies: as is also often reported, the increase at low frequencies is greater than that seen at higher frequencies. There are a plethora of models aiming to predict the increase in viscosity starting with the first work by Einstein [2], through the modifications of Guth [3], Batchelor and Green [4] and the very popular Krieger-Dougherty relationship [5] or MKPD relationship (shown on the right with  $\alpha=2$ ). All of these models predict only a constant vertical shift at all frequencies (no horizontal shift) and so would not predict these results. The increase in viscosity in the low frequency plateau region was found to be predicted well by the Krieger- Dougherty relationship [5] using the most accepted values of the empirical parameters  $\alpha = 2$  and  $\phi_{\max} = 0.68$ .

$$\frac{\eta}{\eta_o} = \left( 1 - \left( \frac{\phi}{\phi_{\max}} \right) \right)^{-\alpha}$$

At higher frequencies the viscosity ratio was lower than predicted by Krieger



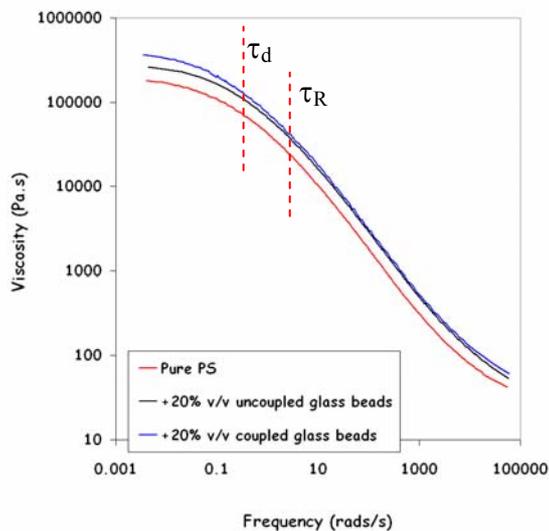
**Figure 2:** Low frequency cross-over for pure PS (—) and filled with 20% coupled glass beads (—)

Dougherty. One possible reason for this can be seen by examining the low frequency cross-over in the real and loss parts of the shear modulus  $G$ . As is shown in Figure 2, the low frequency cross over of the filled material is lower than that of the pure polystyrene, shifting the cross over to the left. This, in turn, leads to the point where the viscosity begins to decrease for the filled material simultaneously shifting to the left, leading to a lower viscosity shift at higher frequencies. Results suggest that the high frequency cross-

over seen in polystyrene is unaffected by the presence of the glass beads.

### 3.2 Linear rheology: polystyrene and uncoupled glass beads

Experimental studies in the literature have reported that the shift in the low frequency



**Figure 3:** Linear shear rheology at 170°C: coupled and uncoupled glass beads in polystyrene

cross-over is sensitive to both particle aggregation and also particle size, suggesting a link to the interaction between the particles and the polystyrene matrix. To investigate this aspect, a second blend was produced using the same glass beads as above but without a coupling agent. Figure 3 shows the linear rheology for this system, again at 170°C. The uncoupled glass bead system shows the same vertical shift at all frequencies, as predicted by the models described above. At higher frequencies the shift is very similar to that seen with the coupled beads, but is smaller in the low frequency region. As expected, the cross-over in

$G'$  and  $G''$  was found to be in the same position for the uncoupled bead system and the pure polystyrene.

An important aspect of the  $\mu$ PP programme is to look for correlations between rheology, processing and molecular aspects, in particular the characteristic relaxation times associated with the polymer structure. In recent years there has been significant progress in linking molecular aspects of polymers to their dynamics and melt flow behaviour [6], building on the original work of de Gennes [7] and Doi and Edwards [8] to more recent studies of, amongst others, Likhtman and McLeish [9]. Most of this theoretical progress has arisen from the insight that polymer chains of sufficient length in the melt state are *entangled*, and that topological entanglements between polymer chains restrict their dynamics. Motion perpendicular to the contour length of the chain is suppressed by entanglements, giving rise to the common theoretical picture that each chain is confined within a “tube” by the surrounding chains. A key result from these molecular theories is that for a monodisperse polymer there are three important timescales,  $\tau_e$ ,  $\tau_R$  and  $\tau_d$ , which are the entanglement, Rouse and reptation times respectively.  $\tau_e$  is the time for a segment between entanglement points to relax, and so is independent of molecular weight. For polystyrene this is given as  $7.13 \times 10^{-4}$  s [6] at a temperature of 170°C. From this, the Rouse time at 170°C (the relaxation of

the whole chain in an unentangled state) can be calculated from  $\tau_R = \tau_e \left( \frac{M_w}{M_e} \right)^2$ . The

Rouse time is considered to be the timescale for retraction towards the equilibrium contour length of a polymer chain within its tube following a non-linear deformation. The reptation time,  $\tau_d$ , is the characteristic time for curvilinear diffusion of the chain along the contour length of the tube, and is given by the equation of Likhtman and Mcleish [9] as

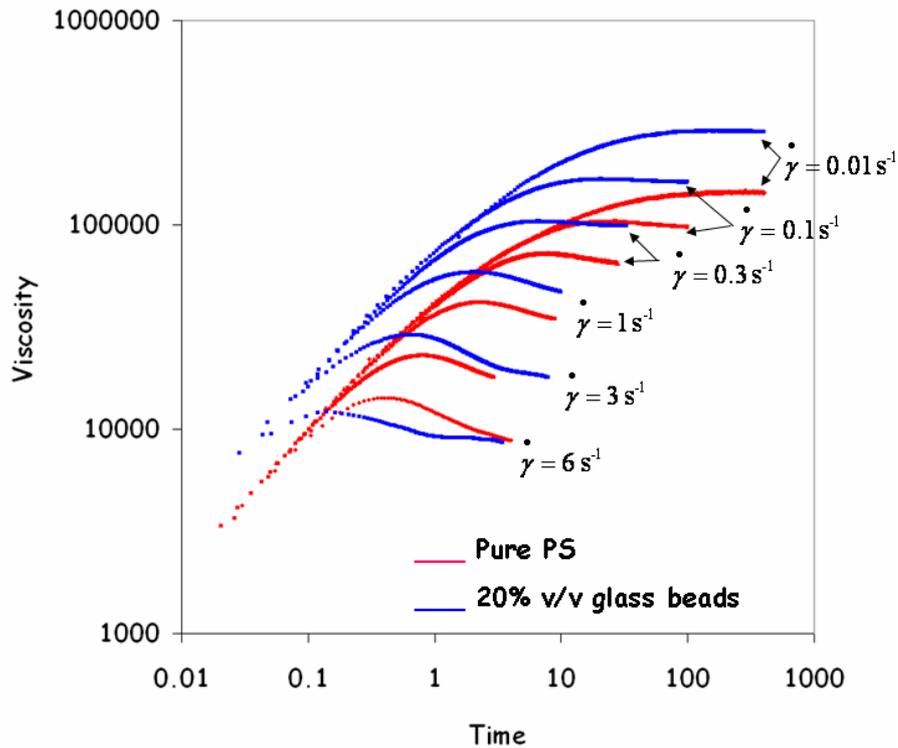
$$\tau_d = \left( 3Z^3 \tau_e \right) \left( 1 - \frac{2C_1}{\sqrt{Z}} + \frac{C_2}{Z} + \frac{C_3}{Z^2} \right)$$

where  $Z = \left( \frac{M_w}{M_e} \right)$ ,  $C_1 = 1.69$ ,  $C_2 = 4.17$  and  $C_3 = 1.55$ .

For a polydisperse polystyrene, such as that used here, we can estimate an average value of these relaxation times from the molecular weight,  $M_w$ , which is 274,000, giving  $\tau_R = 0.3s$  and  $\tau_d = 5.7s$  at  $170^\circ C$ . The positions of these two relaxation processes have been marked on Figure 3 and it can be seen that the deviation of the frequency response, between the uncoupled and coupled glass beads, occurs at around the Rouse time.

### 3.3 Non-linear shear measurements: coupled glass beads.

Non linear shear measurements were carried out on a strain controlled rheometer (Ares L2) using a cone and plate geometry. The measurements were carried out at a temperature of  $170^\circ C$  and a range of shear rates between  $0.01$  and  $6s^{-1}$ .



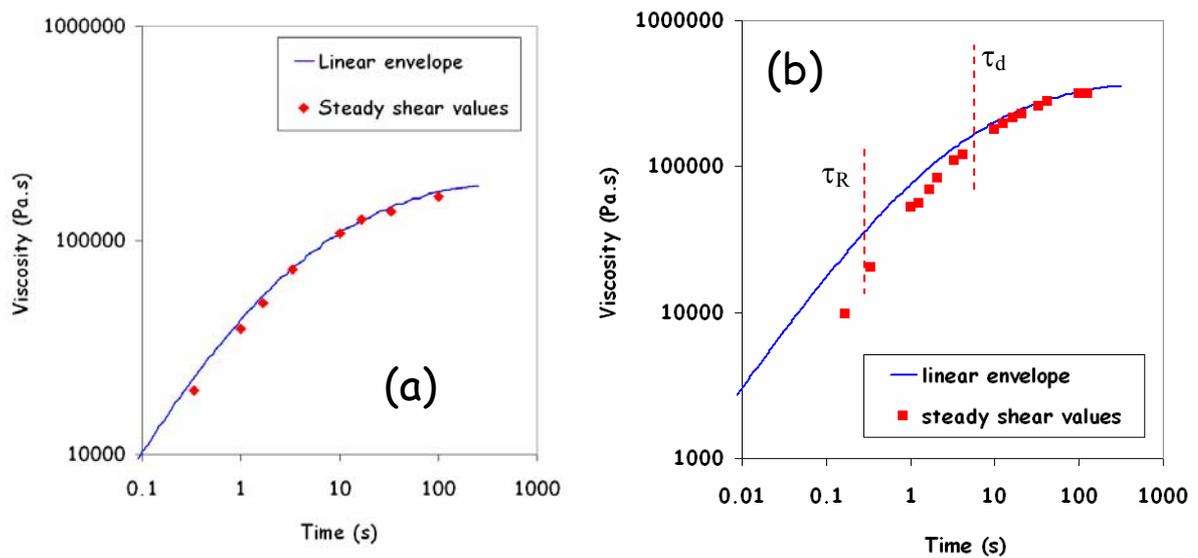
**Figure 4:** Non-linear rheology measurements on polystyrene and 20% coupled glass bead filled polystyrene: tests at  $170^\circ C$ .

It is seen that at low shear rates, and low strains, the shift upwards in viscosity mirrors that of the oscillatory measurements. However at higher strain rates, and at high strains, it is seen that the difference between the viscosity of the pure and filled PS becomes much less. At the highest shear rate used ( $6s^{-1}$ ) the viscosity of the filled polystyrene was measured to be higher in the early part of the test (small strain) but as the strain increases, the viscosity became lower than that of the pure polystyrene material.

One contribution to this reduction in shear viscosity is believed to be due to the increased internal shear rate as a consequence of the presence of the glass beads. This is given by

$$\dot{\gamma}_{\text{eff}} = \frac{\dot{\gamma}}{1-\phi}$$

where  $\dot{\gamma}$  is the external shear rate,  $\phi$  is the glass bead volume fraction and  $\dot{\gamma}_{\text{eff}}$  is the effective increased internal shear rate due to the presence of the rigid glass beads. As the polystyrene is shear thinning then the presence of the glass beads results in a further decrease in viscosity.



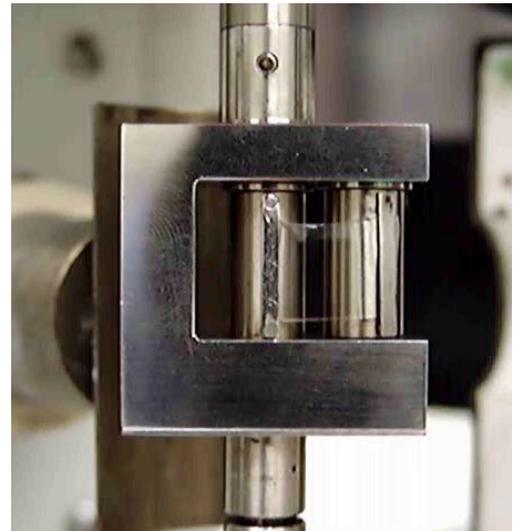
**Figure 5:** A comparison between the linear viscosity envelope and the steady state values from a non-linear shear test: (a) Pure polystyrene: (b) 20% coupled glass bead filled polystyrene.

A common way to compare non-linear and linear measurements is via the empirical Cox-Merz rule [8], which states that the (steady) viscosity versus shear rate curve is virtually identical to the dynamic viscosity versus frequency curve. This has been found to be valid for a range of homogeneous polymers but not always for filled polymers at high loadings which show a yield stress. Figure 5 shows a comparison of the linear viscosity envelope against frequency and the steady shear viscosity values against shear rate for the pure and filled polystyrene. It is seen that the Cox-Merz rule works for the pure polystyrene. For the polystyrene filled with 20% coupled glass beads the steady shear viscosities increasingly lie below the linear envelope suggesting additional shear thinning. The departure of the non-linear measurements from the linear envelope is seen to commence at around the reptation time  $\tau_d$ .

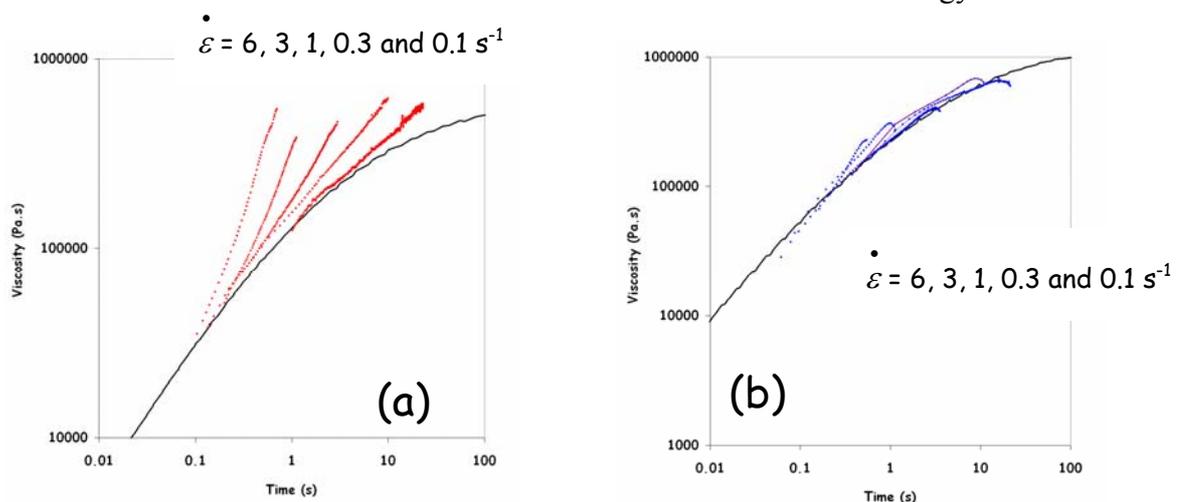
### 3.4 Non-linear extension measurements: coupled glass beads.

The non-linear extensional rheology of the pure and filled polystyrene samples has also been investigated using the Sentmanat Extensional Rheology system (SER) shown in Figure 6. The attachment fits onto a strain controlled torsional rheometer and stretches the polymer between two rotating cylinders.

As with the non-linear shear measurements, tests were carried out at temperatures of 170°C and a range of extensional rates from 0.1 s<sup>-1</sup> to 6 s<sup>-1</sup>. Figures 7a and 7b below show the results for both the pure polystyrene and filled with 20% coupled glass beads.



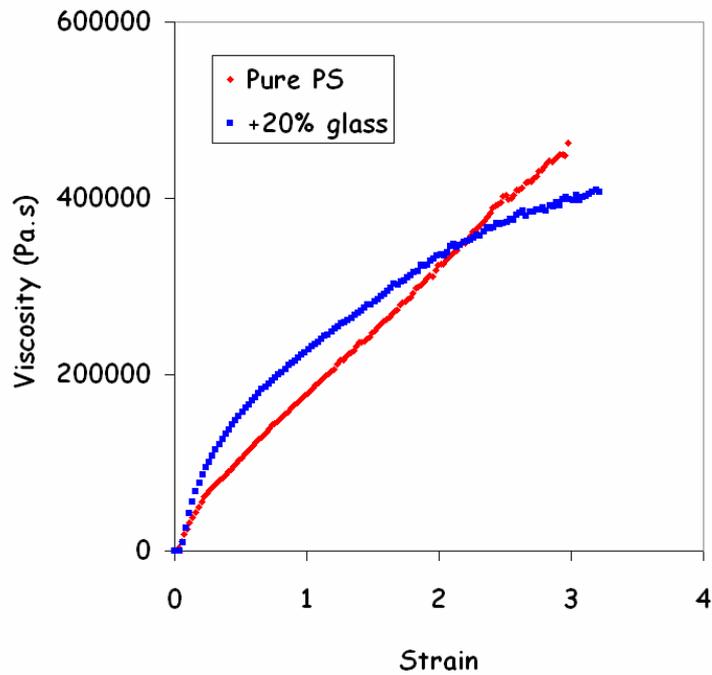
**Figure 6:** SER attachment for extensional rheology



**Figure 7:** Extension viscosity vs time for (a) pure and (b) 20% coupled glass bead filled polystyrene: the linear envelope is indicated by the solid black line.

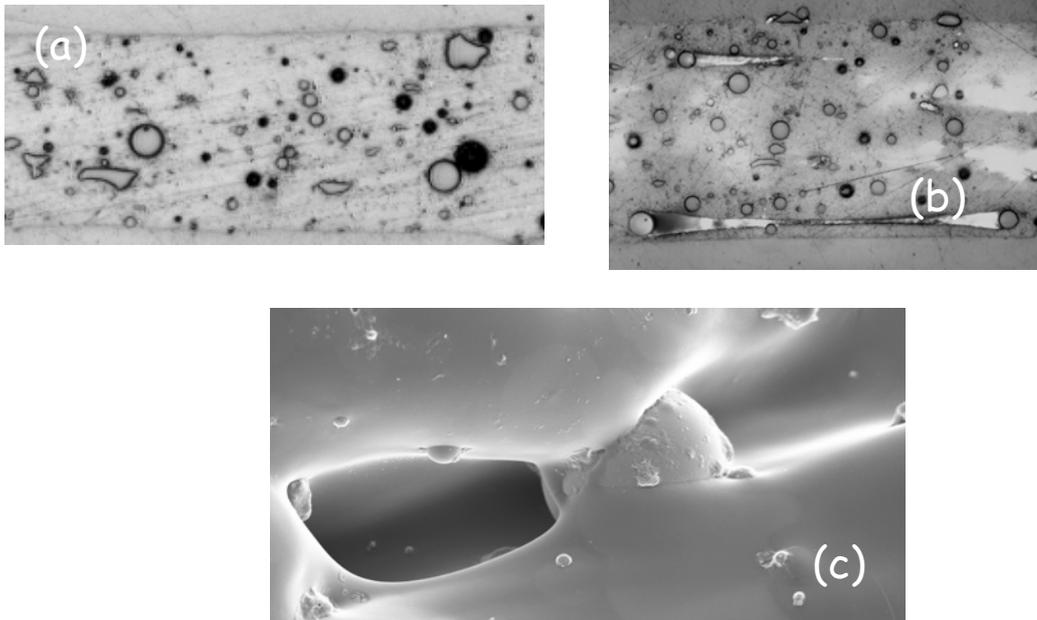
For the pure polystyrene, the samples each show strain hardening. For the glass filled polystyrene, it is clear that the strain hardening of the polymer has been significantly reduced at all strain rates.

Figure 8 shows a comparison of the viscosity vs strain curves at a strain rate of  $1\text{s}^{-1}$ . It is clear that at the beginning of the test, at small strains, the viscosity of the 20% coupled glass bead sample is higher than the pure polystyrene as expected from the linear rheology measurements (in fact it follows the linear envelope). As the strain is increased the viscosity of the filled PS falls below that expected and eventually becomes lower than that measured with the pure PS sample.



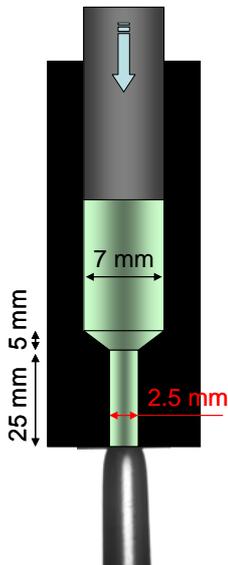
**Figure 8:** Non-linear extension results at a strain rate of  $1\text{s}^{-1}$

To investigate this aspect a couple of samples were examined in the microscope at the end of the test, one for a low extensional rate of  $0.01\text{ s}^{-1}$ , and one at  $1\text{s}^{-1}$ . The samples were embedded in a slow curing epoxy and then polished so that the interior of the samples could be viewed.



**Figure 9:** Details of the interior of the filled PS samples after a non-linear extension test: (a) at a strain rate of  $0.01\text{s}^{-1}$  (b) at a strain rate of  $1\text{s}^{-1}$  (c) details of particle debonding

The pictures show that at the higher extensional rates, particle debonding was occurring, and this is the likely reason for reduction in strain hardening in the filled polystyrene samples at high strains. It is possible that some shear thinning occurs at high strain rate in the non-linear shear experiments, although no particle debonding has yet been seen in post analysis of these samples.



**Figure 10:** Die Swell geometry

### 3.5 Non-isothermal die swell measurements.

The aim of this project is to be able to understand and predict how these materials will respond when processed. To this end we have been investigating a number of model processing rigs, of which extrusion through a die is one. Extrusion through a die is an important industrial process and a cause for concern is the possible swelling of the polymer as it exits from the die.

Figure 10 shows a schematic view of the set up for the die swell measurements. A circular piston of 7mm was driven down at a fixed displacement rate (and hence fixed wall shear rate) using an Instron tensile test machine. The die exit was circular with a diameter of 2.5mm and the length of the narrow section was 25mm. The extruded profile was captured in real time using a video camera and a DVD recorder. Specially designed software was written in Labview to carry out post processing analysis of the extrudate. In order to study the relaxation process occurring during the extrusion, the tangent to the extruded profile at the die exit was determined. This parameter must be strongly related to the relaxation of the polymer and also nearly eliminates the non-isothermal effects of the process.

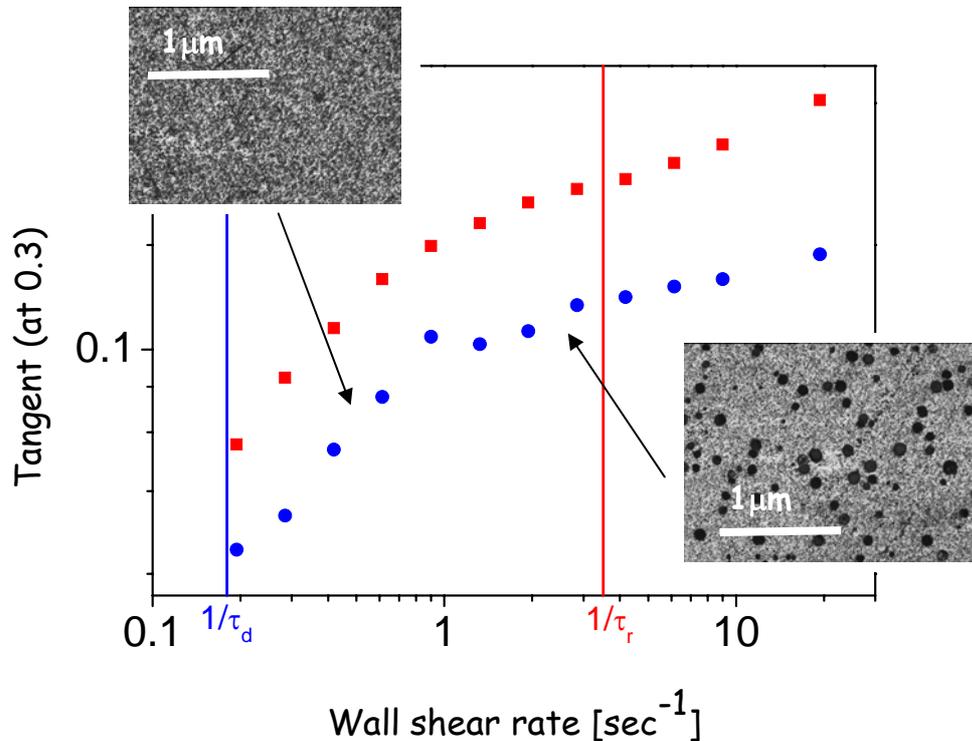


Figure 11: Die Swell results for pure and filled polystyrene.

Figure 11 shows a comparison of the die swell of pure (■) and 20% glass bead filled (●) polystyrene versus apparent wall shear rate with the positions of the characteristic relaxation times indicated. It is seen that when the wall shear rate is greater than the inverse of the reptation time, then die swell increases for the pure polymer. We can interpret die swell as a post-die transverse relaxation of aligned molecules in the die as a result of being stretched faster than the reptation time. The results also show that the glass beads reduce die swell. Additionally, the results show the presence of three regions as the wall shear rate crosses three characteristic times. Post analysis of the extrudates shows that this can again be associated with particle debonding as shown by the inset micrographs. For wall shear rate lower than  $\omega_c$  ( $\sim 1$  rad/s) the sectioned extrudates were seen to be homogeneous (i.e. top left micrograph). For  $\dot{\gamma} > \omega_c$ , the sectioned extrudates were found to contain significant voiding (i.e. bottom right micrograph) and for  $\dot{\gamma} > \tau_R$  the voiding morphology changes furthermore (i.e. Figure 12).

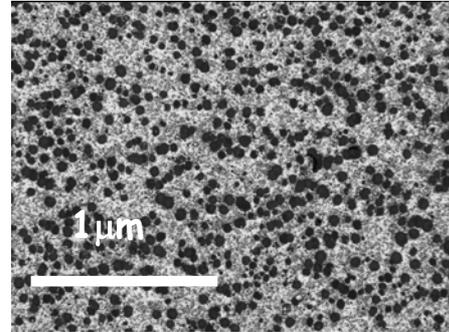


Figure 12: Internal voiding in extrudate at a shear rate of  $10 \text{ s}^{-1}$

#### 4. CONCLUSIONS

The experimental results have shown that the inclusion of glass beads significantly affects both the linear and non-linear rheology (and hence processability) of polystyrene. For oscillatory measurements, the viscosity increases at all frequencies but the increase depends on frequency and coupling between the beads and the polymer matrix. For non-linear shear, the glass beads increase the amount of shear thinning at high shear rates and so no longer follows the Cox-Merz rule. For non-linear extension measurements, the addition of glass beads significantly decreases strain hardening which, through microscopy, has been seen to be linked to debonding around the particles. Die swelling measurements showed that the inclusion of the glass beads reduced die swell and also showed cavitation when  $\dot{\gamma} / \omega_c \geq 1$ .

#### 5. ACKNOWLEDGEMENTS

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