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An investigation into the constriction flow of a particle reinforced polystyrene melt using a combination of flow visualization and finite element simulations

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Synopsis

This paper investigates the flow of a particle filled polystyrene melt through a constriction zone using a combination of experimental techniques and computer simulation. A special blend, containing cross-linked polystyrene beads mixed into a polydispersed polystyrene matrix, was produced for this study. This closely refractive index matched blend allowed visualization of the flow birefringence up to an equivalent particle loading of around 15 vol %. Flow birefringence through a 10:1.4 contraction, measured using a multi-pass rheometer (MPR), was compared with that predicted from finite element simulations, in a similar way to that already published for unfilled polymer melts [Collis *et al.*, *J. Rheol.* **49**(2), 501–522 (2005)]. Numerical predictions were obtained using the finite element solver “EUFLOW” and ranked against the experimental processing data from the MPR. An extensive study of the rheology of the particle filled polystyrene blend was conducted which provided the input to the simulations. The addition of the particles was seen to enhance the shear thinning of the melt, while debonding between the particles and the polystyrene melt during extension testing had the effect of reducing strain hardening. EUFLOW was used to evaluate how these two important aspects could affect the flow birefringence of the filled polystyrene melt. © 2010 The Society of Rheology. [DOI: 10.1122/1.3478307]

I. INTRODUCTION

In recent years there has been a significant progress in linking molecular aspects of polymers to their dynamics and melt flow behavior, for example [McLeish (2002)], building on the original work of de Gennes (1971) and Doi and Edwards (1986) to more recent studies of, among others [Likhtman and McLeish (2002)]. Most of this theoretical

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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 time scales, τ_e , τ_R , and τ_d , which are the entanglement, Rouse, and reptation times, respectively. τ_e is the time for a segment of polymer chain between entanglement points to relax and so is independent of molecular weight. The Rouse time is considered to be the time scale for retraction toward the equilibrium contour length of a polymer chain within its tube following a nonlinear deformation and the reptation time, τ_d , is the characteristic time for curvilinear diffusion of the chain along the contour length of the tube. Both of these latter two relaxation times depend on the molecular weight, as described by, among others, [Likhtman and McLeish \(2002\)](#).

These concepts have proved very successful in predicting the rheology of polymers based on molecular structure. In particular, the study reported by [Collis *et al.* \(2005\)](#) showed that the linear and non-linear rheologies could be accurately predicted from a molecular based theory using a minimum of parameter fitting. A key component of this work was the development of synthesis routes to produce a sufficiently monodisperse polymer (polystyrene and polybutadiene) for experimental rheological studies, thus providing theoreticians with well defined molecular variables for testing their theories. Once verified, the theories were further developed into molecularly aware constitutive equations by [Likhtman and Graham \(2003\)](#) for incorporation into finite element simulation software, in order to predict the flow and processing of a monodisperse polystyrene [[Graham *et al.* \(2006\)](#)].

For industrial practice, polymers are very rarely used in their pure state. Rather, a whole range of additives are utilized in order to tailor their properties for a particular application. These are often particulates of varying shape, size, and mechanical properties; from rigid particles such as glass beads, glass fibers, nanoclay platelets, and carbon nanofibers, to softer particles such as dispersed rubber. The study into the effect of fillers on the linear and non-linear shear rheologies of polymer melts is a well researched area, which has been reported extensively in published journal papers, review articles, and books. Reviews of this vast research area can be found in the books by [Gupta \(2000\)](#) and [Shenoy \(1999\)](#) and the review article of [Barnes \(2003\)](#), while the recent work of [Mueller \(2010\)](#) presents a very nice set of data for the effect of a range of monodisperse particles of different shapes on the rheology of a silicone oil predominantly in shear. In contrast, experimental measurements of particle filled systems in extensional flow are rare and, as commented by [Mewis and Wagner \(2009\)](#) in their recent review of current trends in suspension rheology, analytical solutions for filled particles in viscoelastic media are even scarcer, although they do note a couple of recent examples [[Hwang *et al.* \(2004\)](#); [D’Avino *et al.* \(2008\)](#)].

The work reported here is a continuation of the philosophy of the pure polymer work described above, with the fresh aim of studying the flow of *filled* polymers. As with the pure polymer research [[Lee *et al.* \(2001\)](#)], the ultimate goal is to embed molecularly aware constitutive models [for example, the Rolie–Poly model of [Likhtman and Graham \(2003\)](#)] into flow-solvers in order to predict the processing, and ultimately the mechanical properties.

A closely refractive index matched blend of cross-linked polystyrene beads and a polystyrene matrix was prepared using a solvent blending technique (THF) at a variety of particle loadings. A full description of the linear and non-linear rheologies (shear and

FIG. 1. Scanning electron microscope picture of the cross-linked polystyrene beads.

elongation) was measured over a range of strain rates at the chosen temperature of 170 °C. The addition of the particles was seen to both enhance the shear thinning of the melt and, effectively, reduce strain hardening due to debonding around the particles. The rheology data also provided the input to the finite element simulations.

Visualization of the flow was carried out using the Cambridge multi-pass rheometer (MPR) through a 10:1.4 contraction at a temperature of 170 °C for a range of flow rates. It was found that the use of the closely refractive index matched system allowed flow birefringence to be measured up to an equivalent particle loading of 15 vol % and this blend was the main focus of the comparative study. The measured flow birefringence and pressure drop were compared with numerical simulations carried out using the finite element solver EUFLOW [Tanchev *et al.* (2008)]. While EUFLOW does not currently include constitutive models specifically designed for filled polymers, the strategy here was to use a successfully embedded model for unfilled polymers [the Rolie–Poly model of Likhtman and Graham (2003)] and assess its merit for filled polymers and point the way for future constitutive model development.

II. EXPERIMENT

A. Materials

1. Blending procedure and polymer characterization

In order to develop a blending protocol and produce a range of volume fractions in sizeable quantities with a material that was well-characterized, a commercial polystyrene, which was moderately polydispersed, was our material of choice. The polystyrene was supplied by BASF (grade PS2, $M_w=274\,000$ g/mol, polydispersity 2.7). The particle reinforcement was in the form of highly cross-linked polystyrene beads, manufactured for use in GPC columns, from Polymer Laboratories (PLRPS 1412–2101). Figure 1 shows a

TABLE I. Molecular weights for various polymers and blends.

Blend	M_w
Virgin PS2	287 692
0% Solvent blended PS2	251 116
1% PS beads	268 471
5% PS beads	282 587

scanning electron microscope picture of these particles, taken using a Jeol FEGSEM. The polystyrene beads were observed to be porous and were measured, by image analysis, to have an average diameter of 11.9 μm .

Blending was carried out using a solvent procedure (THF) with a thermal stabilizer (1% weight fraction of Irganox 7610) in order to limit degradation of the polystyrene during the solvent drying process (48 h in a vacuum oven at 140 °C). The solvent technique gave an excellent control of the particle volume fraction compared to other techniques, such as high shear blending, and less molecular degradation through the use of the thermal stabilizer. Infrared spectroscopy carried out post-blending and this confirmed no residual solvent present after the drying procedure. Three blends were created: 10%, 5%, and 1% weight fraction (w.f.), as well as the base PS2 polymer passed through the blending procedure with no filler added, here referred to as a 0% blend. The majority of the work presented in this paper will be carried out on the 5% by weight blend.

Table I shows the molecular weight measured (by GPC) for the polymer blends produced. It is seen that the 0% blend resulted in approximately a 10% reduction in molecular weight compared to the base PS2 polymer, even with the addition of the thermal stabilizer. Adding 1% of the PS beads reduced the molecular weight degradation significantly, while the addition of 5% PS beads gave no reduction in molecular weight within the error of measurement. Hence it can be deduced that the presence of the cross-linked PS beads plays an additional, complimentary, role in reducing the molecular degradation of the base polystyrene during the blending process.

2. Consideration of filler particles

Early rheology measurements (in comparison with commonly used empirical models) suggested that the cross-linked PS beads had a much greater effect on rheology than would be expected based on their weight fraction. Consequently, an investigation was conducted comparing the incorporation of the *porous* cross-linked PS beads with uniform *solid* glass beads of a similar average diameter. Two blends were created using the solvent method described above; a 5% w.f. cross-linked PS bead/PS2 blend and a 5% w.f. solid glass bead and PS2 blend. Linear rheology measurements on the cross-linked PS bead blend compared to the solid glass beads blend showed approximately a three times greater increase in viscosity. In order to investigate this further, shear rheology measurements of a suspension of the polystyrene beads in a Newtonian oil at very low volume fractions (10^{-4} – 10^{-2}) were conducted. In this range, the viscosity of a filled solution (η) can be compared to that of the unfilled solution (η_0) by the simple Einstein relationship [Einstein (1906)]:

FIG. 2. Specific viscosity versus volume fraction of cross-linked PS beads suspended in a Newtonian oil.

$$\eta = \eta_0[1 + 2.5\phi], \quad (1)$$

where ϕ is the volume fraction of the filler. The results were found to fit the Einstein relationship very well (Fig. 2) when the equation was modified to take into account an excess hydrodynamic volume $\Delta\phi$, as follows:

$$\frac{\eta - \eta_0}{\eta_0} = 2.5\phi\Delta\phi. \quad (2)$$

The results (Fig. 2) gave an excess volume fraction of the cross-linked PS beads ($\Delta\phi$) of 3.21 ± 0.06 when compared to the results from the solid glass beads.

This increase in viscosity (over a solid particle) and excess volume is attributed to two main effects. First, as seen in Fig. 1, the beads are porous and as such occupy a greater volume than would be expected from their mass. Thus, at a particular weight fraction they will have a correspondingly larger effective hydrodynamic diameter than that calculated supposing the beads were solid. Second, the cross-linked particles easily swell in THF, which will increase their effective volume if they remain in this swelled state. Swelling measurements in THF showed an increase in the average diameter from 11.9 ± 1.1 to 14.6 ± 1.4 μm . The combined result of these two effects is an increase in the effective volume fraction by approximately three times. Freeze-fractured surfaces of the blended material, examined in the scanning electron microscope (SEM), showed that the interior of the cross-linked PS beads to be completely filled with the PS2 polystyrene matrix.

B. Rheology measurements

The linear and non-linear rheologies of both the pure and filled polystyrene samples were collected using a range of rheometers. Linear oscillatory shear was measured on a strain controlled rheometer (Rheometrics RDA2) with 10 mm diameter parallel plates. Measurements were carried out from 100 to 0.01 rad s^{-1} over a range of temperatures between 130 $^{\circ}\text{C}$ and 210 $^{\circ}\text{C}$. Time-temperature superposition was used to produce a master curve at the chosen temperature of 170 $^{\circ}\text{C}$ and was found to work well for all materials.

FIG. 3. (a) Diagram of MPR insert and (b) grid used for the EUFLOW simulations.

Non-linear shear measurements were carried out on a strain controlled rheometer (Ares L2) using a cone and plate geometry with a 10 mm diameter. The measurements were carried out at a temperature of 170 °C (± 0.1 °C) and a range of shear rates between 0.01 and 6 s⁻¹.

The non-linear extensional rheology of the pure and filled polystyrene samples was investigated using the Sentmanat extensional rheology system. This attachment fits onto a strain controlled rotational 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 in a range of extensional rates from 0.1 to 6 s⁻¹. Post-analysis of the tested samples was carried out by freeze fracturing using liquid nitrogen and examined using a scanning electron microscope (FEGSEM).

C. The MPR

The MPR is a dual piston rheometer which imposes various rheological deformations on the fluid contained within an enclosed volume. Pressure transducers on either side of the central test section enable pressure measurements to be made. The central test section is designed such that flow through different geometries can be observed optically. The basic concept of the MPR is described in detail by Mackley *et al.* (1995) and the use of the optical cell by Lee *et al.* (2001).

An entry-exit slit was used in this work, shown in Fig. 3(a). The operation of the MPR using this geometry has been described elsewhere [Collis *et al.* (2005)]. The geometry used had a depth of 1 mm and channel width of 1.5 mm, giving a depth:width aspect ratio of $\approx 1:1.5$.

Flow induced birefringence was used to observe the principal stress difference (PSD) during flow. Monochromatic polarized light with a wavelength of 514 nm was passed through the midsection and orthogonal analyzer before being captured using a digital video camera. Quarter wave plates were used to eliminate the isoclinic extinction bands to leave only the stress-related isochromatic fringes.

All flow experiments were carried out at 170 °C. Preliminary visualization experiments in the MPR showed that for volume fractions greater than 5%, the system became

FIG. 4. Complex moduli (G' and G'') vs frequency for the pure polystyrene (black line) and the 5% PS bead blend (gray line) measured in a linear shear test at 170 °C.

too cloudy to accurately measure the birefringence, despite the close RI matching. For this reason, the 5% blend (or $\sim 15\%$ effective by volume) was the chosen blend for the remainder of this study.

D. EUFLOW simulations

A finite element simulation code incorporating the Rolie–Poly model [Likhtman and Graham (2003)], EUFLOW [Tenchev *et al.* (2008)], was used to produce a simulation of the MPR experiments. For the MPR simulations used in this paper, a two-dimensional fixed finite element grid was used, shown in Fig. 3(b). The mesh is sufficiently fine to ensure a convergence of the solution. A full description of the simulation method and matching to MPR results (for the unfilled PS2 polystyrene) is given in detail elsewhere [Lord *et al.* (2010)]. The Rolie–Poly model is a molecularly aware constitutive model which incorporates parameters to describe the processes of reptation, contour length fluctuations, and constraint release and is a simplified version of the “full” GLaMM model [Graham *et al.* (2003)]. As with the previous work by Lord [Lord *et al.* (2010)], the β parameter was set to zero therefore suppressing convective constraint release. A stress optical coefficient value of $-4 \times 10^{-9} \text{ Pa}^{-1}$ was used, in line with the value used in previous studies on polystyrene [Macosko (1994); Han and Dexler (1973); Collis *et al.* (2005)].

III. RESULTS AND DISCUSSION

A. Rheology measurements

Figure 4 shows the variation of the elastic (G') and loss (G'') moduli with frequency for the pure polystyrene (black line) and the 5% PS bead blend (gray line) measured in linear shear. It is clear that there is an increase in G' and G'' at all frequencies due to the incorporation of the cross-linked PS beads and that this is close to a pure vertical shift at all frequencies. Barnes (2003) commented that the reported results for the effect of fillers on G' and G'' are contradictory, with some authors reporting a similar increase for G' and G'' (as seen here) and others showing a larger effect for G' . In a more recent contribution [Walberer and McHugh (2001)] noted that G' and G'' always increase with added filler, but the effect depended on the molecular weight of their matrix phase. Linear rheology

FIG. 5. Non-linear shear (a) and non-linear extension (b) results for pure polystyrene measured at 170 °C for a range of strain rates.

can often give insight into whether aggregation, or flocculation, has occurred between the particles, as this is usually associated with a low frequency plateau in G' . This often occurs as the volume fraction of particles reaches a critical value, but this can depend on the size and activity of the particles, with carbon black showing this plateau at only a few percent loading. Wang *et al.* (2006) reported linear shear measurements for a carbon nanofiber/polystyrene composite made by two different processing routes. For melt blending, a purely vertical shift was observed, while for solvent blended samples a low frequency plateau was observed for particle volume fractions greater than 5%. The difference was attributed to longer fibers in the solvent blended samples leading to a network formation. The absence of any low frequency plateau in G' for the measurements reported in the current work strongly suggests no particle aggregation, subsequently confirmed by SEM analysis of freeze fracture surfaces.

The vertical shift factor, for both G' and G'' , was found to be 1.4 for the results shown in Fig. 4. There are many models in the literature for predicting this increase, from the original work of Einstein (1906) for low volume fraction blends to the widely used empirical approach of Maron and Pierce (1956); Vignaux-Nassiet *et al.* (1998)] developed a simplified variation of the Palierne model [Palierne (1991)] for rigid inclusions in

FIG. 6. A comparison of the stress-strain curves for non-linear shear tests carried out for the pure polystyrene and the 5% PS bead blend at 170 °C and at a variety of strain rates. (a) 0.01 s⁻¹, (b) 0.01 s⁻¹, (c) 1 s⁻¹.

FIG. 7. Stress ratio vs strain rate showing the position of the inverse average reptation time.

a viscoelastic media, which predicts a vertical shift factor of 1.44 for the complex shear modulus, close to the values measured here when using the effective volume fraction of 0.15. This is lower than the prediction from the empirical MKPD equation which is 1.6 using the accepted value of 0.68 for ϕ_0 [Kataoka *et al.* (1978)].

Figure 5 shows a typical set of non-linear rheology measurements (carried out at 170 °C), in this case for the pure polystyrene over a range of shear rates from 0.02 to 10 s⁻¹. Figure 5(a) is for non-linear shear and Fig. 5(b) is for non-linear extension. The results indicate that the polystyrene displays shear thinning and extension hardening. Although the polystyrene is a linear molecule, it will still strain harden in extension if the strain rate is greater than the inverse of the average Rouse time.

The two characteristic times describing the polymer dynamics of the whole chain are the Rouse and reptation times [McLeish (2002)]. The Rouse time (τ_R) is defined as

$$\tau_R = \tau_e \left(\frac{M_w}{M_e} \right)^2, \quad (3)$$

where M_w is the average molecular weight and M_e the entanglement molecular weight for polystyrene, 16 518 g/mol [Doi and Edwards (1986)].

The reptation time (τ_d) is accurately given by the expansion formula of Likhtman and McLeish (2002):

$$\tau_d = (3Z^3 \tau_e) \left(1 - \frac{2C_1}{\sqrt{Z}} + \frac{C_2}{Z} + \frac{C_3}{Z^{3/2}} \right), \quad (4)$$

where $Z = (M_w/M_e)$, $C_1 = 1.69$, $C_2 = 4.17$, and $C_3 = 1.55$.

For the polystyrene used here, those two characteristic times have values of $\tau_R = 0.29$ s and $\tau_d = 5.7$ s at 170 °C (considering an average molecular weight of $M_w = 274\,000$ g/mol). It is therefore expected that the pure polystyrene will strain harden for strain rates > 3.4 s⁻¹ although polydispersity will also have an effect.

Similar non-linear rheology measurements were carried out on the blend. Figure 6 shows some chosen comparative results comparing the non-linear shear rheology of the blend (gray line) and the pure polystyrene (black line). Figure 6(a) shows the stress/strain curve for a low strain rate of 0.01 s⁻¹. As with the linear shear results, the shape of the

curves looks very similar, with the filled material shifted upward by a constant factor. This is confirmed in Fig. 6(b), which shows the addition of a prediction of the filled stress/strain data by multiplying the stress by the same factor at all strains. For these data, a multiplication factor of 1.72 gave an excellent overlay of the measured data. This shift factor was chosen to give the best match to the data at all values of strain. For low strains (<0.1) there was evidence that a lower shift factor would be more appropriate. Interestingly, this lower shift factor (~ 1.4) was more in line with that seen from the linear shear measurements of G' and G'' shown in Fig. 4. Figure 6(c) shows a similar comparison, but for a higher strain rate of 1 s^{-1} . Again, it is seen that the curves have a very similar shape but this time the multiplication factor needed to overlay the data was lower (1.4 in this case). Finally, Fig. 6(d) shows the same comparison for a strain rate of 1 s^{-1} . Here a factor of 1.25 gave a good overlay for small strains, but at strains greater than 1 the filled material showed a lower value than would be expected from just a simple shift.

The factor required to superpose the data was determined for all the measured strain rates and is shown in Fig. 7. It is seen that this has a constant value (~ 1.7) up to a strain rate of $\sim 0.1 \text{ s}^{-1}$ at which point this falls with increasing strain rate. The onset of this additional shear thinning is seen to correspond quite well with the position of the inverse of the average reptation time ($1/5.7 \text{ s} = 0.16 \text{ s}^{-1}$), indicated by the dotted line on Fig. 7. In addition to the small increase in the internal strain rate due to the introduction of the particles [by a factor of $1/(1-\phi)$], it is expected that the particles produce additional, and significant, local strain magnification and that creates additional shear thinning. While outside the scope of the present paper, this has been confirmed by parallel finite element studies [Malidi and Harlen (2008)] which showed excellent agreement with these measurements and predicted the shear rheology of the filled material very well at all strain rates (and by inference the enhanced shear thinning/decreasing multiplication factor).

Similar comparisons were made for the non-linear extension measurements and Fig. 8 shows a selection of results. For the lowest strain rate, of 0.1 s^{-1} , the story is similar to that for the non-linear shear measurements. Figure 8(a) shows that if the results for the filled material are shifted upward, that this can be overlaid on the pure polystyrene results by a simple vertical shift of the stress. The multiplication factor of 1.6 is similar to that found for the non-linear shear results (~ 1.7) before the onset of shear thinning. As the strain rate was increased, the results for the blend no longer overlaid a simple shift at all strains. Figure 8(b) shows that results for a strain rate of 0.3 s^{-1} . Here, the stress for the filled material follows a simple shift at low strains (mirroring the linear shear measurements) but then falls below this as the strain increases. Similar results were found for all higher strain rates, with the divergence becoming greater at a strain rate of 1 s^{-1} [Fig. 8(c)] and 3 s^{-1} [Fig. 8(d)].

In order to examine possible reasons for this behavior in non-linear extension, freeze fractured surfaces were prepared from the tested samples. Figure 9 shows a typical SEM picture from a sample tested at a strain rate of 1 s^{-1} . The surface shows a large cavity which has formed between two particles during stretching. Significant debonding was found in all the high shear rate samples. The lower than expected stress in the filled material (and associated apparent suppression of strain hardening) in non-linear extension testing can therefore be associated with debonding between the particles and the polystyrene matrix during stretching and most likely occurs on, or around, the point at which the measured stress/strain curve diverges below the prediction in terms of a simple vertical multiplication factor.

Other authors, for example, Le Meins *et al.* (2003) offered a molecular explanation for the suppression of extension hardening in the filled systems they studied. It has been suggested that the presence of the particles modify a purely extensional strain field into a

FIG. 8. A comparison of the stress-strain curves for non-linear extension tests carried out for the pure polystyrene and the 5% PS bead blend at 170 °C and at a variety of strain rates. (a) 0.1 s^{-1} , (b) 0.3 s^{-1} , (c) 1 s^{-1} , and (d) 3 s^{-1} .

mixture of extension and shear (due to the local strain inhomogeneities) creating a competition between extension hardening and shear thinning phenomena in the polystyrene matrix. This would then result in a decrease in strain hardening. Katsikis *et al.* (2007) studied the elongational viscosity of a range of PMMA/nanoclay composites and came to a similar conclusion. They found strain softening behavior with increasing nanoclay content which they attributed to the development of shear flow around the fillers. While this is still a possibility for the system studied here, the over-riding mechanism would appear to be internal debonding around the particles, which has the effect of suppressing strain hardening. It is possible that debonding around the particles was also present to some degree in the previously reported studies but that it was not observed. The filled elongation results of a variety of authors [Kobayashi *et al.* (1996); Takahashi *et al.* (1999); Le Meins *et al.* (2003); Lee and Youn (2008)] all show a very similar signature to that seen here although none attribute this to debonding but as a reduction in the strain hardening parameter. Crucially, Lee and Youn (2008) showed that when their silicate/PP blend was compatibilized blend, then the strain hardening was no longer reduced, fitting in with the idea of debonding often being the driver for the strain hardening reduction.

Whether the debonding of the polymer matrix from the bead surface is common to all particle filled systems or specific to the special blend made for the visualization experiments reported in this paper is an interesting question. It is to be expected that debonding

FIG. 9. A scanning electron microscope image of the 5% PS bead blend ($\sim 15\%$ v/v) tested at a strain rate of $\dot{\epsilon} = 1 \text{ s}^{-1}$ and at a temperature of 170°C . The sample was freeze fractured and then viewed in the SEM.

will depend on, among other things, particle size, particle coupling agent [Lee and Youn (2008)], particle/matrix interactions, and particle volume fraction. These will be the subject of future research.

B. MPR results

Figure 10 shows the flow birefringence and pressure drop values for flow of the pure PS2 polystyrene through the MPR 10:1.4 constriction at 170°C . Experiments were carried out at three piston speeds of 0.16, 0.5, and 1 mm/s. Measured pressure drops for these three speeds were 17.9, 61, and 78.3 bars, respectively. All three piston speeds showed a significant amount of flow birefringence, which increased with increasing pis-

FIG. 10. MPR slit flow principal stress difference contours of the pure polystyrene at a temperature of 170°C and at three different piston speeds. dP is the measured pressure drop across the slit. Flow is from the top to the bottom.

ton speed. There was also evidence of considerable asymmetry along the vertical center line for the two higher strain rates. The three piston speeds of 0.16, 0.5, and 1 mm s⁻¹ corresponded to the apparent wall shear rates of 38.5, 120.2, and 240.4 s⁻¹, respectively. Even at the lowest piston speed, this is still significantly faster than the inverse of both the Rouse and reptation times at this temperature ($\tau_R=0.3$ s and $\tau_d=5.7$ s at 170 °C from above) indicating that both molecular orientation and stretch would be expected.

The same experiment was repeated with the 5% PS bead blend, and the results are shown in Fig. 11. At the lowest piston speed of 0.16 mm/s, it is seen that the number of fringes has increased accompanied by an increase in the pressure drop dP from 17.9 bars for the pure polystyrene to 41.1 bars for the filled polystyrene. As the piston speed was increased, this difference between the two materials became much less significant. It also became quite difficult to visualize the fringes at the higher piston speeds. A possible reason for this could be a slight mismatch in the refractive index of the two phases, but a more compelling reason is the debonding between the particles and the polystyrene melt under the high elongational strain field of the convergent flow already seen in the rheology experiments. The non-linear rheology results showed that as the strain rate was increased, debonding became more apparent. This transition was seen at a lower strain rate compared to the MPR results, but in the MPR experiments an overall compressive pressure is applied to the system, which could have the effect of delaying debonding to higher strain rates (and hence higher stresses).

Confirmation of debonding during the MPR flow experiment was obtained by examining the cell after flow had ceased. Figure 12 shows a view of the MPR cell a few minutes after flow was stopped (flow from top to bottom). Large voids were seen to form

FIG. 12. Bright-field view of the MPR slit a few minutes after flow from top to bottom had ceased. The material was the polystyrene filled with the PS beads.

FIG. 13. Theoretical fit to the pure PS non-linear rheology: (a) shear and (b) extension. The gray lines are the measured non-linear rheology (from Fig. 5) and the black lines are the best fit using the Rolie-Poly theory.

FIG. 11. MPR slit flow principal stress difference contours for the 5% cross-linked PS bead blend at a temperature of 170 °C. dP is the measured pressure drop across the slit. Flow is from the top to the bottom.

FIG. 14. Theoretical fit to the filled PS non-linear rheology: (a) shear and (b) extension. The gray lines are the measured non-linear rheology (from Fig. 5) and the black lines are the best fit using the Rolie-Poly theory and the same parameters as for the pure PS.

in the downstream region, which can be attributed to smaller voids formed during flow and convected downward. Once the pressure is released on the sample, then these can grow to a size which is visible. A similar experiment was carried out using a pure polystyrene melt that had been through the same solvent processing route and no voids were seen.

One final comment on the MPR visualization studies is the difference of the birefringence seen in the downstream region. The pure polystyrene showed the presence of characteristic “fangs” in this region. This has previously been attributed [Lee *et al.* (2001)] to highly stretched molecular material which is convected downstream of the slit into the outflow region. In the filled polystyrene, the fangs are much less obvious due partly to the turbidity of the mixture (from the internal voiding). However, the reduction in the fangs is evidence for the material being less stretched during its progress through the contraction zone due to particle/melt debonding and hence reduced stress in the melt.

2D simulation

MPR

dP = 65.6 bar

dP=39.5bar

FIG. 15. A comparison of the experimentally measured PSD contours (right hand side) and computer simulation from EUFLOW (left hand side) for the filled 5% PS blend. Measured at a temperature of 170 °C and a piston speed of 0.16 mm s⁻¹. Simulation results based on the dynamics of the pure polystyrene. dP is the measured pressure drop, either experimentally measured or simulated.

C. EUFLOW predictions

In the final part of this study, the EUFLOW finite element program was used to simulate flow birefringence and compare with the measured results from the MPR trials. The input to the simulations is the measured rheology (both linear and non-linear). A nine mode Maxwell mode spectrum was first fitted to the linear shear rheology. The choice of nine modes is arbitrary but has been found to give a good fit to the G' and G'' curves without having too many modes [Lord *et al.* (2010)]. To fit the non-linear rheology, the four

FIG. 16. Rolie–Poly fit to the non-linear extension rheology of the filled PS blend: no stretching modes. The gray lines are the measured extensional rheology and the black lines are the theoretical predictions.

slowest modes were given stretch relaxation times, while the other five fastest modes were designated as non-stretching. The Rouse relaxation times for the four slow modes were as follows, 5, 3, 1.5, and 0.1 s. These were arrived at by first fitting a single arbitrary shear rate in the center of the measured range (0.6 s^{-1}) and varying these four times to get a good fit for both the non-linear shear and non-linear extensions.

Figure 13 shows the theoretical predictions (Rolie–Poly) for both shear and extension over the measured strain rate range, using these parameters. Apart from the highest strain rates in shear, it is seen that the predictions are satisfactory for this slightly polydispersed material at all strain rates. The previous paper on the unfilled polystyrene showed that this approach gave excellent correlation with the experimentally measured flow birefringence.

Next the rheology for the filled PS blend was fitted to the Rolie–Poly model. It was found that the linear rheology could be fitted very well using the same Maxwell mode positions used for fitting the pure polystyrene but increasing the amplitude of the modes. As a first pass, the non-linear rheology was predicted using these new Maxwell mode parameters but the *same* Rolie–Poly parameters as the unfilled polystyrene (four stretching modes). The implied assumption of this approach is that the incorporated particles increase both G' and G'' (and hence the fluid viscosity) but do not change the underlying dynamics of the polystyrene matrix. Figure 14 shows a comparison of the measured non-linear rheology and the prediction from the Rolie–Poly model using this approach. As would be expected, the Rolie model overpredicts both the shear stress (as it does contain the additional shear thinning due to the particles) and the extension rheology (as there is no debonding incorporated into the current constitutive model). Figure 15 shows a comparison of the flow birefringence from the MPR tests with that predicted by EU-FLOW based on this fit to the rheology. Due to the asymmetry seen in the center line for the experimental MPR measurements for the two higher piston speeds, this is shown only for the piston speed of 0.16 m/s. As would be expected from all of the above, the simulation overpredicts the birefringence and has strong downstream fangs which are not present in the experimental measurements.

While the present version of the Rolie–Poly model does not contain either the additional shear thinning from the particles or the debonding, it can be used to assess what difference these might make to the predicted flow birefringence. In particular, debonding

2D simulation MPR
dP = 47.5 bar dP=39.5bar

FIG. 17. A comparison of the experimentally measured PSD contours (right hand side) and computer simulation from EUFLOW (left hand side) for the filled 5% PS blend. Measured at a temperature of 170 °C and a piston speed of 0.16 mm s⁻¹. Simulation results based on the dynamics of the pure polystyrene but with no stretching modes. dP is the measured pressure drop, either experimentally measured or simulated.

in the non-linear extension rheology tests can be equated to turning off the strain hardening. Figure 16 shows a second prediction of the non-linear extension rheology of the filled polystyrene but reducing the Rouse times of the three slowest modes to 1. It is seen that this gives a much better prediction of the non-linear extension rheology and Fig. 17 shows that these parameters give a better agreement with the measured flow birefringence when incorporated into EUFLOW. Switching off the strain hardening in extension eliminates the fangs, as the material is no longer stretched within the constriction zone and therefore not convected into the downstream region. The shape of the fringes in the

upstream region is not a perfect match but the number of fringes is a good match. It can be concluded that although the current form of the Rolie–Poly constitutive model does not contain the correct physical interpretation to accurately model the flow of filled polymer melts, it can give valuable insights into the underlying mechanisms and points the way for future constitutive model development for filled polymers.

IV. CONCLUSIONS

This paper has presented a study of the flow of a particle filled polystyrene melt through a 10:1.4 constriction using a combination of experimental measurements and computer simulation. A blend of cross-linked polystyrene beads in a mildly polydispersed polystyrene melt allowed flow birefringence to be measured in the Cambridge multi-pass rheometer. This was compared to computer simulations of the flow birefringence based on the Rolie–Poly constitutive model. The input to this model was a full characterization of the linear and non-linear rheology of the filled and polystyrene melt. The incorporation of the particles was found to increase shear thinning and, by virtue of debonding around the particles at high levels of strain, reduce strain hardening in extension. Switching off the strain hardening in the simulation, by having no stretching modes, gave better agreement with the experimental measurements, particularly the reduction in the fangs in the outflow region.

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