EXTRUSION VISUALIZATION- FROM BLEND STRUCTURE TO SHARKSKIN

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Abstract

Over the last five years, we have developed optical technologies for in-line monitoring of extrusion. We review two areas where we have succeeded in uncovering important concepts and phenomena by shedding light on processes that were previously unobservable. In the area of polymer blends, we have made real-time observations of blend microstructure during extrusion. we found conditions by which droplets could align in the vorticity axis. In the area of sharkskin and polyolefin extrusion, we have visualized how polymer process additives act and what causes sharkskin.

Introduction

We have developed optical based technologies for in-line measurements during polymer processing. As described below, applications of the technology include velocimetry and slippage, quality control, and morphological measurements of blends, fibers and dispersions.

We have utilized two different flow cells. The first one, which we call an optical slit die, is show in Fig. 1 It is located at the exit of a twin screw extruder[1]. Molten polymer travels through either the horizontal slit or the vertical bypass valve. Two transparent sapphire windows are flush mounted on opposite sides of the slit. (In figure 1, only the top window is visible.) This provides access for the optical instrumentation. A second flow cell is based on flow through a round transparent tube.

We conduct our studies in both real space through optical microscopy and in reciprocal space through optical lights scattering. The optical microscopy is useful for structures larger than approximately 1 μm, whereas the optical light scattering gives indirect information about structures that are as small as 0.1μm. The optical hardware is configured for rapid switching between these two modes of operation so that nearly simultaneous measurements may be conducted.

The first use that we demonstrate is the determination of structure during processing. Due to the complex flow and thermal history of the polymeric blend components, it is difficult to apply the well known droplet dispersion laws to the case of polymer blends extrusion. Furthermore, the phenomena of coalescence, compatibilization and component elasticity are only now being understood. Therefore, it is essential to have an in-situ method for determination of blends structure, to allow for rapid screening and direct determination.

Figure 2 shows the case of a polystyrene/polyethylene (PS/PE) blend as it flows through the slit die. At low shear (left column) the minor component (PS) is nearly spherical as seen by microscopy (bottom row). At intermediate throughput, the PS is strongly elongates into string like structures. At the highest throughput, the morphology reverts back to the nearly spherical droplets[2].

The droplet size is comparable in the low throughput case and the high throughput case, which was unexpected. Intuitively, one would anticipate that such a morphological reversal occurs due to a sharp decrease in droplet size and the concomitant reduction in capillary number. We have proposed that the elastic forces in the droplet component become important at high shear. It is known that high droplet elasticity can retard droplet elongation.

In the upper panel of Fig. 2, we show optical light scattering images of the blend structure. There is a complementarity between the direct images in the upper panel and the reciprocal images in the bottom one. In the case where the blend structure can be determined by microscopy, the scattering is of secondary importance because it relays indirect morphological information that is averaged over the flow profile. On the other hand, there are cases where the polymer blend structure cannot be seen from microscopy. For example, the size scale of the structure may be too small to be seen with a microscope, or the index of refraction mismatch may be too small, as with immiscible polyolefin blends. In these cases optical light scattering plays an important role.

A more surprising result was found in this same blend system near the wall, where the highest shear stresses and shear rates occur[3]. In this case (see Fig. 3), there is a transition as throughput is increased from droplets to strings and then to structures aligned along the vorticity axis. There was only one other recorded case of droplets aligned in the vorticity axis[4]; thus it was not expected here. Again, the most likely explanation for the vorticity alignment is the elastic forces in the droplet, which act to force the droplets to elongate perpendicular to the flow direction, in a manner similar to the well known rod-climbing phenomena in polymers.

Based on these results, we designed carefully controlled experiments to sort out what causes the vorticity alignment phenomenon[5]. We carried out the experiments in a

transparent plate-plate set-up, to minimize the issues of the complex flow field and flow history. The blends components were as simple as possible. One component was a Newtonian PDMS, and the other was a polyisobutylene (PIB). We adjusted the elasticity of the PIB by adding a small quantity of very high molecular weight PIB- the high molecular weight species dramatically increases the elasticity (normal forces) while leaving the viscosity relatively unchanged. We consider the case where the viscosity ratio of the two phases is near unity but the elasticity ratio of the droplet to the matrix is greater than 100.

In the limit of weak shear and small droplets (Fig. 4A), the droplet alignment is along the shear direction, whereas for strong shear and large droplets, the alignment is along the vorticity direction (Fig. 4B). There is a range of conditions for which alignment can be along either axis. For droplets aligned along the vorticity axis, the distribution of aspect ratios is broad. The kinetic transformation from droplet flow alignment to vorticity alignment upon increase of shear flow was observed, as well as the relaxation back to a spherical shape upon cessation of shear. Thus, using the visualization apparatuses, we were able to observe and isolate the factors that lead to the vorticity alignment phenomenon. It is possible that the vorticity alignment phenomenon is quite common, yet due to the paucity of direct visualization studies, it has not been appreciated.

Sharkskin and Polymer Process Additives

A second use for the device is in the area of sharkskin and polymer process additives. It has been known for many years that a surface defect known as "sharkskin," occurs in the extrusion of certain polymeric materials beyond a critical throughput[6]. The particular importance of sharkskin is that it is the first instability to occur as a function of throughput, thus it limits the rate at which these polymers can be processed. In the 1960's, it was accidentally discovered that fluorocopolymer process additives (PPA) can eliminate sharkskin, thus enabling the growth of key segments of the polyolefin industry such as linear low density polyolefins (LLDPE).

However, despite years of research, the cause for sharkskin in polyolefins, and the precise reason that the PPAs eliminate it, are still under debate[6]. The critical questions all revolve around the nature of the velocity fields in the capillary die, and the velocity fields just after the polymer leaves the die.

We utilize particle tracking velocimetry[7, 8]. We track either intentionally imbedded particles, so as 5 μm alumina, or the naturally occurring dust and other impurities in the material. As the throughput is increased, we see a transition from parabolic flow at low throughput, to plug like flow at high throughput.

In polyethylene, we have carried out carried out a series of measurements to address several questions. First, what are the boundary conditions between the polyethylene and the capillary wall, and how are they modified by the presence of the PPA? How does the PPA coat the internal surface of the capillary wall? What is the cause of sharkskin? To answer these questions, we utilize in-situ optical measurements in the exit region of a transparent sapphire capillary tube. Upstream of the die exit, the polymer, a linear low density polyethylene (LLDPE), sticks at the wall-acceleration occurs in the last 25 microns from the exit. Downstream of the exit, high-speed video-microscopy reveals that the material splits via cohesive failure into a slow moving surface layer and a fast moving core region. Figure 5 below shows the polymer just after it exits from the capillary tube. In this picture, we can see that there are two distinct regions, labeled as surface and core. The surface region moves much slower than the core. It accumulates at the exit and then peels off via adhesive detachment. Thus there are two failure mechanisms that occur during sharkskin. The first is a cohesive failure that splits the material into a core region and a surface region. The second is an adhesive failure in which the surface region splits off from the die exit.

Thus we see that through direct visualization, we are able to discern phenomena that are pervasive in the extrusion process, yet have been hitherto not possible to observe. The power of the visualization is its raw simplicity. We thus hope to continue to address critical new issues in polymer processing as they arise.

References

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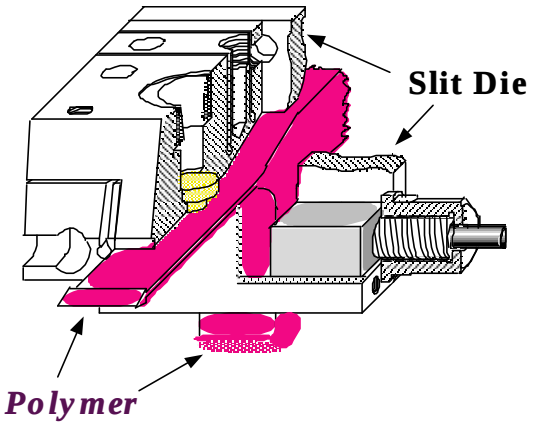

Fig. 1: Optical slit die. Polymer traversing the slit die can either pass through the narrow slit where it is optically detected, or it can pass through the lower bypass valve.

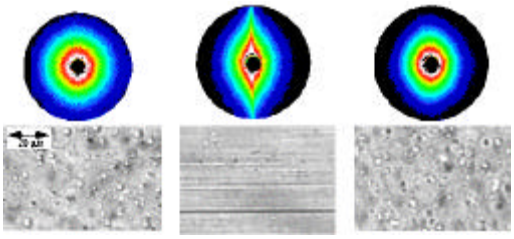

Fig. 2: Optical microscopy (bottom) and optical light scattering images of the flow of a polystyrene/ polyethylene blend through the slit die. Throughput increases from left to right. The flow direction is from right to left.

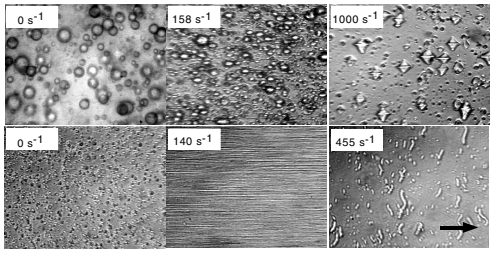

Fig. 3 Droplet morphology as a function of shear rate for 1% PS dispersed in PE. The width of each micrograph is 200 μm. In the upper panel the ratio of droplet to matrix viscosity is approximately 22 whereas for the lower panel the ratio is approximately 1.8.

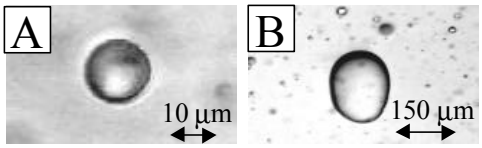

Fig. 4 Droplet morphology between in a transparent rotating plate geometry. The droplet component is a high elasticity polyisobutylene and the matrix is a low viscosity PDMS. Flow from right to left.

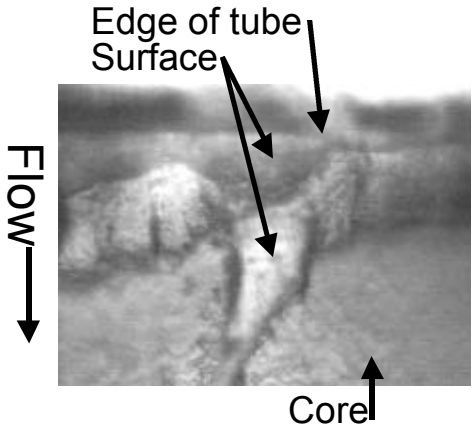

Fig. 5 Sharkskin formation in polyethylene at the exit of a capillary die. The surface and core regions are clearly visible.

Keywords: Extrusion, visualization, blends, sharkskin