LAYERED POLYMERIC SYSTEMS:
NEW PROCESSING METHODS AND NOVEL MECHANICAL DESIGN IN
EXTENSIONAL RHEOLOGY

By

PATRICK JAMES HARRIS

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Department of Macromolecular Science and Engineering

CASE WESTERN RESERVE UNIVERSITY

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We hereby approve the thesis/dissertation of

Patrick J. Harris

Candidate for the degree of Macromolecular Science and Engineering *

Committee Chair
Dr. Joao M. Maia

Committee Member
Dr. Eric Baer

Committee Member
Dr. David Schiraldi

Committee Member
Dr. Roger Bonnecaze

Date of Defense
September 4th, 2014

*We also certify that written approval has been obtained for any proprietary material contained therein.
DEDICATION

I dedicate this dissertation to a man after God’s own heart. You were a hardworking, family loving, free-spirited, friend. You will never be forgotten; always remembered and in our hearts and thoughts. To my brother and friend,

Than.
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all the glory and praise.

Joshua 1:9
ABSTRACT

Layered Polymeric Systems:
New Processing Methods and Novel Mechanical Design in Extensional Rheometry

Patrick James Harris

This dissertation presents novel mechanical designs and advances in both polymer layer multiplication and extensional rheology. In Part I, advances in polymer layer multiplication include the investigation of typical thermoplastic layer multiplication extrusion dies and the redesign of such by means of experimental and computational investigation. Results show a decrease in flow instabilities including viscous encapsulation and elastic instabilities. Similarly, an innovative layer multiplication system for highly filled and elastic rubber compounds is presented. Both of these novel systems for thermoplastic and thermosetting polymer systems are validated and understood by numerical methods using ANSYS Polyflow and CFD-Post. These advances in multilayer coextrusion allow for layering of new families of rheologically complex and as well mismatched materials, thus widening the processing capabilities at the Center for Layered Polymeric Systems. In Part II, advances in extensional rheology include a newly developed extensional rheometer for achieving high Henky
strains. The Meissner Extensional Rheometer Accessory or MERA is limited in strain only by sample rupture. Experimental validation is performed using two materials, a styrene-butadiene rubber (SBR) and a linear polystyrene (PS); the results are compared with those obtained using the well-known SER. Due to its design, it was possible to achieve homogeneous extensional flow up to unprecedented real Hencky strains in excess of 8. The second half of Part II covers a rheological understanding behind the mechanism of sharkskin, a melt fracture instability during extrusion. Solution-styrene-butadiene-styrene blended with various polybutadienes is studied. Experimental extrusion results show a behavior difference depending on the molecular architecture of the latter, polybutadiene. Extensional rheological techniques are used to investigate the behavior. Results show a higher sensitivity to stress relaxation after a step-strain rather than typical stress growth coefficients in extension.
CHAPTER 1

IMPROVED SYSTEM FOR THE CO-EXTRUSION OF
MICRO- AND NANOLAYERED THERMOPLASTIC POLYMER SYSTEMS

This chapter is partially based on:

**Journal articles:**


**United States Patent:**

Layer multiplying die for generating interfacial surfaces J Maia, J Silva, P Harris -

**Polyflow Simulations by:**

Benjamin Huntington, Roger Bonnecaze at the University of Texas at Austin
1.1 Introduction

Polymer co-extrusion is a manufacturing process in which two or more polymers feed a common die system to form a single product. This single product typically contains a layered section consisting of one or more different materials (Harris 2004; Rauwendal 1986). Upon joining the materials in a common location, typically known as a feedblock, the materials are joined and allowed to flow together into a die system (Rauwendal 1986). Dies are typically tubular, sheet, and film shaped, among others (Rauwendal 1986). Co-extrusion has the unique advantage of producing a composite material with the combined the thermal, electrical, barrier, and/or mechanical properties of the constituent materials (Harris 2004; Rauwendal 1986).

Materials that possess structures in the range of several micrometers to several nanometers in size that act in unison so as to provide synergistic effects are referred to as hierarchical structures. The final properties derived from a product are strongly dependent upon its structure; structure and property are likewise dependent upon the processing of the material (Chung 2011). Studies have shown micro- and nanolayered polymeric structures derived from forced assembly co-extrusion create a novel structure-property relationship (Jarus et al 2008; Wang et al. 2009). For example, Ponting et al. (2012) used a series of uneven, varying thickness layer multiplication dies to produce a final polymeric film product containing gradient layers, beneficial for optics and photonic films. Hierarchical helical structures have also been shown to store elastic energy and form an efficient adhesive (Pokroy et al.; 2009). Barrier performance is greatly
enhanced when using a hierarchical micro-layered polymeric structure. A high aspect ratio, impermeable phase can greatly enhance the barrier properties of a material. In generating aligned and oriented polymeric sheets, the diffusion distance is increased by creating a long pathway for the diffusing species (Jarus et al; 2001). By creating the nonconventional multilayer film, Jarus et al. (2001) was able to enhance material barrier properties by up to five-fold (Jarus et al; 2001).

Although multilayer co-extrusion capably produces materials with interesting properties, it is very susceptible to the presence of flow instabilities and non-uniformities during manufacturing. Previous studies have shown layer non-uniformities in both material composition as well as cross-section (Anderson et al. 2006). Several material properties adversely affect the flow pattern, which causes these non-uniformities; the most important of these, viscous encapsulation (Dooley 2002; Hatzikiriakos, Migler 2005; Torres et al. 1993), will be discussed in depth throughout Chapters 1 and 2. Figure 1.1 and 1.2 displays such flow flow non-uniformities; these figure shown are from Dooley (2002).
Similarly, elastic rearrangement (Dooley 2002; Hatzikiriakos, Migler 2005) adversely affects the uniform cross-section. In this work, relatively inelastic materials will be used experimentally and computationally in order to decouple the elastic from the viscous rearrangements. Viscous encapsulation, again shown in Figure 1.2 is the tendency of a material with a relatively lower viscosity to encapsulate a material with a relatively higher viscosity (Hatzikiriakos, Migler 2005). This phenomenon has been widely investigated, as exemplified by this extensive and systematic work of Joseph Dooley (2002). For example, he noted that when viscosities of two flows were similar, the interface location changed much slower than when the viscosities had a higher mismatch ratio (Hatzikiriakos, Migler 2005). Similarly, Torres et al. (1993) examined these phenomena via computation. Results from Torres (1993) predicted “stick” and “slip” conditions of a polymer-polymer-solid interface and the resulting flow effect.
If a “stick” condition was present along the steel or solid wall, a thin layer of more viscous material would become trapped between the less viscous and solid.

![Viscous encapsulation in a circular channel; entrance (left) and exit (center); exit of a square channel (right)](image)

Another rheological principle, which will be investigated, is the result of forces acting perpendicular to the direction of flow; i.e. second normal stress difference ($N_2$), (Barnes et al, 1989; Jenson, Christiansen, 2008; Morrison 2001). In general, the second normal stress difference is the difference between the amount of stress applied in the flow gradient and neutral directions. When considering plastic extrusion factors such as the frictional force along the steel wall, channel geometry, flow direction, extrusion velocity, and material type, among others, will affect the direction and magnitude of the second normal stress difference (Morrison 2001). Co-extrusion with large amounts of second normal stress differences will have an equivalent amount of layer rearrangement, thus resulting in undesirable non-homogenous final product properties (Dooley 2002).

In this chapter, we analyze experimentally and computationally the performance of two multiplier dies. The previously reported die design (Carr et al. 2012,
Ponting et al. 2012), or “standard” design, is compact and has been found to be effective for co-extruding low elasticity materials with closely matched rheological properties. This multiplication die will be termed throughout the chapter as the CLIPS first-generation die or standard die. The second-generation die is a proposed design that ensures a constant area for a balanced flow. The flow, layering, and pressure drop for these two generations of dies are compared to establish design rules for co-extruding multiplier dies.

Following the work of comparing the performance of the two dies, several small research studies are presented including feedblock and a third generation multiplier die with a rectangular shape and high aspect ratio.

1.2 CLIPS First Generation Multiplier: Layer Visualization

The standard layer multiplying die, shown in Figure 1.3, multiplies the amount of plastic layers entering the die by a factor of two. That is, after a single multiplying step, a two layer A/B system will be multiplied from two layers, to four layers. Similarly, if a system houses ten complete multiplier dies, then the polymer will enter at two horizontal layers and exit with $2^{11}$ or 2,048 horizontal layers. Assuming flow is in the ‘x’-direction, the standard multiplier works by splitting the plastic flow, compressing in the ‘z’-direction, and then expanding in the ‘y’-direction.
The standard multiplier has several potential design issues because of the compression and expansion. First, there is a cross-sectional area decrease of 50%, resulting in large stress and pressure drops. Likewise, as the plastic flows through the channel, there is asymmetry during both the compression and expansion steps which needs minimized. For example, during the expansion step, the flow expands only in one direction. The reduction in cross section and non-symmetry both play a large role in the non-uniformities produced during standard layer multiplication.
Figure 1.4 displays the CLIPS first generation multiplier die. In order to best understand the flow through the CLIPS first generation multiplier die, a special visualization die was manufactured. The visualization die could be split after
extrusion and cooling to pull solid plugs of extrudate form the die packs. These extrudates were cut at the planes shown in Figure 1.4 and studied. The work was completed by Jessica Patz at CLIPS and summarized (Huang, submitted 2014).

To best co-extrude two or more polymers, typically two approaches are used. First, the processing temperature is selected so that both materials have the same viscosity. If that is not possible, then two differing extruder temperatures are used to yield similar viscosities. However, this course of action is not always possible because of the thermal gradients that develop in the films, which can break-up the layered structure. A novel solution is needed in order to co-extrude high viscosity ratio materials while minimizing or eliminating viscous encapsulation.

### 1.3 CLIPS Second Generation Multiplier: Proposed Design

The first generation multiplier has historically worked well with rheologically matched materials (Jarus et al. 2001; Ponting et al. 2010); however, in order to expand the window of capable materials, a new design is proposed. The new multiplier (Figure 1.5) has a constant cross-sectional area and ensures a balanced and symmetrical flow through the die. In order to overcome the compression-then-expansion step of the standard multiplier, the proposed die simultaneously compresses the material in one direction and expands in another while keeping the cross-sectional area constant. That is, a single channel of the
proposed die has a 2:1 vertical height to width ratio, expands and compresses the material to a 1:2 vertical height to width ratio.

Figure 1.5: Proposed layer multiplication process – second generation die

Upon layer multiplication, normal stresses built up within the flow are relaxed by flat die land at the exit of the die. This design is modular and can be adapted to different materials and desired flow ratios by changing the relative length of the different zones, the incorporation of intermediate die lands, or the height to width ratio. Figure 1.6 displays the second-generation die proposed within a round channel. The Figure 1.6 shows how the segmented die can be split and interchanged with different length geometries.
In this work, we only show the comparison between the basic design and the standard multiplier. The basic design has a 1:1 height to width ratio and four similar length zones, for a total length equal to the standard design. In future work, we will present results for different geometries.

Due to the complexities of the proposed die system, the modular system was machined using both ram and wire EDM machining processes. The internal geometry of the die systems were held to a tolerance of 0.001”. The steel chosen for the internal segments as well as the die holders are H-13.

Figure 1.7 – 1.12 display the detail drawings for each of the components.
Figure 1.7: Proposed multiplier housing for the CLIPS second-generation die

Figure 1.8: First segment in the flow path
Figure 1.9: Second segment in the flow path

Figure 1.10: Third segment in the flow path
Figure 1.11: Fourth segment in the flow path
Figure 1.12: Key for the assembly of the proposed segments

Figure 1.13 outlines the final assembly and flow proposal of the flow multiplication. In all isometric views, the arrows represent the flow direction. The four rows represent each of the four steps in a single multiplier. The entering material is first split and flows horizontally. Next, a horizontal structure forms by simultaneous compression and expansion. In the final two steps, the die rearranges the polymer forming the final structure displayed. As discussed previously, the components are housed within the housing shown in Figure 1.7.
1.4 Experimental

1.4.1 Materials

Two commercial poly (methyl methacrylate), Plexiglas® VS100 and Plexiglas® V826 and one polystyrene (PS), Styron 615APR were used. Styron 615APR will be referenced throughout the remainder of this study as material “A”. Plexiglas® VS100 will be referenced as “B_m” (representing ‘matching’ viscosity) and the Plexiglas® V826 referenced as “B_{nm}” (representing ‘non-matching’ viscosity).
1.4.2 Rheological Measurements

The primary purpose of rheology for this study is to evaluate the material's rheological properties for the use as inputs for computational simulation. The shear flow properties were performed in a rotational rheometer (Thermo Fisher Scientific MARS III) equipped with parallel plates of 25 mm diameters. Sample thickness was 1 mm. All samples were vacuum dried for 8h at 70°C prior to the rheological experiments. The experiments were conducted under a nitrogen atmosphere in order to preclude oxidative degradation of the samples. The frequency sweeps were performed at different temperatures between 180°C and 240°C with the angular frequency ranged between 0.01 and 100 rad/s. The time-temperature superposition was performed using IRIS software.

The uniaxial extensional flow measurements were conducted on an Paar Physica MCR 501 from Anton Paar, coupled with the Sentmanat extensional fixture (Sentmanat; 2004) The temperature for the uniaxial extensional flow measurements was set in a way to avoid the sagging of the sample, at 160 °C for the PS 615 and PMMA VS100, and 190 °C for the PMMA V826; both under different constant rates of deformation, ranging from 0.01 to 10 s\(^{-1}\). Rectangular specimens of length 17.7mm, width 12.5mm and thickness of 0.8 mm were molded at 200 °C in a compression mold. The specimens were subjected to 200 °C for 5 min during molding. Prior to testing, the rheometer was first heated and kept at a set temperature for 5 min to reach equilibrium.
Figure 1.14: Dynamic moduli of PS 615, PMMA VS100, and PMMA V826 at 230 °C (open symbols: $G''$; closed symbols: $G'$)

The dynamic moduli of the materials used in this work are shown in Figure 1.14. PS 615 and PMMA VS100 have similar values for loss moduli whereas the storage modulus at low frequencies for PS615 is slightly higher than the storage modulus at low frequencies for PMMA VS100. PMMA V826 exhibits higher dynamic moduli than the PS 615 and PMMA VS100. Nevertheless, the three materials are relatively inelastic. The relaxation spectra, which were calculated by IRIS software, are shown in Table 1.1 and the respective fittings are in Figure 1.14.
Table 1.1: Relaxation spectrum of PS 615, PMMA VS100 and PMMA V826 at 230 °C

<table>
<thead>
<tr>
<th>Mode (i)</th>
<th>PS 615 (G_i) (Pa)</th>
<th>(\lambda_i) (s)</th>
<th>PMMA VS100 (G_i) (Pa)</th>
<th>(\lambda_i) (s)</th>
<th>PMMA V826 (G_i) (Pa)</th>
<th>(\lambda_i) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(1.82 \times 10^5)</td>
<td>(3.14 \times 10^{-4})</td>
<td>(4.20 \times 10^5)</td>
<td>(5.96 \times 10^{-5})</td>
<td>(1.84 \times 10^5)</td>
<td>(2.99 \times 10^{-5})</td>
</tr>
<tr>
<td>2</td>
<td>(7.40 \times 10^4)</td>
<td>(2.53 \times 10^{-3})</td>
<td>(1.51 \times 10^5)</td>
<td>(6.22 \times 10^{-4})</td>
<td>(7.23 \times 10^4)</td>
<td>(3.93 \times 10^{-4})</td>
</tr>
<tr>
<td>3</td>
<td>(2.68 \times 10^4)</td>
<td>(1.26 \times 10^{-2})</td>
<td>(7.22 \times 10^4)</td>
<td>(3.24 \times 10^{-3})</td>
<td>(7.96 \times 10^4)</td>
<td>(2.35 \times 10^{-3})</td>
</tr>
<tr>
<td>4</td>
<td>(7.11 \times 10^3)</td>
<td>(5.32 \times 10^{-2})</td>
<td>(2.27 \times 10^4)</td>
<td>(1.36 \times 10^{-2})</td>
<td>(6.59 \times 10^4)</td>
<td>(1.12 \times 10^{-2})</td>
</tr>
<tr>
<td>5</td>
<td>(9.43 \times 10^2)</td>
<td>(2.33 \times 10^{-1})</td>
<td>(3.08 \times 10^3)</td>
<td>(6.02 \times 10^{-2})</td>
<td>(3.66 \times 10^4)</td>
<td>(5.12 \times 10^{-2})</td>
</tr>
<tr>
<td>6</td>
<td>(3.62 \times 10^1)</td>
<td>(1.26 \times 10^0)</td>
<td>(1.91 \times 10^1)</td>
<td>(7.85 \times 10^1)</td>
<td>(1.11 \times 10^1)</td>
<td>(2.24 \times 10^1)</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td>(9.06 \times 10^2)</td>
<td>(1.03 \times 10^0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td>(4.50 \times 10^1)</td>
<td>(9.22 \times 10^0)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The multi-mode Phan-Thien-Tanner (PTT) model (Thien; Tanner; 1977) was used to fit the rheological data. Each mode of the PTT model obeys Equation 6 where \(G_i\) and \(\lambda_i\) are the relaxation modulus and relaxation time of mode \(i\) and \(D\) is the rate of deformation tensor. The adjustable parameters \(\xi\) and \(\alpha\) were kept constant for all relaxation modes.

\[
\nabla \frac{\tau}{\tau} = \frac{1}{\lambda_i} \exp \left( \frac{\alpha}{G_i} tr \tau \right) + \xi (D \cdot \tau + \tau \cdot D) = 2G_i D
\]

\[
\nabla \frac{\tau}{\tau} = \frac{\partial \tau}{\partial t} - \nabla \tau^T \cdot \tau - \tau \cdot \nabla \tau
\]
Figure 1.15 shows the shear viscosity for the three materials. PS 615 and PMMA VS100 have similar zero shear viscosities and shear-thinning behavior. PMMA V826 is about 10 times more viscous at low shear rates and shows a more pronounced shear-thinning.

![Graph showing shear viscosity](image)

**Figure 1.15**: Steady shear viscosity at 230°C for PS 615, PMMA VS100 and PMMA V826 and PTT model fitting. PTT parameters: PS 615 ($\xi=0.51s^{-1}$; $\alpha=0.072s^{-1}$), PMMA VS100 ($\xi=0.55s^{-1}$; $\alpha=0.49s^{-1}$) and PMMA V826 ($\xi=0.34s^{-1}$; $\alpha=0.47s^{-1}$). Cox-Merz rule is assumed to be verified.

In order to find the PTT parameters that best fit to the rheological behavior of the materials uniaxial extensional experiments were also performed; shown in Figure
However, as stated in the experimental section, the extensional experiments were not conducted to 230°C but rather at lower temperatures.

![Figure 1.16: Uniaxial extensional viscosity for PS 615 at 160°C and PTT model fitting. PTT parameters: $\xi=0.55s^{-1}$; $\alpha=0.49s^{-1}$.](image)

For extensional experiments, the PTT fitting was not done for the higher deformation rate, 10s$^{-1}$, since at this deformation rate the material is in the elastic regime and therefore cannot be described by the model. PMMAs, shown in Figure 1.17 and Figure 1.18, do not exhibit any strain hardening at intermediate and low deformation rates. PS 615 in Figure 1.16 has a relatively small strain hardening at 1 s$^{-1}$. 
Figure 1.17: Uniaxial extensional viscosity for PMMA VS100 at 160°C and PTT model fitting. PTT parameters: \( \xi = 0.51 \text{s}^{-1} \); \( \alpha = 0.072 \text{s}^{-1} \).
Thus, the PTT parameters, $\xi$ and $\alpha$, that best fit to both shear and extensional experimental results were determined. Although there is a slight over prediction of shear-thinning at high shear rates, the model is able to accurately describe the
rheological behavior of the materials and it is therefore a good choice to use in the numerical simulations of co-extrusion.

1.4.3 Multilayer Co-extrusion

Prior to co-extrusion, all materials were dried for 24 hours at 80°C. Co-extrusion was performed using two Killion extruders, model number 19782; and Zenith melt pumps, model number K46LP56. Screw RPMs were set to a constant 5.0 RPM.

When performing co-extrusion of similarly matched viscosities (A-Bm-A), melt temperatures were set to 230°C. When using non-matched viscosities (A-Bnm-A, Bnm-A-Bnm), the polymer melt was set to 240°C.

1.4.4 Simulation Method

The flow through the multiplier dies was computed with Ansys POLYFLOW®. The flow is assumed to incompressible and isothermal and the rheology of the polymers is assumed well described by the Phan-Thien Tanner (PTT) constitutive model (see below). The equations governing the flows are the Cauchy-momentum equation given by

\[
\rho \frac{Du}{dt} = \nabla \cdot T + \nabla p + \rho g, \quad (2)
\]
and the continuity equation

\[ \nabla \cdot \mathbf{u} = 0, \quad (3) \]

where \( t \) is the time, \( \mathbf{u} \) is the velocity vector, \( p \) is the pressure, \( \rho \) is the fluid density, \( \mathbf{g} \) is the gravitational field and \( \mathbf{T} \) is the stress tensor described by the PTT model.

The tensor \( \mathbf{T} \) is split into a viscoelastic component \( \mathbf{T}_1 \) that is computed according to the chosen PTT model (Phan-Thien & Tanner 1977) and a purely viscous term \( \mathbf{T}_2 \). (This decomposition helps the convergence of the numerical method (Ansys POLYFLOW user’s guide)). Therefore, the stress \( \mathbf{T} \) is given by

\[ \mathbf{T} = \mathbf{T}_1 + \mathbf{T}_2. \quad (4) \]

\( \mathbf{T}_2 \) is considered as the stress response associated with the fastest relaxation time and \( \eta_2 \) is the viscosity factor associated with it so that

\[ \mathbf{T}_2 = 2 \eta_2 \mathbf{D}. \quad (5) \]

\( \mathbf{T}_1 \) according to the PTT model is implicitly given by
\[
\exp\left(\frac{\varepsilon \lambda}{\eta_1} T_1 + \lambda \left[ \left(1 - \frac{\xi}{2}\right) T_1 + \frac{\xi \Lambda}{2} T_1 \right]\right) = 2 \eta_1 D. \tag{6}
\]

The symbol \( \overset{\cdot}{T}_1 \) the upper-convected time derivative of \( T_1 \), and \( \overset{\wedge}{T}_1 \) is the lower-convected time derivative. The rate of deformation tensor \( D \) is

\[
D = \frac{1}{2} (\nabla u + \nabla u^T). \tag{7}
\]

The viscosity \( \eta_1 \), is given by

\[
\eta_1 = (1 - \eta_e) \eta, \tag{8}
\]

\[
\eta = \eta_2 + \eta_1, \tag{9}
\]

Where
\[ \eta_r = \frac{\eta_2}{\eta_2 + \eta_1}. \]  

While the complete relaxation spectra of the polymers studied here were measured, only the longest relaxation times were used in the simulations. This was sufficient to capture the flow behavior of these materials in the two multiplier dies. The parameters for three different polymers used in the simulations are summarized in Table I.2.

Table 1.2: Material parameters at 230 C for the three polymers simulated with ANSYS POLYFLOW.

<table>
<thead>
<tr>
<th></th>
<th>PMMA VS100</th>
<th>PS 615</th>
<th>PMMA V826</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta_r ) (Pa.s)</td>
<td>0.63</td>
<td>0.56</td>
<td>0.015</td>
</tr>
<tr>
<td>( \eta ) (Pa.s)</td>
<td>39.99</td>
<td>102.47</td>
<td>926.50</td>
</tr>
<tr>
<td>( \xi )</td>
<td>0.546</td>
<td>0.510</td>
<td>0.336</td>
</tr>
<tr>
<td>( \epsilon )</td>
<td>0.490</td>
<td>0.072</td>
<td>0.468</td>
</tr>
<tr>
<td>( \lambda ) (s)</td>
<td>0.785</td>
<td>1.260</td>
<td>9.220</td>
</tr>
</tbody>
</table>

At the upstream portion of the die, the polymer layers are split in half and flow in the two halves of the die. The split is assumed perfect and so only one-half of the multiplier die is simulated. The boundary conditions for the simulations are as follows. At the inlet the total flow rates of the two types of polymers in the multiplier are specified (\(1 \times 10^{-7}\) or \(3 \times 10^{-7}\) m\(^3\) s\(^{-1}\) for each polymer). At the outlet
it is assumed that the normal force and tangential velocities vanish. On solid boundaries where there is no interface, the no slip condition is assumed. On the surfaces where the interface touches, a slip condition is applied to allow the position of the interface to evolve as it propagates downstream from the inlet. On the slip surface, the shear force $F_s$ is assumed to be proportional to the slip velocity $u_s$ according to $F_s = -k u_s$ with $k = 667,300 \text{ kg s}^{-1}$.

1.5 Results and Discussion: Proposed Second Generation Multiplier

1.5.1 Experimental

Figure 1.19 displays the exit of the extrusion feedblock and the resulting viscous encapsulation (from left to right: A-B$_m$-A, A-B$_{nm}$-A, and B$_{nm}$-A-B$_{nm}$). Noticeably, the matched viscosity materials have 10-15% encapsulation, whereas the non-matched viscosity materials show complete encapsulation.

Figure 1.19: Exit of extrusion feedblock, 3 layers (shown left to right: A-B$_m$-A, A-B$_{nm}$-A, B$_{nm}$-A-B$_{nm}$)
The $B_{nm}-A-B_{nm}$ system has a much poorer performance compared to the $A-B_m-A$ system; however, it shows better layering performance when compared to the $A-B_{nm}-A$ system. This can be explained by the higher amounts of stress at the wall promoting the flow of the lower viscosity material the $B_{nm}-A-B_{nm}$ system has less lower viscosity material along the wall, hence encapsulation is delayed. Since layer multiplication begins directly following this stage, it is important to have a balanced and symmetric flow into the multipliers.

Figure 1.20: Extrusion results $A-B_m-A$ (shown top to bottom: 5 layers, 9 layers, 17 layers; left to right: standard, proposed)
The first set of images, using the matched system, Figure 1.20, compares the standard multiplier in the left column and the proposed multiplier in the right column. The amount of layers derived (shown from top to bottom) is five, nine, and seventeen respectively. The proposed multiplier shows as good of a multiplication performance, as standard multiplier. In both cases, viscous encapsulation is kept to a minimum and, therefore good layering structure is promoted.

The second set of data, shown in Figure 1.21, displays the non-matched system A-B_{nm}-A. Overall format of the images remains the same as before.

Figure 1.21: Extrusion results A-B_{nm}-A (shown top to bottom: 5 layers, 9 layers, 17 layers; left to right: standard, proposed)
Unlike the matched system, both the standard and proposed multipliers result in an entrance having encapsulated material. Since the material entering here is encapsulated, the multiplier which adds the most shear stress will result in a greater layer rearrangment. Similar layer capability is shown for five layers; however, the results begin to diverge at nine layers. The proposed multiplier tends to minimize encapsulation and is able to maintain remnants of a horizontally layered structure, much better than the standard multiplier. This increased encapsulation in the latter, results in a poorer layer structure. As the material develops into 17 layers (bottom), the proposed die has much better performance in creating layers than the standard multiplier.

Lastly, the $B_{nm}-A-B_{nm}$ results are displayed in Figure 1.22. Again, the proposed multiplier is better able to handle the mismatch in viscosity, resulting in a more uniform layer structure. Here, there is evidence of the great importance of placing the higher viscosity material on the outside rather than inside.
1.5.2 Polyflow Simulation

The following results were produced by Ben Huntington in the research group of Dr. Roger Bonnecaze at the University of Texas at Austin in collaboration with the CLIPS program at CWRU.

Results from computational simulation are formatted similarly in Figure 1.23 thru Figure 1.25; that is, with the standard multiplier shown in the left column and the proposed shown in the right column; from top to bottom rows, the results show A-Bm-A, A-Bnm-A, and Bnm-A-Bnm. The first computational study looks at the
velocity of the polymer in the flow direction; Figure 1.23. In general, an even
distribution, or more consistent color, is desirable as this implies that the polymer
will be subjected to similar shear stresses. In all six images, encapsulation can
be seen in the simulation results, confirming the experimental results shown
above. The greatest change in velocity across a single profile is in the standard
multiplier. The basis for this is the reduction of the cross-sectional area in the
standard multiplier. As the flow enters this region, the velocity is greatly
increased as the system tries to maintain the overall flow rate. Though a velocity
profile distribution can be seen in the proposed multiplier, the results are much
more balanced and will result in a lesser pressure drop, as will be shown later.

![Figure 1.23: Flow velocity (grouping shown left: standard multiplier; right
proposed multiplier)](image)
The results for the second normal stress differences can be seen in Figure 1.24. Similar to the velocity profiles, the standard multiplier contains the highest variations in N2. This is true for all material systems as the compression then expansion stages of the standard multiplier places a large amount of normal stresses on the polymers. Since the proposed multiplier has a constant cross sectional area, the channels are required to move side to side and up and down, in the y and z axes. This channel movement places a low, yet clear normal stress on the polymer.

Figure 1.24: Second normal stress difference (grouping shown left: standard multiplier; right proposed multiplier)
Figure 1.25 shows the in-plane velocity. Unlike the previous results, the material in the proposed multiplier is subjected to the highest in-plane velocity, although all material systems display relatively similar results that stems from the fact that in the third module, whereupon the channels physically converge. Thus, this is by and large a geometrical effect and not a material one. The greatest amount of in-plane velocity is shown in the proposed multiplier using the A-B_{m}-A system (top left). This can be explained as the average viscosity of the system is lower than the other two systems. As the directional change occurs, polymer with the lowest overall viscosity changes direction the most easily.
The pressure drop through a single multiplier was next investigated computationally. Figure 1.26 displays the approximate system pressured drops of the three material systems. When moving from the standard to the proposed die of the A-B_m-A system, a total pressure drop reduction of 40% is achieved. Similarly, the A-Bnm-A system is decreased 45%, and the Bnm-A-Bnm system is decreased 41%.

![Layer Multiplication System Pressure Drop Reduction - Polyflow Simulation Results](image)

Figure 1.26: Pressure drop reduction (left to right: A-B_m-A, A-Bnm-A, and Bnm-A-Bnm)

The advantages of this 40-45% pressure drop reduction are a decreased facility energy usage and the ability to use more layer multiplication dies which will result in a total number of layers achievable.
1.6 Nine Layer Feedblock Design

1.6.1 Design A: Round Channels

As discussed previously, a challenge in multilayer co-extrusion is the ability to layer both compatible and incompatible viscoelastic materials. Over the last chapter, we’ve discussed how to, at least in a large improvement, layer viscoelastically mismatched materials by using a proposed “second generation” CLIPS die. We showed that by maintaining a constant cross-sectional area, the multi-layered structure is drastically improved.

The relatively poor layer structure entering the multiplier dies from the feedblock only complicates the instabilities. Starting with a wider aspect ratio than 1:1 improves layer uniformity. Dooley (2002) first showed this theoretically and experimentally. Thus, we want to investigate the feedblock and propose a new design for a feedblock that will maximize the horizontal layering structure as it enters the first layer-multiplying die.

First, we will look at using round channels, or more specifically half-round channels, which would be ball-milled into two-halves; similar to what would be seen in injection molding. Figure 1.27 shows an isometric design representation of what would a round style nine-layer feedblock would look like. The overall design proposal would be a three component feedblock, two outer blocks each having one inflow on the outboard to allow connection to a single screw extruder. The outboard steel blocks would contain either a four flow split or a five flow split.
Figure 1.27: Nine-layer feedblock concept with a half round channel into three blocks

A mating center block will have both flow patterns on either side of the block. Also in this center block is a complex geometry which brings all nine flows into a common location. From here, the multiplication dies can be attached.

Although this geometry proposal for the nine-layer feedblock is appropriate, the machining challenge is great and an alternative design is proposed.

1.6.2 Design B: Rectangular channels

Alternative to half-round style geometry for a nine-layer feedblock is a rectangular geometry. Again, the standard 3 or 5 layer feedblock geometry
which was used throughout the thesis chapter is displayed in Figure 1.28. At CLIPS at CWRU, the geometry in Figure 1.28 is used almost exclusively for multilayer coextrusion. Again, the primary goal of redesigning this flow merging geometry is to reduce any flow instabilities in the feedblock prior to the layer multiplication steps directly following the feedblock.

![Figure 1.28: Standard 3 or 5 layer feedblock used at CWRU CLIPS facility](image)

Figure 1.29 display the isometric assembly detail drawing. The final proposed design contains five major steel blocks and several small standard “stock” components. First, similar to the half-round nine-layer design above, the two outer blocks have a four-flow or five-flow geometry, which are combined into the center block. From here, the center block feeds into two more geometries, which ease the flow fronts together into a wide-aspect horizontal structure. Other
general stock components include hardware, dowel pins for alignment, stick heating cartridges, and temperature transducer ports.

Concerning the manufacturing of the rectangular nine-layer feedblock, the steel chosen for the five main components are a pre-hardended 420 stainless mold steel. The components were polished to a SPI B-2 finish, or a wire EDM finish. Each flow block has a 0.0625 inch radii in the bottom of the ramped channels. All wire EDM channels have a 0.006 inch radius in the pocket corners. Figure 1.30 and 1.31 show isometric assembly views of the final nine-layer feedblock geometry, except with cutting planes used for visualizing the internal flow path.
Figure 1.30 displays the one of the two material flow paths, which ends as a single layer or the nine-layer output.

Figure 1.30: Assembled nine-layer feedblock with a horizontal cutting plane displaying a single flow path

Similar to the above Figure 1.30, Figure 1.31 displays a cutting plane except vertically through the center block of the main geometry. Figure 1.31 displays the combining flow into a nine-layer structure which converges into a short die land used to allow the material(s) to flow together before reaching the first multiplier die (not shown). Figure 1.32 displays a solid rendering of the assembled geometry. Figure 1.33 – 1.37 displays the remainder of the detail drawings for the final manufacturing of the rectangular nine-layer feedblock.
Figure 1.31: Pressure drop reduction (left to right: A-B_m-A, A-B_nm-A, and Bnm-A-B_nm)
Figure 1.32: Final assembled view of a nine-layer feedblock

Figure 1.33: Detail drawing: Five flow feedblock
Figure 1.34: Detail drawing: four flow feedblock

Figure 1.35: Detail drawing: central block
Figure 1.36: Detail drawing: compression block

Figure 1.37: Detail drawing: Stability block
1.7 Rectangular Multiplier

Throughout the prior chapter, we’ve worked through several challenges in improving the layered structure in multilayer coextrusion. As discussed, flow instabilities are prevalent in standard equipment and in order to minimize instabilities such as viscous encapsulation and elastic effects due to high values of N2, geometry of the equipment needs properly designed. Learning from redesigning the “standard” or first generation multiplication die, a constant cross-section must be maintained. A third generation design is proposed in the final section of this dissertation chapter. The flow geometry proposed is an 8:1 geometry and is displayed in Figure 1.38. Similar to the second generation die, the steel components are designed in a segmented fashion for future studies of geometry length.

Figure 1.38: High aspect ratio, rectangular polymer layer multiplier (flow top-right to bottom-left)
Again, the primary purpose of designing a multiplier with geometry shown in Figure 1.38, is due to the high aspect ratio. Dooley (2002) recognized viscous encapsulation was minimized or at least held to the outer edges when a wider-than-tall geometry was used. To build off the success of the previous nine-layer geometry, a nine-layer feedblock was incorporated. The main components from Figure 1.33 – 1.35 were used for this study, while the components from Figure 1.36 – 1.37 were redesigned to have an output to match the inflow of the geometry in Figure 1.38. The final isometric assembly view is shown in Figure 1.39 below.

Figure 1.39: Solid isometric view of a nine-layer feedblock with a high aspect ratio output to flow into a rectangular layer multiplier.
Figure 1.40: A rendering of the proposed nine-layer feedblock and high aspect ratio rectangular multiplier die.

Figure 1.41: Solid isometric view with flow channel (left), solid isometric view with solid proposed manufactured multiplier dies.
1.7.1 Validation

Huang (submitted IPP 2014) studied validation of the entire system in detail. Shown in Figure 1.42 is the rheology of several materials. The first row houses the rheology of the materials described earlier (Figure 1.14 – 1.16). A second set of material was chosen for this study to investigate the elastic effects of a material combination. The materials chosen are two thermoplastic polyurethanes. Figure 1.42 displays the gross mismatch of elastic stresses from the TPUs.

Taken from Huang (submitted IPP 2014), the results of coextrusion are displayed in Figure 1.43. The image at left in Figure 1.43 displays a TPU layered structure taken from standard equipment, while the image on the right displays the layering results from a nine-layer feedblock into a rectangular multiplier. The results as outlined in Huang’s thesis and research paper (IPP 2014) show conclude excellent layering capability with the final layering system. The final layering system capably performs on a wide range of viscosity and elasticity ratio systems.
1.8 Conclusion

Microlayer co-extrusion technology shows promise in applications ranging from films, to membranes, optics, and electronic system but is currently limited to the layering of materials with very similar viscosities. A proposed next generation die
design was engineered and incorporated into this experimental work, one that allows for a balanced and symmetric flow that, and in turn allows for lower viscous encapsulation. In fact, experimental results show matched performance when layering matched viscosity materials and enhanced layering performance of nonmatched viscosity materials when contrasted to the standard die design. Computational results using Polyflow simulation based upon PTT models correlate well with co-extrusion images and provide guidance to further optimization. High velocity gradients are present in the standard multiplier, while a more balanced flow is displayed in the proposed multiplier. Similarly, second normal stress differences are minimized in the proposed multiplier. Though larger amounts of in plane velocity is displayed in the proposed multiplier, the overriding factor controlling layer rearrangement and viscous encapsulation is shown to be a cross sectional area reduction and subsequent normal stress derived in the standard multiplier.
1.9 References

6. Ponting, Michael; et al., **49**, 12111-12118 (2012)
CHAPTER 2

MULTILAYER CO-EXTRUSION OF HIGH VISCOSITY ELASTOMER SYSTEMS:
PLATFORM DEVELOPMENT AND IMPLEMENTATION

This chapter is partially based on:

Journal article:

P. Harris, et al., (2014) Submitted

United States Patent:

Methods for Layer Multiplication of High Viscous Elastomer Polymeric Systems,
Application 2014-2630
2.1 Introduction

In recent years, advances in co-extrusion technology have led to the development of micro- to nano- layered polymeric structures via layer multiplication extrusion [1, 2, 3]. Due to limitations in the existing technology, layered polymers are confined to a window of standard thermoplastic materials. Consequently, current layering technology is not applicable to low viscosity systems (such as thermotropic liquid crystalline polymers [tLCPs]), as well as high viscosity systems (such as elastomers and unvulcanized rubber). Limitations are due to several factors including rheologically incompatible materials, die design, gear pump capability in manufacturing, and extrusion instabilities. Overcoming and expanding this processing window is possible in specific situations, for example, by chemically altering tLCP to allow for a higher viscosity at processing temperatures viscosity [1]; other methods include geometric correction of the multiplication die [2, 3]. The aim of this study is to develop a full-scale multilayer co-extrusion process capable of layer multiplication of high viscosity materials for the elastomer and rubber industry.

Plastics co-extrusion is an industrial manufacturing process by which two or more polymers feed into a common die system to form a single product. This single product typically contains a layered section consisting of one or more different materials. After leaving the extruders, the materials meet and converge in a feedblock. In the case of continuous multilayering co-extrusion, the materials are then allowed to flow together into the multiplication die packs. The primary advantage of multilayer co-extrusion is the ability to produce a composite
material with the combined thermal, electrical, barrier, and/or mechanical properties of the constituent materials in a continuous extrusion process [4, 5]. The final properties derived from a product are strongly dependent upon its structure; structure and property are likewise dependent upon the processing of the material [6].

The development of co-extrusion began in the early 1930s by the Wingfoot Corporation when two unvulcanized rubber materials were joined in a feedblock [7]. Later, D.N. Lehman described a co-extrusion process for joining tire tread and side wall rubber together [8]. Companies such as the U.S. Rubber Company, B.F. Goodrich Company, Goodyear Tire and Rubber Company, and Bridgestone Tire Company, all followed suit in developing novel concepts to join several unvulcanized rubber materials for the manufacturing of rubber goods [9].

Co-extrusion research and manufacturing accelerated in the thermoplastics industry beginning in the 1960’s when the Dow Chemical Company developed the continuous multilayer co-extrusion system [10]. However, only very limited research has been performed in the area of multilayer co-extrusion of unvulcanized rubbers thus far, because of various processing difficulties. First, multilayer co-extrusion dies are confined geometrically, which means the pressure requirements for such processing techniques are high. Secondly, as with any unvulcanized processing technique, there is a high risk of vulcanizing the compound in the extrusion die. This is the case in multilayer co-extrusion where longer residence times and longer flow paths may abound.
Figure 2.1 displays the general concept of how polymer layer multiplication works. An incoming flow front is typically split vertically, rearranged, and then restacked, forming an outflow multiplication of the original inflow.

![Generic polymer multiplier](image)

**Figure 2.1: Generic polymer multiplier**

Research has shown that micro- to nanolayered polymeric structures produced via multilayer co-extrusion can create novel structure-property relationships. For example, Ponting et al. [11] used a series of uneven, varying thickness multiplier dies in order to produce a gradient-thickness layered product for the optics and photonic industry. These optical lenses achieve outstanding properties based on varying the refractive index of each lens. Barrier properties are also typically enhanced with multilayer co-extrusion. A high aspect ratio, impermeable phase can greatly enhance the barrier properties of a sheet; this is typically performed by creating a tortuous path for the diffusing species [12]. Jarus et al. [12] were
able to enhance the gas barrier properties five-fold by comparison with conventional co-extruded films.

Though multilayer co-extrusion adeptly produces materials with interesting properties, the process is very susceptible to the presence of flow instabilities and non-uniformities during manufacturing. Studies have shown layer non-uniformities in both material composition as well as cross-section [2, 3]. Several material properties adversely affect the flow pattern that causes these non-uniformities. One example of important flow non-uniformity is viscous encapsulation [13, 14, 15]. Viscous encapsulation is the tendency of a material with a lower viscosity to encapsulate a material with a higher relative viscosity [13, 14]. This phenomenon has been widely investigated, as exemplified by the extensive and systematic work of Joseph Dooley [13]. When secondary flow patterns exist due to high second normal stress differences then elastic rearrangement of the melt is possible. This rearrangement of the melt stream has a direct effect on the outcome of layer structure and quality. Torres et al., Dooley et al., and several others, studied several instabilities numerically [2, 3, 13, 15]. Similarly, elastic rearrangement adversely affects the cross-section uniformity. One such study by Debbaut et al. [16] observed secondary motions using a single polymer with different pigmentation in non-circular channels. Debbaut's results displayed deformations of the interface due to the action of secondary normal stress difference. The experimental results were confirmed numerically.
2.1.1 Pressure Drop Reduction – Improved Interfacial Surface Generator

In our previous work [2], we compared two polymer co-extrusion multiplication dies experimentally and computationally. The two dies are shown in Figure 2.2.

![Figure 2.2: CLIPS first (left) and second (right) generation multipliers](image)

The first generation die is compact and has been used successfully for thermoplastics with mid-level viscoelastic properties for decades; as depicted in Figure 2.3 along with a range of other polymers.
The flow channel of the first generation die contains a gradual cross-sectional area reduction ending at a 50% reduction halfway through the overall length of one multiplier die. When considering highly viscous materials, this geometric constraint is likely to cause not only equipment (extruder, gear pump, and/or multiplier) failure due to increased pressure drops originating in the compressive section, but is also likely to induce the previously described flow instabilities due to the non-uniform flow paths and residence times inside the multiplier die. The second-generation die was designed to maintain a constant cross-sectional area, as well as to minimize flow non-uniformities, and showed promising results experimentally and computationally. The results, depicted in Figure 2.4, show that the second-generation die decreases the overall pressure in the multiplier by more than 40%. This general geometry was the underlying design basis for the
layer multiplying dies for this work and will be discussed in detail in the following section.

![Layer Multiplication System Pressure Drop Reduction - Polyflow Simulation Results](image)

**Figure 2.4:** Pressure drop reduction by use of the CLIPS second generation multiplier

In this work, a multilayer co-extrusion processing line based on the second-generation die showed above, but quadrupling the number of layers in each pass, and capable of layering high viscosity materials for the elastomer and rubber industry was developed. Three unvulcanized rubber materials were used throughout the study; two butyl rubber systems and a polyisoprene rubber. First, each unvulcanized rubber was rheologically characterized, then processed as either a rheologically matched or a mismatched system in order to investigate the possible existence of flow phenomena such as elastic rearrangement and viscous encapsulation. Numerical simulations using ANSYS Polyflow® were performed to investigate a four-channel layer multiplying die proposed for the experimental layering. The numerical calculations in the present study using
ANSYS Polyflow® do not focus on the possible development of instabilities. Instead, flow paths, velocity profiles, and flow rate distribution were investigated at the exit of the die. Upon co-extrusion, the layered polymeric structure was visually validated using optical microscopy. Outside of varying the inherent viscoelastic properties via matching and mismatching polymeric materials, a single process processing parameter of flow rate, via gear pump revolutions per minute (RPM) was altered to visualize the influence of melt velocity in the layer multiplication die packs on flow phenomena.

2.2 Method

2.2.1 Co-extrusion Equipment

The extrusion system was specially designed for the multilayer process of very high viscosity systems. The system houses two single-screw extruders, which feed into separate gear pumps. The screws have a diameter of 30 mm with an L/D of 10:1. Each gear pump, specifically designed and build for this extrusion system, is capable of 80 kg/h throughput with a maximum of 50 RPM and pressures up to 100 MPa, approximately 3x the maximum pressures in typical thermoplastic co-extrusion processes. Extreme pressures in the developed system were crucial for the layering of the high viscosity rubber systems. Layer multiplication was performed with similar dies used in the work by Harris et. al. [2]. Instead of using a two-channel multiplication die, the dies in this system were
designed with four channels, as shown in Figure 2.5, thereby multiplying the layers at a rate of:

\[ N = 2^{2n+1} \]  

where \( N \) is the total number of layers, and \( n \) is the number of multiplication die packs.

Following the layer multiplication dies, the process transformed the layered structure from a 39x39 mm flow channel, into a 100x2.5 mm sheet via a single roll roller die designed and manufactured specifically for this process.

Processing temperatures and roller die speed were not changed in this work, since all materials show similar temperature dependency on the viscosity. Thus,
the single processing condition varied to investigate layer distribution was gear pump RPM. Similarly, two layering conditions were studied, a 8-layer system and a 32-layer system, developed from one die pack and two multiplication die packs, respectively.

2.2.2 Materials

Three unvulcanized rubber systems were used for this study; two butyl rubbers (poly[isobutylene-co-isoprene]) and a polyisoprene rubber. One of the butyl rubbers, termed ‘yellow butyl’ throughout, is compounded with silica, clay, and a yellow pigment. The other butyl rubber is a carbon black containing compound.

2.2.3 Rheological Measurements

Each of the rubbers used in this work were first characterized under small angle oscillatory shear using a Haake MARS III rotational rheometer. An 8 mm parallel plate system and a heated bottom plate were used for all shear experiments. Oscillatory stress sweeps were first performed to identify the region in which the storage modulus (G’) and the loss modulus (G”) respond linearly as a function of applied shear stress, i.e., the linear viscoelastic region. A shear stress in this region was then chosen for each of the materials and applied during the oscillatory frequency sweeps. Figures 2.6 and 2.7 display G’, G” and η* (complex viscosity) as a function of frequency. Apparent shear rates of the
multilayer co-extrusion process fall in the range of 2.6 s\(^{-1}\) and 131 s\(^{-1}\), depending on the sectional area and RPM conditions, which is equivalent to 0.4 Hz to 20 Hz under oscillatory shear conditions. This frequency range is represented in Figure 2.6 and 2.7 by the red box.

Figure 2.6: Frequency moduli of rubber compounds for layering
The material system identified to be a rheologically ‘matched’ system, was the yellow butyl and polyisoprene system, while the ‘mismatched’ rheological system was yellow butyl and black butyl. Both elasticity and viscosity are matched for the yellow butyl/polyisoprene system, while both elasticity and viscosity are mismatched for the yellow butyl and black butyl system.

The viscosity and elasticity ratios are shown in Table 2.1 below. The ratio represents either the polyisoprene or black butyl to the yellow butyl. The viscosity and elasticity ratio for the ‘matched’ pairing of compounds are 0.89 and
0.87, while the mismatched pairing has larger ratios of 2.47 and 2.44, respectively.

<table>
<thead>
<tr>
<th></th>
<th>Polyisoprene/Black butyl</th>
<th>Black butyl/Yellow butyl</th>
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<tr>
<td></td>
<td>Yellow butyl/“Matched”</td>
<td>Yellow butyl/“Mismatched”</td>
</tr>
<tr>
<td>Viscosity ratio</td>
<td>0.89</td>
<td>2.47</td>
</tr>
<tr>
<td>Elasticity ratio</td>
<td>0.87</td>
<td>2.44</td>
</tr>
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</table>

Table 2.1: Viscosity and elasticity ratios of each paired material

The extensional rheology characterization is shown in Figures 2.8 thru 2.11. The extensional viscosity of yellow butyl displayed in Figure 2.8 shows strain-softening behavior. Typical polymers, especially filled polymers, will undergo strain-hardening due to polymer chain entanglement and extensibility limitations. The opposite happens with the yellow butyl, likely due to filler type.
Figure 2.8: Extensional viscosity of the yellow butyl compound at 0.01 s\(^{-1}\), 0.1 s\(^{-1}\), and 1.0 s\(^{-1}\)

Figure 2.9 and 2.10 display the extensional viscosities the polyisoprene and black butyl compounds. These compounds display similar behavior with regards to strain-hardening, however, there are major differences in extensibility and stress growth. To investigate the differences, Trouton ratios are plotted in Figure 2.11 and show the polyisoprene contains a higher amount of stress at a particular deformation or time, compared to the black butyl.
Figure 2.9: Extensional viscosity of the polyisoprene compound at 0.01 s$^{-1}$, 0.1 s$^{-1}$, and 1.0 s$^{-1}$
Figure 2.10: Extensional viscosity of the black butyl compound at 0.01 s⁻¹, 0.1 s⁻¹, and 1.0 s⁻¹
2.2.4 Optical Microscopy

The extrudate was cut with a razor for visualization of the cross-section near Tg temperatures to promote a clean investigation surface. Cross-sectional images were taken with a digital camera, for the 39 mm thick samples and with an Olympus optical microscope for the thinner 2.5 mm thick samples.

2.2.5 Simulation Method

Flow through the feedblock and multiplier dies was numerically solved using ANSYS Polyflow®. The primary purpose for using this software was to
investigate the effect of a fourfold channel multiplier on the velocity profile at the exit, ultimately determining the flow rate exiting the multipliers.

The full 3D geometric calculation was solved using a steady-state simulation task. The material model as described below was fitted to experimental data using ANSYS POLYMAT®. The simulation used a constant inflow condition at two faces, defining the inflow of the two materials per simulation. Normal and adjacent forces were applied to the exit of the multiplication dies allowing for straight channel exit out of the multiplier die. A slip condition, k, is applied along the wall of the flow domain; k is increased incrementally until a wall velocity of 1-3% of the maximum velocity in that relative section is achieved. A fixed interface condition was used between the two materials, starting at the end of the feedblock and finishing at the exit of the multiplication die. A moving interface with several re-meshing techniques, including but not limited to Optimesh 3D, Streamwise, and Improved Elastic was attempted but convergence could not be achieved due to geometric issues with sharp angles in the outer flow domains.

Flow was assumed to be incompressible and isothermal. The following equations are field equations governing the incompressible fluid flow. First is the conservation of mass, or the continuity equation:
\(\nabla \cdot \mathbf{v} = 0\)  \hspace{1cm} (1)

where \(\mathbf{v}\) is the velocity. The conservation of momentum is described by:

\[-\nabla p + \nabla \cdot \mathbf{T} + f = \rho \frac{d\mathbf{v}}{dt}\]  \hspace{1cm} (2)

where \(p\) is the pressure, \(\rho\) is the density, and \(\mathbf{T}\) is the extra-stress tensor. The governing equation for a generalized Newtonian fluid is:

\[\mathbf{T} = 2\eta(\dot{\gamma})\mathbf{D}\]  \hspace{1cm} (3)

where \(\eta\) is the viscosity which is dependent only on the shear rate, \(\dot{\gamma}\). Due to the isothermal assumption in our calculation, temperature dependency on viscosity is neglected. Local shear rates in the calculation are defined as:

\[\dot{\gamma} = \sqrt{2\text{tr}(\mathbf{D}^2)}\]  \hspace{1cm} (4)

where \(\mathbf{D}\) is the rate-of-deformation tensor defined as:
\[
D = \frac{1}{2} (\nabla \nu + \nabla \nu^T)
\]  \hspace{1cm} (5)

The flow was assumed to be incompressible and isothermal, and the rheology of the polymers is assumed well as described by the well-known Cross model:

\[
\eta(\dot{\gamma}) = \frac{\eta_0}{1 + (\dot{\gamma}/\lambda)^m}
\]  \hspace{1cm} (6)

where, \(\eta(\dot{\gamma})\) is the shear rate dependence on viscosity, \(\eta_0\) is the first Newtonian plateau, \(m\) is the power law, and \(\lambda\) is a relaxation time constant of the material.

Upon convergence of the simulation, results were analyzed using ANSYS CFD-Post®. As discussed above, the final convergence was the direct result of an iterative process solving for the correct \(k\) parameter. Though much effort was used to allow for the interface to adjust vertically as a result of velocity distribution and flow rate, the software was not able to solve the calculation of a moving interface with the available re-meshing techniques.
2.3 Results and Discussion

2.3.1 ANSYS POLYFLOW Results

The results from computational flow modeling using ANSYS Polyflow® are displayed in Figures 2.12 - 2.14. As discussed previously, the aim of the computational work was to first of investigate the influence of geometry on the velocity profiles, flow paths, and flow rates. Secondly, we attempted to solve the moving interface problem with re-meshing techniques along with evolution iterations. As stated, the second task did not come to fruition as the outer geometry contains approximately a 90° bend causing the calculations to diverge.

With regard to the velocity profiles through the flow length, the rheologically matched system displayed in Figure 2.12 showed a high velocity through in the center of the square inflow, as expected. The high flow rate through the center channel is compounded from the fact that the material that starts with highest velocity also has the shortest flow length. This potential design flaw was recognized during the initial design, but was accepted as a trade-off for a pressure drop reduction of approximately 50%. In other words, with this geometry it is possible to achieve the same amount of layers in half the flow length, thereby reducing pressure requirements by half. It is expected that as the number of layers is increased this discrepancy in layer thickness will decrease by virtue of the successive layer-multiplication cycles.
Figure 2.12: Velocity profiles through the feedblock and multiplier die using a rheologically matched system

Similar results are displayed in Figure 2.13 with the exception of the influence of having a lower viscosity material in the lower of the two extruders. As the layered material advanced down the length of the multiplication dies, the lower viscosity material tends to advance at a higher rate, therefore theoretically increasing the layer thickness. The exit of the flow domain is displayed in Figure 2.14, with the rheologically matched system displayed on the left, and the rheologically mismatched system displayed on right.
As discussed previously, the highest flow rate through the multiplier length comes to completion as the top and bottom channels in the flow exit. These layers have the highest velocity at around 8 mm/s. Conversely, the outermost
channels down the multiplier flow length result in the center two channels of the flow domain exit. These two layers display a much lower velocity at around 3.5 mm/s.

2.3.2 Experimental Results

Two initial parameters were first studied with the polyisoprene compound only, in both extruders, multiplied to 32 layers. Figure 2.15 displays the gear pump head pressure and extrudate temperature as a function of material throughput. Head pressure was measured directly following the gear pumps, before the separate streams start flowing together into the multiplication dies.

![Figure 2.15: Head pressure and melt temperature as a function of throughput](image)

Figure 2.15: Head pressure and melt temperature as a function of throughput
Two phenomena commonly seen in polymer processing can be seen in Figure 1.1. First, the increasing and subsequent levelling of head pressure is attributed to slip along the die wall. The maximum 27 MPa of head pressure is relatively low and encouraging in that the system is only using approximately 1/4 of the maximum gear pump pressure with two multiplication die packs. This insinuates that up to an additional 4 die packs are possible, resulting in a possible 8,192 total layers according to formula (1). Secondly, extrudate temperature is important for rubber compounds and is commonly measured during rubber processing due to potential vulcanization. Shear-induced heating caused by friction within the polymeric material is the primary reason for the significant and steady increase of temperature in Figure 2.15. Temperatures in the region displayed here are not of concern as they are well below vulcanization temperature.

The layer distortion of the extrudate in columns 1 and 3 in both Figure 2.16 and 2.13 are attributed to the high levels of second normal stress difference [10, 13, 16]. For this reason, the square 39x39 mm channel displayed a large amount of die swell.

Layer quality is important for defining the effect on material properties as well as processing conditions on the final structure. In Figures 2.16 and 2.17 the first and third columns are images of the layered structure directly out of the multiplication dies. In these images, there is a noticeable distortion in the bottom and top layers. The dimensions of these images are 39 mm². The second and
fourth columns display the layered structures post-roller die, when the samples have spread to the final thickness of 2.5 mm.

In the case of the rheologically matched, 8-layer systems (Figure 2.16), thicker regions in the top and bottom two layers. In the 32-layer matched system, the thicker layers are displayed every four layers. These phenomena are also observed in the mismatched system (Figure 2.17).

Figure 2.16: Layering structure results of the rheologically matched system
Figure 2.17: Layering structure results of the rheologically mismatched system

To get a quantitative layer distribution, Image J® analysis software was used on the images in the second and fourth columns of Figure 2.16 and 2.17. The layer distribution for both matched and mismatched 8-layer systems (5 RPM pump rate) is shown in Figure 2.18. Layer numbers 1, 2, 7 and 8 all display thicker layers while the center layers are much thinner. These layer numbers correspond to the bottom and top 25% of the layered structure. The mismatched system displayed in red bars has an overall larger thickness compared to the matched system shown in black.
The layer distributions for both 32-layer material systems are displayed in Figure 2.19. While the bottom and top 25% of the layered structure display the thickest layers for both material systems, there also exists non-uniformity in the layered structure within each quarter channel. For example, layers 1-8 have an average layer thickness greater than that of 9-16 and 17-24. However, within layers 1-8, the top and bottom 2 layers (layers 1, 2, 7, and 8) have the largest relative thickness.

Figure 2.18: Measured layer thickness distribution in both 8-layer rubber extrudates
Figure 2.19: Measured layer thickness distribution in both 32-layer rubber extrudates

Average thickness, standard deviation, and the coefficient of variation of each layered system are displayed in Table 2.2 below. The overall average layer thickness is much larger in the mismatched system. Although a 2.5 mm thick die was used for the 32 layer system, the samples displayed a large amount of extrudate swell. Specifically, the mismatched system has double the thickness compared to the matched system. The standard deviation of the layer thickness in both systems is large, as displayed in Figure 2.18 and 2.19, and the relative
amounts are quantitatively displayed by the variation coefficient. While the mismatched system has a more stable variation coefficient, 44% moving from 8 layers into 32 layers, as expected, the matched system shows more unbalanced values, 32% and 51%.

<table>
<thead>
<tr>
<th></th>
<th>Polyisoprene/ Yellow butyl</th>
<th>Black butyl/ Yellow butyl</th>
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<tbody>
<tr>
<td></td>
<td>”Matched“</td>
<td>”Mismatched“</td>
</tr>
<tr>
<td>8 Layers</td>
<td>0.366</td>
<td>0.581</td>
</tr>
<tr>
<td>32 Layers</td>
<td>0.084</td>
<td>0.146</td>
</tr>
<tr>
<td>Mean (mm)</td>
<td>0.366</td>
<td>0.581</td>
</tr>
<tr>
<td>Std. Dev. (mm)</td>
<td>0.117</td>
<td>0.256</td>
</tr>
<tr>
<td>Variation Coefficient</td>
<td>32%</td>
<td>44%</td>
</tr>
</tbody>
</table>

Table 2.2: Layer thickness statistics

Through the quantitative layer analysis, we show good semi-quantitative agreement with computational results. Layer non-uniformities in both experimental and computation show the effect of longer flow paths and subsequent lower flow rates. This is compounded by a higher flow rate in the center of the feedblock prior to layer multiplication. Moreover, the layer non-uniformity is attributed to this geometric effect and only small differences, if any, could be attributed to a matched or non-matched rheology effect.
2.4 Conclusions

The primary goal of this research work was to design and develop a multilayer coextrusion system capable of layering high viscosity and high elasticity materials such as unvulcanized rubber material or thermoplastic elastomers. For this work, three unvulcanized rubber systems were used, a higher relative viscosity and elasticity black butyl rubber and two lower relative systems of yellow butyl and polyisoprene. Each rubber was rheologically characterized under oscillatory shear conditions, then processed in the new co-extrusion system. The computational work performed with ANSYS POLYFLOW® predicted a layer non-uniformity due to geometric constraints and the influence on velocity through the feedblock and multiplication dies. Each material system, whether matched or mismatched rheologically, was layered to a total of 8 layers or 32 layers, with gear pump RPMs of 5 and 15. Quality and layer thickness distribution were judged to be of good quality given the design constraints, and correlated well with the computational results.
2.5 References


CHAPTER 3

INFLUENCE OF POLYBUTADIENE ARCHITECTURE ON THE PROPENSITY OF RUBBER COMPOUNDS TO FLOW DEFECTS; AN EXTENSIONAL RHEOLOGY PERSPECTIVE

This chapter is partially based on:

Journal article:

P. Harris, et al., (2014) Submitted
3.1 Introduction

Over the better part of a half century, polymer processing instabilities have been heavily sought after in research fields. The current need for studying these instabilities is at the manufacturing level, where the reward for investment is a better grasp on process capability and in turn, a higher quality product at lower costs. One such instability studied in depth is a phenomenon in polymer extrusion coined *sharkskin*. Sharkskin is the tendency of a polymer under flow conditions to exhibit periodic skin fracturing not contained in the core of the extrudate. Understanding the phenomenon is important for certain polymers such as linear low density polyethylene (LLDPE) where the linear-style architecture is highly prone to sharkskin and gross melt fracture, the latter typically occurring at higher shear rates than the former. LLDPE is relatively inelastic in nature, which potentially leads to melt instabilities. On the other hand, a highly branched polymer, such as some standard LDPEs, has a higher elasticity and therefore an increase in melt strength. With an increase of branching along the polymer backbone, the stress applied during extrusion is carried and then dissipated along the side branches, whereas in a linear material the ability of the polymer to inherently absorb energy is much lower, resulting in the backbone giving way and fracture. These two polymers have been used in depth for understanding the mechanism behind sharkskin and melt fracture, among other melt flow instabilities.
3.1.1 General Understanding of Sharkskin

Researchers have taken numerous angles at studying the material, the process of extrusion, and sharkskin. In order to capture these angles, we first discuss the influence of converging flow then the velocity profile within an extrusion die. Finally, we show experimental rheology results in relation to sharkskin.

Cogswell [1] studied the stretching of polymers at the exit of an extrusion die, concluding that there is a quantitative relationship between the phenomena of sharkskin and cohesive failure of polymer melts. He proposed a question, why don’t all polymer melts display sharkskin, and then suggests the answer is held in the theory of elasticity, as mentioned previously. “The elastic response of polymer melts retards the stress growth so that if the total deformation is small even very rapid stretch rates may only produce low stresses.” Several studies have investigated molecular architecture and the role this plays on slip-stick transitions and melt fracture/sharkskin. “Slip-stick” is a term for the adhesion and slip along an extrusion die wall. One such study by Zhu [2] used 4-arm star polybutadiene, PBD, in capillary flow to study the effect of molecular architecture independently of molecular weight. The star PBDs displayed a faster non-linear response than the linear counterpart, as well as a weaker (nearly non-existent) stick-slip transition. This allowed Zhu to suggest that the sharkskin instability, especially for PBD, does not originate from an oscillating stick-slip transition, but does originate from a “rotating-breaking” hypothesis. The hypothesis was best shown with the flow-splitting phenomena where the extrudate physically breaks into multiple strands and rotates. The flow splitting phenomena was
accompanied by sharkskin and melt fracture. Park et al. [3] studied linear polybutadiene and the effect of architecture on wall slip and spurt flow. Park used a sliding plate rheometer to investigate the slip velocity of the PBDs. Rojo et al. [4] also studied sharkskin and melt fracture with polypropylenes (PP). The study looked at linear and branched PP and again showed that with an increase in elasticity with the slightly branched PP, the sharkskin and melt fracture is delayed to a higher shear rate. Wang and Drda et al. [5] summarized findings prior to 1996 and moved the research on the molecular origins of sharkskin, partial slip, and slope change in the flow curves of LLDPE. Again using capillary rheometry, their research showed sharkskin dynamics precisely correlate with chain relaxation processes.

Huang and Shroff [6] concluded there is a relationship between the level of long-chain branching and the onset of melt fracture. The study looked at the dependency on the flow into an extrusion die where there is a converging effect leading to a dominating extensional deformation. Xue et al. [7] studied cis-1,4 polybutadiene (PBD) and found that the processability of unvulcanized PBD is related to the entrance extensional effects which is sensitive to the branching architecture and molecular weight distribution of the melt. In terms of geometric dependency, Nigen and Walters [8] also studied converging flows; however, they investigated the flow in the form of axisymmetric and planar comparisons. The geometric nature of the research provided a good insight to the relationship between elasticity and die configuration and cross-section; however, it did not look at extensional behavior. They concluded by showing that planar contraction
behavior of the same fluid is “provocatively” different from the axisymmetric contraction. Vortex enhancement was absent in the planar contraction but was prevalent as expected in the axisymmetric configuration. A similar study by Kamerkar and Edwards [9] investigated the effect of a semi-hyperbolical converging die (SHCD) and compared the slip velocity to that of a straight channel converging die. LDPE was used throughout the work. They also studied the slip velocity as a function of a viscosity reducing agent. Results showed that there was a substantial increase in slip velocity with the viscosity reducing agent only in the straight die. This was explained by the degree of orientation was much greater with the straight wall channel and that the local shear rate aligned the polymer chains to allow for an easier flow.

The well-studied fundamental understanding of the velocity profile within an extrusion die shows that the velocity along the die wall is zero, or at best, near-zero. Conversely, downstream from the die, the melt is flowing unconstrained and therefore has a constant velocity throughout the polymer melt’s cross-section. With these two pieces of knowledge, it is easy to say that there is thus a transition period near the die exit that the skin-layer accelerates and the core region decelerates [1]. Several studies have exhaustively investigated this changing linear velocity and have shown the extensional flow dependency on how a polymer melt will respond. One such study by Inn et al. [10] visually scrutinized the velocity profile near the die exit and how this velocity change affected sharkskin and melt fracture. Using PBDs they showed that sharkskin developed with the cohesive failure at the die exit as the skin layers at the die
wall peeled off. By the addition of a soap solution at the die exit, an interfacial slip mechanism reduced the sharkskin again showing the velocity profile dependency on the proposed mechanism. Another study by Munstedt [11] uses a technique called Laser Doppler Velocimetry (LDV) to investigate the true melt velocity through the extrusion die. The results from this study showed velocity fluctuations in the melt which correspond to well-known pressure fluctuations; however, with different shaped amplitudes. Munstedt proposes a hypothesis relating this to the entanglement and disentanglement of the molecules, leading to a stick-slip periodicity. Another study by Arda and Mackley [12] investigated the effect of die exit curvature, roughness, and fluoropolymer additive on the sharkskin phenomenon. Their results confirmed previous studies stating that the onset of sharkskin is correlated with the magnitude of stress at the die exit. By decreasing the stress via die lip curvature or fluoropolymer additive, the onset of sharkskin is subsequently decreased. Another study by Legrand and Piau [13] used stress birefringence and flow visualization to look at polydimethylsiloxane flow through a slit die. The results showed that flow instability is generated in a contraction plane upstream, which restricts the slit channel. The contraction plane was shown to be the place where the extensional stress reaches its maximum. Choi et al. [14] studied the effect of adding low molecular weight polybutadiene to high-silica containing styrene-butadiene rubber compounds. The architecture of the PBD component is not explicit, however, the amount of die swell decreased with the addition of PBD. This was explained by a decrease in void space when adding the low molecular weight PBD.
3.1.2 Rheological Fingerprinting of Sharkskin

Kasehagen and Macosko [15, 16] studied the rheological behavior of long-chain randomly branched polybutadiene, with regards to shear, storage and loss moduli increase with branching especially at low oscillation frequencies. The extensional behavior was found to be extremely sensitive to changes in the relaxation spectrum, which is the direct result from both branching and an increase in the high-end of the molecular weight distribution. Therefore, changes in these two material characteristics have a direct effect on the strain-hardening behavior of the material. The research contribution to the understanding of sharkskin accelerated when Sentmanat et al. [17] were able to fingerprint the mechanism of sharkskin in LLDPE and LDPE with the use of the SER tool by Xpansion Instruments for measuring extensional properties of polymer melts [18]. The mechanism was studied through extensional properties using the SER as well as capillary extrusion and peeling experiments. With regards to the stress growth curves in uniaxial extension, at short times and high rates of extension the influence of branching had a tensile retardation effect via energy dissipation. This energy dissipation is believed to delay the propagation of any sharkskin in the melt. Minegishi et al. [19] studied the correlation between the partial cross-linking of styrene-butadiene-styrene (SBS) and the ability of the rubber material to strain-harden in extensional flows, where this particular material wouldn’t otherwise strain-harden without partial cross-linking. Stress relaxation in uniaxial extension followed by a step strain was studied by Barroso and Maia [20]. The study probed the microstructure of the materials (polyisobutylene) and the
sensitivity of shear and extensional tests. A benefit to the research allowed for 
the step strain to occur in either the linear or non-linear viscoelastic region 
followed by stress relaxation in extension. Similarly, their follow-up work [21] 
showed that the technique in extension is more sensitive to molecular structure 
than oscillatory shear experiments.

3.1.3 Research Problem

Based on the reviewed literature, sharkskin and melt fracture are flow 
phenomena that have been studied via converging flows, velocity profile 
changes, and extrusion die exit velocity distribution adjustments. On the material 
rheology side, the phenomenon has quantitatively been studied using shear and 
extensional rheology. These studies use ideal and well-characterized linear and 
branched polymer systems; for this reason we propose the question: is the 
rheological fingerprinting valid for complex, multi-component materials? A study 
of sharkskin investigation using highly filled and complex styrene-butadiene-
styrene and polybutadiene (SSBR-PBD) blends and single component PBD is 
presented in this work.

Two production compound rubber blends are used initially, then the 
polybutadiene phase is studied independently later. The blended materials that 
will be studied are presented in Table 3.1 below. Each blend contains 
approximately 250 total phr (parts per hundred rubber) including 150 phr of filler 
components including but not limited to: carbon black, silica, curing agents and 
processing oils. Each of the two blends contain identical levels of SSBR and
each type of filler. The final component is a PBD component at a level of 30 phr in each blend. Subscript ‘L’ represents a linear architecture PBD, while the subscript “B” represents a brush architecture PBD where the brush architecture is a relatively high frequency, short branch off of the main PBD chain.

Table 3.1: Parts per hundred rubber and filler levels

<table>
<thead>
<tr>
<th>Material</th>
<th>SSBR phr</th>
<th>PBD phr</th>
<th>Filler phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSBR-PBD&lt;sub&gt;L&lt;/sub&gt;</td>
<td>70</td>
<td>30</td>
<td>150</td>
</tr>
<tr>
<td>SSBR-PBD&lt;sub&gt;B&lt;/sub&gt;</td>
<td>70</td>
<td>30</td>
<td>150</td>
</tr>
</tbody>
</table>

Table 3.2 displays the Mooney viscosity tests at ML1+4 at 100 °C. The latter part of the research will focus solely on the pure PBD polymer component. Table 3.3 identifies some important molecular characteristics of the linear and brush PBD used in the blends as described above. Interesting to note is the large difference in when comparing the ML1+4 Mooney results of the full compounds to the pure PBD. The full compounds show a relatively small difference in Mooney viscosity, however, the pure PBD displays a much larger difference. These differences are a direct result of the amount of filler the full rubber compounds. Each polybutadiene contains at least 97% cis 1,4 PBD. The linear architecture PBD molecular weights are slightly higher than the brush PBD. The polydispersity is significantly larger, however, for the brush PBD compared to the linear PBD.
Table 3.2: Mooney viscosity of full rubber compounds

<table>
<thead>
<tr>
<th>Material</th>
<th>ML1+4 @100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSBR-</td>
<td>64.9</td>
</tr>
<tr>
<td>PBD_L</td>
<td></td>
</tr>
<tr>
<td>SSBR-</td>
<td>61.6</td>
</tr>
<tr>
<td>PBD_B</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.3: Molecular characteristics of each polybutadiene used in the blends

<table>
<thead>
<tr>
<th>Material</th>
<th>ML1+4 @100 °C</th>
<th>Cis 1,4 %</th>
<th>Mw</th>
<th>Mn</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBD_L</td>
<td>55</td>
<td>97</td>
<td>445,867</td>
<td>138,496</td>
<td>3.22</td>
</tr>
<tr>
<td>PBD_B</td>
<td>40</td>
<td>97</td>
<td>426,197</td>
<td>101,741</td>
<td>4.19</td>
</tr>
</tbody>
</table>

Each blended material was extruded through a lab scale extruder and rectangular die system. The rectangular die geometry was 2.5 mm high by 15.25 mm wide by 6.35 mm in length. The inflow into these final dimensions from the extruder gently converges from a circular channel into the rectangular channel over a total length of 47 mm. The extrudates are shown in Figure 3.1 and 3.2. Shown in Figure 3.1 is an example of the sharkskin observed in the blend of
SSBR-PBD$_L$. The inset image is a blown up view of the surface fracture. The periodic rupturing of the skin is highly prevalent.

Figure 3.1: SSBR-PBD$_L$ compound displays sharkskin phenomenon along the edges and surfaces of the extrudate. Inset is the magnified view of the sharkskin

Conversely, the SSBR-PBD$_B$ shown in Figure 3.2 does not display any sharkskin. Upon extrusion, the sample is smooth and does not have any sign of surface rupture.

Figure 3.2: SSBR-PBD$_B$ compound does not display sharkskin phenomena at any location in the extrudate. Inset is the magnified view of the smooth surface
The approach of this study is to first investigate the dynamics of the sharkskin of the two fully compounded productive rubber blends using the methodology of Sentmanat et al., as discussed previously. We then move on to the individual polymer components.

3.2 Experimental

3.2.1 Rheological Method

Blended samples supplied for the oscillatory shear measurements, extensional testing, and stress relaxation tests were kept frozen at -20 °C until needed for testing to minimize the possibility of early vulcanization. The samples were hot pressed in a compression molding machine. The compression molder was first pre-heated to 110 °C. The samples were cut into several small cubes ranging in size around 1mm³ and then placed in a stock sheet steel mold with a thickness of 1.0 mm. The loaded mold was placed between sheets of Teflon paper and steel plated and then placed in the compression molder for three minutes without pressure. Upon pre-heating, the samples were then held under pressure for three additional minutes, and then cooled to room temperature under pressure by water cooling for approximately 4-5 minutes. The process was repeated one additional time then removed. The samples showed some elastic recovery upon removal from the mold. Identical conditions were used for the pure PBD component only; however, an additional cycle was used given the PBD-only material did not contain a curing agent within the material.
Oscillatory shear measurements were conducted on an Anton Paar Physica MCR 501 rheometer with using the forced convection oven CTD 450. Sample size from compression molding was 25 mm in diameter and 1 mm in thickness. The oscillatory shear conditions were performed at 110 °C within the linear viscoelastic region as chosen by a stress sweep test prior to the frequency conditions. Stress conditions used for the frequency sweeps were 100 Pa.

Extensional testing was performed using the SER device using an Anton Paar Physica MCR 501 rheometer and the forced convection oven CTD 451. Oven temperature was maintained at 110°C through testing. Sample size was 1mm x 5mm x 20 mm; however, exact sample size was measured prior to each test and inputted into the software at the start of each test. After the oven was pre-heated, each sample was placed in the clamps of the SER and allowed to pre-heat for 3 minutes prior to the start of the extensional test. Blended samples were stretched at strain rates of 0.01 s⁻¹, 0.10 s⁻¹, and 1.0 s⁻¹. The pure PBD samples were also prepared in the same manner and were extended at strain rates of 0.01 s⁻¹, 0.10 s⁻¹, 1.0 s⁻¹, and 10 s⁻¹. The additional strain rate of 10 s⁻¹ was used to further verify results, which will be explained later in detail.

Stress relaxation tests were performed using the SER device using an Anton Paar Physica MCR 501 again as the host rheometer. Oven temperature was maintained at 100°C throughout testing. Several tests were performed on the blended materials including an instantaneous strain then held to allow for the stress to relax from the compounds. Strains of 50%, 75%, 100%, and 115% were used. Both compounds ruptured at 120%.
Finally, dynamic data from the frequency sweeps was imported into the IRIS® rheological software. The full relaxation spectrum was collected for all four materials. The extensional data was analyzed using an Excel spreadsheet developed at the University of British Columbia for analyzing extensional rheology results from the SER device. Primarily torque vs time was imported to the spreadsheet along with sample dimensions of each test. The extensional data was fitted to fall along the $3\eta$ data from the relaxation spectrum.

### 3.3 Results and Discussion

![Diagram showing time sweep to investigate early vulcanization during sample preparation and extensional testing.](image)

Figure 3.3: Time sweep to investigate early vulcanization during sample preparation and extensional testing.
3.3.1 Oscillatory Shear Measurements- Full Compounds

Before oscillatory shear frequency sweeps, a time sweep was performed for the investigating possible vulcanization of the compounds during testing. This preliminary test was run at 1 rad/s at 100 °C. After 25 minutes of examination, the compounds did not crosslink and all subsequent testing can be assumed unvulcanized within a window of at least 25 minutes.

In order to gain an understanding of the viscosity and elasticity of each full blend, SSBR-PBD\textsubscript{L} and SSBR-PBD\textsubscript{B}, frequency tests as explained above were performed. The results of the test are shown in Figure 3.4. Furthermore, to gain an understanding of the ratio of loss modulus to storage modulus, tangent δ is used in Figure 3.5. Each of the graphs display very similar rheological behavior and results fall within the error bars based on the standard deviation of the testing.

The relaxation spectrums for each of the blends are displayed in Table 3.4. Each of the modes shown were used in calculating a viscosity. The Trouton ratio was applied whereby multiplying the calculated viscosity by a factor of three.
Figure 3.4: Storage ($G'$) and loss ($G''$) moduli of full compounds

Figure 3.5: $	an(\delta)$ for both full SSBR-PBD compounds
As discussed, the dynamic shear properties of the full compounds are very similar, and the similarity is again displayed by Figure 3.6. Figure 3.6 is the complex viscosity of both of the compounds.

Figure 3.6: Complex viscosity of the full SSBR-PBD compounds.
Table 3.4: Relaxation spectra of both rubber compounds

<table>
<thead>
<tr>
<th></th>
<th>SSBR-PBD&lt;sub&gt;L&lt;/sub&gt;</th>
<th></th>
<th>SSBR-PBD&lt;sub&gt;B&lt;/sub&gt;</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G (Pa)</td>
<td>λ (s)</td>
<td>G (Pa)</td>
<td>λ (s)</td>
</tr>
<tr>
<td>3.09E+05</td>
<td>6.69E-03</td>
<td></td>
<td>2.82E+05</td>
<td>5.91E-03</td>
</tr>
<tr>
<td>1.86E+05</td>
<td>4.19E-02</td>
<td></td>
<td>1.61E+05</td>
<td>3.65E-02</td>
</tr>
<tr>
<td>9.97E+04</td>
<td>1.84E-01</td>
<td></td>
<td>9.99E+04</td>
<td>1.53E-01</td>
</tr>
<tr>
<td>5.90E+04</td>
<td>8.92E-01</td>
<td></td>
<td>5.65E+04</td>
<td>8.29E-01</td>
</tr>
<tr>
<td>4.06E+04</td>
<td>5.25E+00</td>
<td></td>
<td>3.93E+04</td>
<td>4.99E+00</td>
</tr>
<tr>
<td>5.96E+04</td>
<td>2.21E+02</td>
<td></td>
<td>5.85E+04</td>
<td>2.31E+02</td>
</tr>
</tbody>
</table>

3.3.2: Extensional – Steady Strain Measurements – Full Compounds

Figure 3.7 displays the stress growth curves of the SSBR-PBDL compound. Each of the three strain rates shown displayed a small amount of strain-hardening. Strain-hardening is depicted by the departure from 3η. The amount of strain-hardening at each strain rate plateaus then ruptures, representing a ductile rupture mechanism.
Figure 3.7: Stress growth curves of SSBR-PBD$_L$ compound which show strain-hardening behavior.

Figure 3.8 displays the stress growth curves of the SSBR-PBD$_B$ compound. Each of the three strain rates shown displayed a small amount of strain-hardening similar to that of the SSBR-PBD$_L$ compound. Strain-hardening is again depicted by the departure from $3\eta$. The amount of strain-hardening at each strain rate plateaus then ruptures.
Although visually different in sharkskin, the two fully blended compounds show identical extensional behavior, both in magnitude and shape. According to literature as discussed above, the linear architecture compound should rise in stress as elongated; similarly, the brush compound should dissipate the stress inherently. Results in the stress growth curves did not show this difference in behavior.
To further elucidate these results, the extensional viscosities are divided by $3\eta$ and are displayed in Figure 3.9. These results show the departure from the linear, Newtonian region and strain-hardening behavior can be compared more appropriately. The normalization shows very similar results between the two compounds.

![Figure 3.9: Trouton ratios for both full SSBR-PBD compounds](image)

Furthermore, Table 3.5 displays the maximum Trouton ratio achieved which relates to the stress required for rupture. The behavior is again very similar, with only small levels detected which fall within error.
Table 3.5: Trouton ratio at break in extension

<table>
<thead>
<tr>
<th>Strain Rate (s⁻¹)</th>
<th>η⁺ / 3η @ Break</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SSBR-PBDₐ</td>
<td>SSBR-PBDₖ</td>
</tr>
<tr>
<td>0.01</td>
<td>2.23</td>
<td>2.57</td>
</tr>
<tr>
<td>0.1</td>
<td>1.92</td>
<td>1.86</td>
</tr>
<tr>
<td>1.0</td>
<td>1.38</td>
<td>1.39</td>
</tr>
</tbody>
</table>

3.3.3 Stress Relaxation Measurements- Full Compounds

To further investigate possible mechanisms of sharkskin in the full compounds, we looked at stress relaxation under extension conditions. Several strains were used throughout testing, including two along the 3η curve and two within strain-hardening region. Figure 3.10 displays the stress relaxation data directly following an instantaneous strain. When the compounds were stretched around 120%, the samples ruptured during flow. A large difference between the two full compounds was found, with the largest difference in a strain of 50%.
Figure 3.10: Stress relaxation SSBR-PBD_L (top) and –PBD_B (bottom); each graph displays four strains: 50%, 75%, 100%, and 115%. Samples ruptured at approximately 120% strain.
Figure 3.11 displays the strain of 50%, where the differences are more significant, of both compounds. Each data set was fitted and used in Table 3.6. It can be assumed that the stresses within the compounds are nearly the same (as learned during initial extension testing above) at the start of the relaxation process in the stress relaxation tests. After 1000 seconds, the stress held within the sample is lower in the brush material. Several interpretations from this result can be proposed. First, the brush compound potentially has additional free volume, allowing for easier flow and relaxation as discussed by Kamerkar and Edwards [9]. Secondly, the brush compound, as described earlier, inherently dissipates the energy and stress applied as discussed by Sentmanat et al [17].
The characteristic relaxation times of each compound are displayed in Table 3.6. The blends show a 7.4% difference in relaxation times according to the stress relaxation tests at 50% strain.

Table 3.6: Characteristic relaxation times of each compound SSBR-PBD$_L$ and SSBR-PBD$_B$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Charact. Relax. Time (s)</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSBR-PBD$_L$</td>
<td>3.32</td>
<td>7.4%</td>
</tr>
<tr>
<td>SSBR-PBD$_B$</td>
<td>3.09</td>
<td></td>
</tr>
</tbody>
</table>

Concluding the previous analysis of the full SSBR-PBD$_L$ and the full SSBR-PBD$_B$ compounds containing high levels of filler proved extensional testing to not display a difference or causality for the highly prevalent sharkskin phenomenon. The only test that showed any significant difference was that of stress relaxation in extension, and even then, the difference in relaxation times was only approximately 7%. Because of the findings in stress relaxation, we propose the hypothesis that a masking of properties exists, either or in combination, from the SSBR component or the high levels of filler. Based on these findings we moved forward with examining the pure polybutadienes without the additional 70 phr SSBR and 150 phr of filler.
3.3.4 Oscillatory Shear Measurements- PBD Component

Similar to the studies above, the PBDs, both linear and brush architecture, were studied first in oscillatory shear conditions. The storage and loss moduli are shown in Figure 3.12.

![Figure 3.12: Storage (G') and loss (G'') moduli of the PBD components only](image)

These results show a difference between the two materials not shown in the full compounds. Unlike the full compounds, the individual PBDs display a different magnitude of viscoelastic properties. Interestingly, here we show the brush style architecture PBD to have a slightly higher storage modulus and loss modulus. This agrees with literature [17] in stating that with an increase in elasticity in a
brush or branched polymer, the tendency of a material to display sharkskin or melt fracture is diminished. Tan δ is displayed in Figure 3.13 below; the graph shows the comparison between the loss modulus and storage modulus of the pure PBD polymers. Finally, the full relaxation spectrum calculated in IRIS is shown in Table 3.7.

Figure 3.13: Tan(δ) as a function of frequency for both of the pure PBDs
Table 3.7: Relaxation spectra of both PBDs

<table>
<thead>
<tr>
<th>PBD_L</th>
<th>PBD_B</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>G (Pa)</strong></td>
<td><strong>λ (s)</strong></td>
</tr>
<tr>
<td>6.42E+05</td>
<td>4.23E-04</td>
</tr>
<tr>
<td>4.65E+04</td>
<td>1.76E-02</td>
</tr>
<tr>
<td>2.57E+04</td>
<td>7.17E-02</td>
</tr>
<tr>
<td>1.63E+04</td>
<td>2.57E-01</td>
</tr>
<tr>
<td>1.07E+04</td>
<td>9.56E-01</td>
</tr>
<tr>
<td>7.72E+03</td>
<td>3.88E+00</td>
</tr>
</tbody>
</table>

3.3.5 *Extensional Measurement – Steady Strain – PBD Component*

Finally, the results from extensional testing are displayed in Figure 3.14 and 3.15. The departure from $3\eta$ occurs in both materials similar to that of the full blends in above. However, these materials behave more as expected and line up with what has been proven in literature.
Figure 3.14: Stress growth curves of $PBD^{-L}$ component only which shows strain-hardening behavior
In Figure 3.14, following departure from $3\eta$, the linear PBD continues to rise in stress. In Figure 3.15, at a similar strain, the brush polymer contains lower levels of stress at each of the four strain rates used. This result correlates with Sentmanat’s [17] findings and can be explained by the capability of a branched material to dissipate energy supplied, be it via free volume or a side chains carrying the stress initially. These results are shown via Trouton ratios in better detail in Figure 3.16. The departure and overall trend of the materials at all strain
rates are nearly identical, however, the linear PBD displays much higher Trouton ratios.

![Figure 3.16: Trouton ratios of the pure PBD component](image)

To best explain these findings, Table 3.8 displays the Trouton ratios at break for both polymers at four strain rates. The elevated Trouton ratios at break for the linear polymer provide insight to the stresses at comparable deformations.
Table 3.8: Trouton ratios of the pure PBDs at several strain rates

<table>
<thead>
<tr>
<th>Strain Rate (s⁻¹)</th>
<th>( \eta^+ / 3\eta @ Break )</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PBD₇</td>
<td>PBD₇</td>
</tr>
<tr>
<td>0.01</td>
<td>6.30</td>
<td>2.80</td>
</tr>
<tr>
<td>0.1</td>
<td>4.39</td>
<td>1.74</td>
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<tr>
<td>1.0</td>
<td>2.84</td>
<td>1.82</td>
</tr>
<tr>
<td>10.0</td>
<td>2.39</td>
<td>1.53</td>
</tr>
</tbody>
</table>

3.3.6 Stress Relaxation Measurement- PBD Component

Again, to further investigate possible mechanisms of sharkskin in pure polybutadiene, we looked at stress relaxation under extension conditions. Several strains were used throughout testing, including two along the 3\( \eta \) curve and two within the strain-hardening region. Figure 3.17 displays the stress relaxation data directly following an instantaneous strain. After each sample was stretched they ruptured at approximately 170% for PBD₇ and 145% strain for the PBD₉. For this reason, common strains of 80%, 100%, 120%, and 140% were used.
Figure 3.17: Stress relaxation PBDL (top) and PBDB (bottom); each graph displays four strains: 80%, 100%, 120%, and 140%. Samples ruptured at approximately 170% for PBDL and 145% strain for the PBDB.
Figure 3.18 displays the strain of 120%, again the one at which the differences were more significant, of both compounds. Each data set was fitted and used in Table 3.9. It can be assumed that the stresses within the compounds are nearly the same (as learned during initial extension testing above) at the start of the relaxation process in the stress relaxation tests. After 100 seconds, the stress held within the sample is less in the brush material. As discussed previously, there are two interpretations to this result. First, the brush PBD has additional free volume, allowing for easier flow and relaxation as discussed by Kamerkar and Edwards [9]. Secondly, the brush compound, as described earlier, inherently dissipates the energy and stress applied as discussed by Sentmanat et al [17].
The characteristic relaxation times of each compound are displayed in Table 3.9. The pure PBD polymers show an 11.4% difference in relaxation times according to the stress relaxation tests at 120% strain.
Further studies on both the full production-style compounds as well as the individual components are ongoing, including geometric effects and the effect of secondary flows which may be prevalent in one type of architecture. The influence of N₂, the second normal stress difference, may play a significant role and potential results may line up with the findings of Nigen and Walters [3], as discussed previously.

### 3.4 Conclusions

Two production style rubber compounds were investigated due to the occurrence of extrudate sharkskin dependent on molecular architecture according to findings in literature. Based on the findings, the full compounds containing small amounts of either a linear or brush style polybutadiene did not show a difference under steady strain, uniaxial extensional conditions. However, the full compounds displayed a relatively small but significant difference in stress relaxation following an instantaneous strain. This led to further testing to investigate the possibility of either the larger content rubber, solution-styrene butadiene rubber, or the high level of filler, being masking differences in the extensional properties of the

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**Table 3.9: Characteristic relaxation times of each compound PBD_L and PBD_B**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Charact. Relax. Time (s)</th>
<th>% Difference</th>
</tr>
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<tbody>
<tr>
<td>SSBR-PBD_L</td>
<td>2.75</td>
<td>11.4%</td>
</tr>
<tr>
<td>SSBR-PBD_B</td>
<td>2.43</td>
<td></td>
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</table>
rubber. Upon uniaxial testing of the polybutadiene component as a stand-alone material, results show that the differences are much higher between materials in extensional flows. In particular there are large differences in the Trouton ratios at rupture and in the stress relaxation behavior.

At the beginning of the study we asked the question of whether the rheological fingerprints proposed in the literature for homopolymers was still valid for highly complex, multicomponent materials. The results show that the presence of multiple additives to a large degree mask the differences in rheological behavior of the polymeric components that are only slightly different from one another to begin with. Therefore, one should test the base polymers in extensional flows instead of the full compounds whenever possible. In the case of the polybutadienes tested, the most sensitive tests to the presence of brushes along the main polymer chain, which were enough to alter the propensity of the compounds sharkskin completely, were the Trouton ratio at rupture and tensile stress relaxation.
3.5 References


CHAPTER 4

HIGH-STRAIN EXTENSIONAL RHEOMETRY OF POLYMER MELTS:
INSTRUMENT DESIGN AND IMPLEMENTATION

This chapter is partially based on:

Journal article:

United States Patent:
Controlled stress extensional rheometer

4.1 Introduction

Extensional rheology has played a key role in theoretical, experimental, and computational polymer research over the years [1, 2, 3, 4, 5, 6, 7]. In extensional flow, polymer elements are stretched very rapidly along flow streamlines. For example, Figure 4.1 displays the three main types of simple extensional flow: uniaxial, equibiaxial, and planar [8].

![Figure 4.1: Sketch showing the three main types of simple extensional flow: uniaxial, equibiaxial, and planar. Image from: [8]](image)

When considering theoretical polymer flow models such as tube models, nonlinear flow can be viewed from tube orientation as well as tube stretch. Tube
orientation is easily probed using shear flows; however, tube stretch is best understood and studied using extensional flow properties [8].

Understanding the mechanism behind extensional rheology is important for two main reasons. First, the primary form of deformation in several major plastics processing is extension. These processes include fiber spinning, film blowing, and blow molding. Other plastics processes also contain extensional elements, specifically, injection molding and extrusion of sheet and film. The second reason, which makes extensional rheology so important of a field to study, is the understanding of molecular structure. Nonlinear behavior in extensional deformations provides molecular structural features, which cannot be understood with shear data alone, in particular, molecular weight, molecular weight distribution, degree of branching, and the nature and strength of the interface in a polymer blends, etc. [9, 10, 11].

Measuring the properties of an elongational flow or stretching flow is much more difficult than shear deformations and since extensional tests predict aspects of nonlinear rheology which cannot be identified otherwise, it’s critical to develop a proper testing method for the behavior of a material under extensional flow. Historically, several techniques have been deployed for measuring the elongational properties of polymer melts. Two main types of instruments include filament stretching with length variation otherwise known as “end-separation” [8] and filament stretching at constant length, referenced further as “fixed length” [6, 12, 13, 14, 15, 16, 17, 18, 19, 20].
4.1.1 Constant Length Design

The first of the constant length extensional rheometers which was accurate and reliable was from Meissner [21] at the BASF Company. Figure 4.2 below shows device invented by Meissner.

The device in Figure 4.2 contains two pairs of rollers which counter-rotate. The rollers are machined in a way to grip the polymer sample between them as noted above as “P”. The constant length Meissner rotates at a constant velocity, and assuming there is no slip at the rollers, the deformation of the sample is considered uniaxial. In fact, this deformation creates a constant Henky strain.
rate in the sample. The device uses a heated oil bath which suspends the polymer while in the molten state.

Meissner later simplified the device and switched the rollers with rotating belts. This design is displayed in Figure 4.3. A downfall to this design is that the sample must be rectangular in cross-section which may lead to a planar deformation easier. Higher temperatures could be achieved with this design as there was no oil bath required. The design uses an air bath which filtered through a porous medium and lifted the sample.

![Diagram of rotating melt belt design](image)

Figure 4.6: Rotating melt belt design using a fixed length. Design by Meissner and Hastettler [13]. Image from: [8]
The last device, and most recent, was developed by Martin Sentmant [20]. The sketch for his device is shown in Figure 4.4. The device is the most widely used and is the industry standard with regards to extensinoal rheology of polymer melts. The primary operation of the device works by installing the entire instrument in a standard host rheometer. The instrument comes equipped for installation in all major rotational rheometers.

![SER device by Sentmanat](Image from: [8])

**Figure 4.7: SER device by Sentmanat [20]. Image from: [8]**

Though the setup in Figure 4.4 is meant for a strain-controlled rotational rheometers, the principle operation is the same for a stress-controlled rheometer.
The host rheometer simultaneously rotates a drive shaft on the SER. Meanwhile, the SER, which contains two gears, translates the rotational movement into a linear stretching force on a sample. The sample is clamped on two drums. As the sample is stretched at a fixed length and constant strain rate, the material flows under uniaxial conditions. The clamped sample is limited to one revolution on the roller drum before wrapping onto itself, thus ending the test. For this reason, Henky strain is limited to approximately 4. Currently, accessories based on this fixed length fiber wind-up design are offered commercially by TA Instruments under the designation of Extensival Viscosity Fixture and by Xpansion Instruments as the SER.

4.1.2 End-Separation Design

In a varying length, or end-separation style extensional rheometer, the polymer sample is glued or fixed to small metal plates, one of which is attached to a force transducer. The operation is similar to a tensile testing machine in solid state. The device developed by Munstedt is displayed in Figure 4.5 [14]. The specimen can reach strain rates of about $5 \text{ s}^{-1}$ and can be used for creep experiments. A downfall to this type of rheometer is the oil bath which the polymer sits within and temperature being limited to 220°C [8].
Finally, another end-separation type extensional rheometer was developed by Bach [16]. The filament-stretching rheometer (a.k.a. FSR or FiSER) is an adaptation. The device shown in Figure 4.6 was initially developed for low viscosity polymer solutions. As the upper and bottom plate move away from each other, a laser measures the change in diameter at the midpoint of the sample.
4.1.3 Introducing MERA

As shown above, all the current extensional rheometer designs suffer from one or more drawbacks that prevent the easy and controlled testing of polymeric samples up to ultra-high strains. We present our extensional rheometer design, which was purposely developed to overcome these issues. In particular, the main design requirements were:
1. It must have the ability to achieve ultra-high Hencky strains, \( i.e. \), in excess of 6. Preferably, maximum Hencky strains should be limited only by sample rupture.

2. The deformation should be homogeneous up to sample rupture or the onset of necking, namely by imposing the same boundary conditions at both edges.

3. It must be adjustable to rotational rheometers as an add-on accessory.

4. It should be simple to use and robust.

5. It must allow visual access to the sample during deformation, in order to allow for control of the deformation kinetics, \( i.e. \), strain rate, or dynamics, \( i.e. \), the tensile stress, using a feedback control loop.

The only design that inherently obeys requirements 1 and 2 above is that of a full Meissner, \( i.e. \), with two pairs of counter-rotating rollers. Thus, the new rheometer, which was miniaturized to fit inside the oven of a rotational rheometer and coupled to a digital camera, an image acquisition software and a feedback control loop, is essentially a miniaturized and user-friendly Meissner. This design is named the MERA, for Meissner Extensional Rheometer Accessory, and its general lay-out and appearance are depicted in Figure 4.7 and 4.8.
Figure 4.10: The MERA
Figure 4.11: Different views of the MERA: (a) Isometric; (b) Side; (c) Front; (d) Back.
This design has the advantage of imparting similar strain histories to both ends of the sample, and facilitates observation, because sample visualization is performed at the mid-point and necking or other experimental problems with any given experiment are easily spotted. Also, it does away with need for a bath for temperature control by having the instrument in a single frame that fits within the high-temperature chamber of the rotational rheometer, similarly to the SER device. Sample loading is easily performed by pulling the front rollers with the aid of a built-in spring, which is also used to keep the clamping force on the rollers constant as the sample decreases in cross section during the experiment. The rollers are readily changeable, so that the best surface finish to avoid slippage for each material can be chosen. Also, there are wedges external to the rollers that guarantee that the sample is ejected from the system after testing and does not wrap around them. A more detailed explanation of the MERA is presented in the next section.

We validate the MERA design in non-controlled mode, i.e., without the control loop, using three representative materials at different ends of the viscoelastic spectrum, namely a linear, relatively inelastic polystyrene, a branched polyethylene and a highly elastic, highly viscous bi-modal styrene-butadiene rubber (SBR) melt. Validation of the instrument in controlled modes of deformation will be the subject of a follow-up work.
4.2 MERA – Meissner Extensional Rheometer Accessory

Our instrument for measuring the extensional viscosity of polymers, the Meissner Extensional Rheometer Accessory, MERA, was designed to provide accurate measurements at high Hencky strains, and can be adapted to any rotational rheometer, although in this work we used an Anton Paar Physica MCR 501 as the host machine.

4.2.1 Operation

The principle of operation of the MERA apparatus is the counter-rotation of two sets of two roller drums, which extensionally deform a sample until rupture. The deformation is conceptually similar to mechanical tensile testing except that it is performed on the melt. Figure 4.9 displays the general principle of operation of the MERA (top) and the general view of the assembled instrument (bottom).
Figure 4.12: Operation principle (top) and assembled view (bottom) of the MERA.
A polymeric sample, in either rod or slab format, is placed between the rollers, and the MCR shaft rotates in a counter-clockwise direction, which in turn rotates gearing (Figure 4.10) in order to rotate the paired counter-rotating rollers. Visualization is performed using a digital camera attached to the exterior of the oven. This is an important trait since, as will be shown later, the nominal and real strain rates are slightly different in both the MERA and the SER.
The internal dimensions of the oven (60 mm diameter), of the host rotational rheometer primarily dictate the size of the MERA. Due to the spacing of gearing of off-center drive axle, the overall dimensions of the MERA is 42.35 mm long by 40.64 mm wide. The device, as shown in Figures 4.2 and 4.3 above, rests on a stationary rod/thermocouple with an upper shaft extending from the air piston head, both of which vertically extend into the Physica’s CTD 450 oven. The former provides a stationary base for the rheometer, while the latter supplies a rotational velocity to the drive axle of the MERA. Similarly, the stationary base contains a thermocouple which allows for temperature measurements within the oven. The drive axle rotates a gear and in turn transmits power to one of the primary axles. In total, there are seven low-friction titanium nitride coated steel and brass gears (see Figure 4.10).

4.2.2 General Components

Figure 4.10 displays the internal components of the MERA, including the roller drums, axles, gearing, and bearings. All meshing gears are made to horology-level precision specifications, and were designed to have equal number of teeth providing a gear ratio and angular velocity ratio equal to 1, thereby producing a torque ratio, or mechanical advantage, also equal to 1. The four smaller gears
have 16 teeth and a pitch diameter of 6.35 mm, while the three bigger gears have 60 teeth and a pitch diameter of 12.7 mm. The five axles are made of stainless steel construction and are coated with a low friction coating. All axles are axially contained within two low friction bearings and contain points at either ends to promote a low normal force. Both the bearings and precision axles are developed for signal integrity and friction (noise) reduction.

The roller drums that make contact with the sample have been coated with a nickel-Teflon coating to promote removal from roller drums and easy cleaning. The roller drums have a major diameter of 6.35 mm, and are spaced 6.35 mm when viewed from the side, allowing the rollers to make slight contact. Similarly when viewed from the front, the rollers have a spacing of 12.70 mm. Several types of surface finishing can be applied to the rollers, including highly polished, sand-blasted to different degrees, vertical grooving, cross-hatching of a diamond pattern, etc. The type of roller to be used during experimentation is dependent upon sample surface and bulk properties and must be chosen to minimize slip at the rollers. Rollers were designed with ease of removal and installation in mind. This is accomplished by removing its base, and sliding the rollers out of the coated axles, as shown in Figure 4.11. Four socket-head cap screws are first removed from the base of the MERA, which allows for the base to slide off of the bottom alignment pins (Figure 4.12). Once the base has been removed, the four roller drums easily slide off of the four roller axles. The reverse process holds for reassembly of new roller drums. The whole process takes only a few minutes.
Slip is further minimized by the existence of four adjustable springs, as depicted in Figure 4.12. This, coupled with the fact that the front rollers of each pair can move in an inward direction (see sample loading section below) provides a constant clamping force as the sample becomes thinner upon testing. The actual clamping force is imposed at the beginning of the experiment by the level of tightening of the springs. It is recommended that prior to the real runs this clamping force is calibrated; if it is too low there will be slippage at high strains, and if it is too high the friction will be too high. Both these effects are easily detected in the torque curve and can be compensated for.
Figure 4.14: Isometric exploded view displaying the disassembly for the interchangeable drum rollers. Four screws release bottom assembly and then the rollers slide off.
Figure 4.15: Isometric view displaying the rear components used for adjusting the compression springs.

Steel brackets containing Teflon material strippers (see Figure 4.13) provide very close spacing to the roller drums, which allows for complete sample material removal (scrapping) during the elongational test. This is important because any residue left on the rollers during testing will negatively impact the integrity of the torque output signal, and deformation homogeneity.
The front assembly is attached using spring-loaded shoulder bolts. Left: Closed position; Right: Open position (~3.0 mm maximum opening).

4.2.3 Sample Loading

Sample loading and unloading is performed in the simple fashion depicted in Figure 4.13. Prior to sample loading, a small handheld pulling device pulls the front of the instrument and subsequently the rollers apart, allowing for the loading the sample. The sample is loaded from the side of the instrument with a pair of tweezers. The sample typically extends past the rollers and material strippers prior to operation. As mentioned before, the spring loaded shoulder bolts control
the compression force applied to the sample. Springs can be replaced as needed to change the amount of normal force applied outside of the compression zone of the supplied springs. When fully tightened, the springs still allow for movement of the front assembly for the capability of sample loading and unloading. An approximately 3.0 mm stroke is imposed to allow for sample placement between the roller drums. Fig. 13 (left) displays the MERA when fully closed, and (right) when opened to a distance of 3.0 mm (small inserted figures display the zoomed near side view). Once a sample has been loaded, the springs supply sample pressure during testing and allows the rollers in each pair to come closer as needed during sample thinning.

### 4.3 MERA Validation

The following validation work was previously reported in our research article [22] as well as the thesis presentation and dissertation of Dr. Ricardo Andrade. His validation work incorporated three rheologically different polymer systems, Polystyrene (PS) Styron 615 (The Dow Chemical Company), polyethylene (LDPE) Petrothene NA940000 (LyondellBasell Company), and a bi-modal blend of styrene-butadiene rubber (SBR) melt, the latter supplied by Professor Shi Qing Wang (University of Akron).

For the purpose of this dissertation, only two will be re-reported, the PS for repeatability testing and SBR, which was chosen for the significance of unprecedented results produced during validation.
For rheological characterization, frequency sweep tests were performed in oscillatory shear flow with 25-mm plate–plate geometry with the Physica MCR501 rheometer and CTD450 convection oven (Anton Paar). From storage and loss modulus, discrete relaxation spectra were calculated using the IRIS software. Partial relaxation moduli $g_i$ and relaxation times $\lambda_i$ as well as the (calculated) zero-shear viscosities $\eta_0$ are presented in Table 4.1 together with the molecular characterization of the SBR.
Table 4.9: PS and SBR molecular characterization and relaxation spectrum obtained by dynamic shear measurement and IRIS Software

<table>
<thead>
<tr>
<th></th>
<th>PS 615</th>
<th>SBR 70K/1M (80:20)</th>
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<tbody>
<tr>
<td>M&lt;sub&gt;w&lt;/sub&gt;</td>
<td>256 kg/mol</td>
<td>453.9 kg/mol</td>
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<tr>
<td>M&lt;sub&gt;n&lt;/sub&gt;</td>
<td>28.4 kg/mol</td>
<td>283.7 kg/mol</td>
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<tr>
<td>η&lt;sub&gt;0&lt;/sub&gt;</td>
<td>8.166 x 10&lt;sup&gt;4&lt;/sup&gt; Pa.s</td>
<td>4.19 x 10&lt;sup&gt;5&lt;/sup&gt; Pa.s</td>
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<tr>
<td>T&lt;sub&gt;g&lt;/sub&gt;</td>
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<th>λ&lt;sub&gt;i&lt;/sub&gt;(s)</th>
<th>g&lt;sub&gt;i&lt;/sub&gt;(Pa)</th>
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Extensional rheology specimens were prepared using a hydraulic press heated to 180°C (PS) and 80°C (SBR). Rectangular polymer samples of dimensions 0.85 x 6.5 x 16 mm (HxWxL) were thus produced. Prior to sample loading, the MERA fixture was heated to 160°C and 25°C for the SBR blend, using the environmental chamber of the host system. Once the oven temperature reached its set point, the fixture sat at temperature for a minimum of 30 min prior to initial sample loading. The loading procedure involved opening the oven chamber door
and, using a pair of fine tweezers, loading and securing the specimen onto the preheated MERA fixture, then closing the oven chamber door all within a time span of about 20–30 s. A second wait period was then imposed prior to starting a test in order to allow the oven and sample specimen to reach the test temperature and the latter to relax any residual stresses from the forming stage. When sample sagging during this stage occurred, it was necessary to bring it back up to the horizontal position manually prior to testing, and monitor stress relaxation. Only when the torque signal read zero and the sample was horizontal was testing initiated. Upon test completion, the drums were carefully wiped clean with a soft disposable laboratory wipe to remove any sample residue off the drum surfaces.

The specimens for the SER were prepared following the same protocol, with strips 12.7 mm long. Sample loading followed the protocol described in Sentmanat 2005.

4.3.1 MERA Repeatability Validation

The first test of an instrument’s precision must be its measurement reproducibility. In the case of the MERA this is depicted in Figure 4.14 for three runs of the PS sample at a nominal strain rate of 1.0 s⁻¹. Clearly, the instrument is very precise with the results from all experiments falling within +/- 5% from each other.
All of the following measurements shown in this study were video recorded to obtain a direct measure of the actual strain rates and Hencky strain imposed on the sample in both devices, MERA and SER, for different elongational rates. For each material, we first report on MERA ability to perform experiment at different constant strain rates. Next, we compare the results between the MERA and the SER. Finally, the extensional viscosities calculated at different rates for both fixtures are compared with each other.
4.3.2 Styrene-Butadiene Rubber Validation

Figures 4.15 and 4.16 show the visual evidence of deformation homogeneity and strain rate calculation for the SBR melt at 25°C in the MERA and, again, the experiments all show uniform deformation up to the onset of yielding and follow the mandatory exponential decay $W(t)=W_0 \exp(-\varepsilon/2)$ for all strain rates and for all times. A rate-dependent yielding of the network is observed at high Hencky strains. Figure 4.17 shows the particular example of a nominal strain rate of 1.0 s$^{-1}$, where it can be seen that in that case a maximum Hencky strain of 8.1 was achieved under homogeneous deformation conditions. This equates to a linear stretch in excess of 3700, and to the best of the authors’ knowledge, these are the first reported results ever of true Hencky strains in excess of 8 being achieved for polymer melts under homogeneous deformation conditions. Finally, Fig. 18 shows the calculated extensional viscosities for both geometries at various true constant strain rates. The results clearly show that the onset and evolution of strain-hardening are detected at very similar strains by both instruments, as expected. However, although the SER results are limited in Hencky strain, those of the MERA are not and it can clearly be seen that accurate viscosity measurements can be obtained with the latter up to much higher strains. These measurements cannot, however, be continued up to rupture because of the aforementioned issue with the superposition of the empty torque signal on the actual torque from sample deformation. In the present case, we only calculated the extensional viscosity up to a Hencky strain of...
approximately 5.5; above this, the influence of instrument friction was noticeable on the torque curve (more than 10% of the measured signal). One final point worth of consideration is that at no point were we able to discern the onset of a steady-state regardless of material, strain rate, or experimental geometry.

MERA experiments in particular should be sensitive to the presence of a steady state due to the high strains involved, but we were not able to observe it.

Figure 4.17: Images of MERA experiments on SBR at various nominal strain rates at 25°C
Figure 4.18: Evaluation of the true strain rates using the MERA for SBR at 25°C
Figure 4.19: Evaluation of the true strain rate at a nominal strain rate of 1 s\textsuperscript{-1} for SBR at 25°C
Figure 4.18: Transient elongational viscosity for both experimental geometries as a function of time for different strain rates for SBR at 25°C
4.4 Conclusions

A new extensional rheometer for high viscosity systems based on the Meissner principle, easy-to-use, versatile and adaptable to commercial rotational rheometers was developed, and in this paper it was demonstrated to be capable of achieving ultra-high deformations, limited only by sample rupture. The rheometer was designed with counter-rotating rollers, thereby imposing similar strain histories to both ends of the sample, and ensures a uniform extensional deformation during the elongational experiments. True strain rate is monitored by visually accessing the sample during deformation using a high-speed digital camera.

Extensional experiments were conducted on three materials representing opposite ends of expected rheological behavior, a highly elastic SBR blend, a branched LDPE and a linear PS, and the results compared with those obtained using the ubiquitous SER design. The main results were:

The MERA was able to accurately replicate the results of the SER in terms of onset of strain-hardening and absolute transient extensional viscosity values, while yielding lower deviations between the nominal and effective strain rates than the SER.

The MERA allowed experiments to be performed up to unprecedented real Hencky strains of 8.1, which corresponds to a linear stretch of 3,700, whereas the SER is limited to one drum revolution, which corresponds to a Hencky strain of 3.5-4.0, or a maximum linear stretch of approximately 50.
No sign of a steady-state was observed at high Hencky strains.

There are intrinsic limitations to coupling instruments such as the SER and MERA to controlled-stress rheometers. In fact, not only is instrument inertia a factor at high strain rates, but at very high strains the sample becomes so thin that if one is not careful to minimize the empty torque of the extensional accessory, the total torque may end up having a non-negligible component due to instrument friction.

In conclusion, the new MERA design maintains all the advantages of the original Meissner concept, namely the possibility of achieving very high strains, while improving in critical areas, such as versatility, ease-of-use, accuracy at ultra-high strains and cost. It also outperforms the SER design in terms of strain rate accuracy and achievable Hencky strains. The MERA concept is currently being expanded to include coupling to controlled-strain rheometers, and the ability to perform controlled strain and/or stress experiments via the use of a feedback control loop.
4.5 References


APPENDIX

Experimental and Numerical Studies of Adapter Design in Counter-Rotating Twin Screw Extrusion

This chapter is partially based on:

*Journal article:*

P. Harris, et al., (2014) Submitted
A1.1 Introduction

The plastics industry commonly uses coathanger and fish-tail style extrusion dies for the production of sheet and film products. A coathanger geometry serves the primary purpose of guiding the molten polymer from a cylindrical shape following an extruder into a wide and sometimes very thin extrudate. The coathanger’s output geometry dictates the final dimensions of manufactured product, unless otherwise shaped further via thermoforming or other post-extrusion process methods.

In typical polymer extrusion, solid-state plastic powder or pellets enter a hopper which feeds into a single, twin, or even triple screw extruder. As the polymer is heated and conveyed through various screw sections, the polymer then enters a transition zone, an adapter, between the extruder screws and a die system. For a single screw extruder, this adapter is typically a straight cylindrical pipe. However, for materials and processes using twin-screw extrusion, the adapter geometry is much more complex due to flow inhomogeneity. Figure A1.1 displays the output scheme of both co- and counter-rotating twin-screw extruders (Wagner, et al., 2014) just prior to flow into the adapter geometry.
The high pressure areas are representative of the high flow areas; likewise, the areas of low pressure are representative of low flow rate regions. As can be deduced, the flow entering the adapter can vary based on the twin-screw style, without even discussing the properties of the material. The internal flow geometry of the adapter in twin-screw extrusion varies not only on the twin-screw style, but also should vary based on the down-stream profile geometry. Selection of the proper style and geometry is critical in maintaining a stable and efficient, cost-saving process. Polymer degradation can occur in poorly designed screws and dies, and the same can be said of the adapters which connect the two flow geometries. Adapter geometries are design to minimize pressure drop and keep the velocity at the wall moving to “self-clean” the walls. In a poorly design channel, the velocity layers nearest to the steel wall move very slowly, if not stopped completely. This layer of static material degrades and becomes brittle, breaking off periodically with high built up pressure. Material related processing issues, however, are critical in designing a proper adapter and are
studied in this work. An industrially-recognized processing instability of a thermally-sensitive chlorinated-polyvinyl chloride (cPVC) has proven to be costly; causing poor raw material-to-product yield. An author in a recent magazine articles states “does degraded or burned polymer seem to show up when you least expect it? If so, it’s probably coming from one of your adapters” (Frankland, 2010).

A1.1.1 Residence Time

Material residence time has been well studied experimentally and numerically in all types of extrusion processes including single- thru triple-screw extrusion as well coathanger and fish-tail style die geometries (Yang, 2014, Edi-Soetaredjo, et al., 2003, Yilmaz, et al., 2014). By using particle tracks and mixing simulation in ANSYS Polyflow, researchers investigate how material, process, and geometry affects the material residence time and residence time distribution. For a thermally sensitive material such as cPVC, understanding regions of high residence time is critical in establishing proper extruder, adapter, and die geometry.

A manufacturing process was first studied and observed during the start-up of the research. Figure A1.2 displays the solid adapter and coathanger die plug. The experimental plug was saved directly after a process shut-down for degraded material showing up within the process.
Upon further investigation of the coathanger and adapter plug from Figure A1.2, noticeable degradation displayed originating in the adapter portion of the system. A closer look at this section of the extrudate is shown in Figure A1.3.
Figure A1.22: Solid adapter plug of cPVC. Noticeable degradation was found primarily in several spots, one darker more prevalent than the other.

The degraded cPVC was heavy near several spots including the top-central of the plug and around the perimeter of the bottom half. The degraded polymer showed up in streaks stemming from the adapter plug as well as solid masses throughout the coathanger and die lands. As stated earlier, the solid masses likely stem from the adapter channel having stagnate regions where the polymer first degrades then breaks apart and is forced into the coathanger die.

We decided to investigate the flow further by performing a residence time study via small amounts of colorant added to the cPVC resin. The resulting sheet shown in Figure A1.4 displays two noticeable traits. First, a parabolic shape occurs, suggesting a highly unbalanced flow through the coathanger die.
Secondly, a long tail stretches down the length of the sheet, in the middle, and continued on for 10.5 minutes.

Figure A1.23: Residence time study of a cPVC process.

The existence of these two flow conditions represent two separate and very important problems which should be studied. However, the long tail resulting from stagnant flow is costly from the manufacturing perspective as previously discussed. In the following research, we propose two hypothesis for study: adapter geometry has a strong influence on residence time in counter-rotating twin screw extrusion; and the material type; i.e. rheological model, has a strong influence on residence time in counter-rotating twin screw extrusion.
A1.2 Method

A1.2.1 Experimental Material

A commercially available chlorinate-polyvinyl chloride (cPVC) from Lubrizol Advanced Materials was chosen for the study. The cPVC chosen was LC 987; the material was dry-blended with titanium-dioxide from DuPont Ti-Pure R104 at a level of 1.5% by weight.

A1.2.2 Rheological Measurements

The primary purpose of shear flow property measurement is for gathering the proper information for computational simulation. Rheological characterization was carried out using a Thermo Fisher Haake Mars II rotational rheometer. Steady and oscillatory shear was carried out using parallel plates of 25 mm diameters. cPVC was first pressed at 190°C using a hot press. Samples are hydroscopic and did not need vacuum drying. Steady shear tests were performed on shear rates ranging from 0.001 s\(^{-1}\) to 20 s\(^{-1}\). Frequency sweeps were carried out at several temperatures then t-T superposition was used in IRIS software to build a master curve at a reference temperature of 190°C.

Steady shear results are shown in Figure A1.5. Shear stress and shear viscosity are plotted as a function of shear rate. The zero shear viscosity is evident at shear rates lower than 0.01 s\(^{-1}\) and shear thinning occurs above the same.
Figure A1.24: Steady shear results of cPVC polymer

Oscillatory shear results are displayed in Figure A1.6. As mentioned above, the reference temperature after t-T superposition was applied is 190°C. Figure A1.6 is used for attaining the relaxation moduli and time, otherwise known as the relaxation spectra and will be discussed in the next section.
A1.2.3 Internal Mixer Process

The stability of the cPVC and titanium dioxide blend is important for understanding how residence time affects degradation. An internal mixer, Thermo Fisher Haake Rheomix Lab Mixer for the Thermo Fisher Haake Polylab OS system was used for mixing. The front plate, back plate, and bowl of the mixer were set to a temperature of 190 C. The rotor chosen for the stability study were a standard roller rotor. Rotor speed was set to a constant 75 rpm. Samples were collected periodically during mixing to investigate color changes.
The mixer was stopped when the torque increased 25% from the stable mixing region.

As shown in Figure A1.7, the internal mixer results displayed a typical sharp initial increase in torque due to the amount of solid, unmelted and unfused cPVC. As the powder begins to melt and fuse, the torque rapidly decreases and remains stable for several minutes. A degradation time of approximately 10 minutes is noticed. At this time in the torque curve, the material becomes very rigid and the
degradation turns the material into a solid char. This solid char is very similar to what is seen in the physical extrusion process and can be related. Due to a difference in shear rates between batch mixing and the extrusion process, however, the degradation times can’t be correlated exactly, however, the degradation behavior can be qualitatively related.

A1.2.4 Computational Method

The full adapter and coathanger flow geometry is shown in Figure A1.8. The geometry was modelled using Dassault Systems Solidworks 3D modeling software. For numerical simulations, ANSYS Polyflow version 14.5 and 15.0 were used. In general, the material flows directly from the counter-rotating twin-screws and enters the adapter (top-right). Since the material is extruded in a fashion similar to Figure A1.1, the flow channel leaving the adapter is vertically offset. The offset nature of the adapter channel leading to the coathanger is to promote the flow in the lower pressure regions leading from the extrusion screws.
Figure A1.27: Full coathanger and adapter channel designed using 3D Solidworks

To lower the computational cost of the simulations, half symmetry was applied to the geometry model leaving a geometry design shown in Figure A1.9.

Figure A1.28: Half symmetry geometry; mesh for ANSYS Polyflow
The mesh used throughout the Polyflow simulations used a combination of Sweep and Patch Conforming methods. Due to the nature of the coathanger land thickness, an Edge Sizing feature was used in the mesh to allow for three elements through the thickness of the geometry. As will be discussed later, there are three geometries used; the mesh counts of each range from 158,919 – 164,456 nodes and 578,155 – 640,451 elements.

Other conditions used in the setup of the computational modeling included three inflows, a plane of symmetry, zero normal and tangential velocity at all adapter and coathanger die walls, and a zero normal and tangential force condition at the die outflow. The three inflows were estimated and when summed, the total mass flow rate matched the mass flow rate of the physical extrusion being replicated.

The experimental rheology discussed previously was fitted with three rheology models. First, a Newtonian rheological model with the viscosity chosen from the zero-shear viscosity experimental data. Secondly, a shear-thinning rheology model, the Cross model, was chosen. This rheology model has the same zero-shear viscosity as the Newtonian fluid, however, has a viscosity thinning region, or Cross law index of 0.774. The final rheological model chosen includes elasticity and is a fully viscoelastic model. This differential viscoelastic model is the Phan-Thien Tanner (PTT) model. The experimental and modelled curves are displayed in Figure A1.9.
The flow was assumed to be incompressible and isothermal. The equations governing the flows are the Cauchy-momentum equation given by

$$\rho \frac{D\mathbf{u}}{dt} = \nabla \cdot \mathbf{T} + \nabla p + \rho g,$$  \hspace{1cm} (1)
\[ \nabla \cdot \mathbf{u} = 0, \]  

(1)

where \( t \) is the time, \( \mathbf{u} \) is the velocity vector, \( p \) is the pressure, \( \rho \) is the fluid density, \( \mathbf{g} \) is the gravitational field and \( \mathbf{T} \) is the stress tensor described by the PTT model.

The tensor \( \mathbf{T} \) is split into a viscoelastic component \( \mathbf{T}_1 \) that is computed according to the chosen PTT model (Phan-Thien & Tanner 1977) and a purely viscous term \( \mathbf{T}_2 \). (This decomposition helps the convergence of the numerical method (Ansys POLYFLOW user’s guide)). Therefore, the stress \( \mathbf{T} \) is given by

\[ \mathbf{T} = \mathbf{T}_1 + \mathbf{T}_2. \]  

(3)

\( \mathbf{T}_2 \) is considered as the stress response associated with the fastest relaxation time and \( \eta_2 \) is the viscosity factor associated with it so that

\[ \mathbf{T}_2 = 2 \eta_2 \mathbf{D}. \]  

(4)

\( \mathbf{T}_1 \) according to the PTT model is implicitly given by

\[ \exp \left( \frac{\xi \lambda}{\eta_1} \mathbf{T}_1 \right) \mathbf{T}_1 + \lambda \left[ \left( 1 - \frac{\xi}{2} \right) \mathbf{\nabla} + \frac{\xi}{2} \mathbf{T}_1 \right] = 2 \eta_1 \mathbf{D}. \]  

(5)
The symbol \( \mathbf{T} \) the upper-convected time derivative of \( \mathbf{T} \), and \( \mathbf{T}' \) is the lower-convected time derivative. The rate of deformation tensor \( \mathbf{D} \) is

\[
\mathbf{D} = \frac{1}{2} (\nabla \mathbf{u} + \nabla \mathbf{u}^T) .
\]

(6)

The viscosity \( \eta \) is given by

\[
\eta_i = (1 - \eta_r) \eta ,
\]

(7)

\[
\eta = \eta_2 + \eta_1 ,
\]

(8)

Where

\[
\eta_r = \frac{\eta_2}{\eta_2 + \eta_1} .
\]

(9)
The full relaxation spectrum was calculated using IRIS software from the oscillatory shear data above. The relaxation spectrum and the PTT parameters are first shown in Table A1.1.

Table A1.10: Full relaxation spectrum of the cPVC compound

<table>
<thead>
<tr>
<th>Mode #</th>
<th>G1 (Pa)</th>
<th>lambda (s)</th>
<th>Viscosity</th>
<th>η1</th>
<th>η2</th>
<th>η</th>
<th>η ratio</th>
<th>η*</th>
<th>η* ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>5.71E+06</td>
<td>8.44E-06</td>
<td>4.82E+02</td>
<td>48.20</td>
<td>48.20</td>
<td>96.39518</td>
<td>0.5</td>
<td>0.108</td>
<td>0.194</td>
</tr>
<tr>
<td>7</td>
<td>4.48E+05</td>
<td>3.51E-04</td>
<td>1.57E+01</td>
<td>156.85</td>
<td>48.20</td>
<td>205.04634</td>
<td>0.323057061</td>
<td>0.108</td>
<td>0.194</td>
</tr>
<tr>
<td>6</td>
<td>3.11E+05</td>
<td>1.60E-03</td>
<td>4.97E+02</td>
<td>497.42</td>
<td>48.20</td>
<td>545.61859</td>
<td>0.088335682</td>
<td>0.108</td>
<td>0.194</td>
</tr>
<tr>
<td>5</td>
<td>1.90E+05</td>
<td>6.03E-03</td>
<td>1.14E+03</td>
<td>1143.89</td>
<td>48.20</td>
<td>1192.08859</td>
<td>0.040431215</td>
<td>0.108</td>
<td>0.194</td>
</tr>
<tr>
<td>4</td>
<td>1.02E+05</td>
<td>4.77E-02</td>
<td>4.85E+03</td>
<td>4846.01</td>
<td>48.20</td>
<td>4894.20259</td>
<td>0.009487894</td>
<td>0.108</td>
<td>0.194</td>
</tr>
<tr>
<td>3</td>
<td>4.96E+04</td>
<td>2.85E-01</td>
<td>1.41E+04</td>
<td>14102.67</td>
<td>48.20</td>
<td>14150.86259</td>
<td>0.003405982</td>
<td>0.108</td>
<td>0.194</td>
</tr>
<tr>
<td>2</td>
<td>1.18E+04</td>
<td>1.77E+00</td>
<td>2.10E+04</td>
<td>20956.86</td>
<td>48.20</td>
<td>21005.05759</td>
<td>0.0022949571</td>
<td>0.108</td>
<td>0.194</td>
</tr>
<tr>
<td>1</td>
<td>2305.00</td>
<td>54.40</td>
<td>125392.00</td>
<td>125392.00</td>
<td>48.20</td>
<td>125440.3976</td>
<td>0.000384228</td>
<td>0.108</td>
<td>0.194</td>
</tr>
</tbody>
</table>

While the complete relaxation spectra of the polymers studied here were measured, only a single relaxation time as used in the simulations. This was sufficient to capture the flow behavior of these materials in the two multiplier dies. The final input parameters for three different rheological models used in the simulations are summarized in Table A1.2.
Table A1.11: Parameters for each material model

<table>
<thead>
<tr>
<th>Rheological model</th>
<th>$\eta$ (Pa*s)</th>
<th>$\eta_o$ (Pa*s)</th>
<th>$\eta_t$ (Pa*s)</th>
<th>$\eta_r$ (Pa*s)</th>
<th>$\lambda$ (s)</th>
<th>$\xi$</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Newtonian</td>
<td>157,763</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Cross</td>
<td>--</td>
<td>157,763</td>
<td>--</td>
<td>--</td>
<td>0.774</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Phan-Thien</td>
<td>--</td>
<td>--</td>
<td>119</td>
<td>0.040</td>
<td>0.006</td>
<td>0.108</td>
<td>0.194</td>
</tr>
</tbody>
</table>

where $\eta$ is the viscosity, $\eta_o$ is the zero-shear viscosity, $\eta_t$ is the total viscosity (using $\eta_1$ and $\eta_2$ for calculating the purely viscous component in the extra stress tensor, $\eta_r$ is the viscosity ratio ($\eta_1$ to $\eta_2$), $\lambda$ is the relaxation time, $n$ is the cross-law index, $\xi$ is the fitting parameter for shear behavior, and $\varepsilon$ is the fitting parameter for regulating elongational behavior.

A1.3 Presentation of Simulation Results

A1.3.1 Residence Time Influence Part I Results

We first investigate the influence of geometry on material residence time in the adapter channel. Three different adapter geometries are used, each dependent upon the previous simulation results, excluding the initial geometry. This original geometry used was based off of the physical geometry used in manufacturing.
Figure A1.30: Detail drawings of the design changes involved in the two modified adapter flow channels

The details of the three flow channels are displayed in Figure A1.11. The first design modification involved increasing the radii around the perimeter to promote flow at the top of the adapter. The second modification again increased the radii, except with the promotion of flow via large radii near the bottom of the adapter.

The fully viscoelastic PTT rheological model was chosen for the first analysis to for the purpose of properly designing the adapter flow channel. Figure A1.13 shows the residence time study of the original design. The results are broken
into three categories and displays the material residing in the adapter during each time interval.

Figure A1.31: Residence time study showing the original design using the PTT model

For example, the left picture in Figure A1.12 displays the material residing in the adapter between the times of four and six minutes. That is, the shaped regions in this figure, shows how much material and for how long the material has resided in the adapter. This format is used throughout the remainder of the study. Table A1.3 below shows the maximum residence time in the adapter channel and the average residence time. The cPVC remains in the adapter channel for 23.49 minutes, while the total average residence time is 0.32 minutes.
Table A1.12: Residence time values of the original design using PTT model

<table>
<thead>
<tr>
<th>Residence Time in Adapter Channel (min)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max Residence Time</td>
<td>23.49</td>
</tr>
<tr>
<td>Average Residence Time</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Based on a qualitative investigation of the locations of high residence times, a first redesign was proposed and completed in Solidworks. The areas we promoted the flow is displayed in the red box in Figure A1.13. This region was increased in the flow domain (reduction in theoretical adapter steel) to remain "steel-safe". The results for this study are shown in Figure A1.13.

Figure A1.32: Residence time study showing the first redesign using PTT model

Table A1.4 below shows the maximum residence time in the adapter channel and the average residence time of the first redesign. The cPVC remains in the
adapter channel for 28.84 minutes, while the total average residence time is 0.29 minutes.

Table A1.13: Residence time values of the first redesign using PTT model

<table>
<thead>
<tr>
<th>Max Residence Time in Adapter Channel (min)</th>
<th>28.84</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Residence Time in Adapter Channel (min)</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Due to an increase in residence time in the region identified by the blue box and a decrease in the red box in Figure A1.13, a second redesign is proposed. The second redesign, again, is proposed based off of the qualitative flow in the geometry of the original and first redesign. The results for the second redesign are displayed in Figure A1.14 below.
Table A1.5 below shows the maximum residence time in the adapter channel and the average residence time of the second redesign. The cPVC remains in the adapter channel for 15.84 minutes, while the total average residence time is 0.30 minutes.

Table A1.14: Residence time values of the second redesign using PTT model

<table>
<thead>
<tr>
<th>Max Residence Time in Adapter Channel (min)</th>
<th>15.84</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Residence Time in Adapter Channel (min)</td>
<td>0.30</td>
</tr>
</tbody>
</table>

A1.3.2 R.T. Influence Influence Part II Results

The residence time study in Part II is a study of material model dependency on residence time. Here we again use the geometry models developed for Part I when the fully viscoelastic PTT model was used. For the first study in Part II, we investigate how a constant viscosity model flows through the adapters and coathanger. Figure A1.15 displays the results within the adapter of a Newtonian,
constant viscosity material (as outlined in Table A1.2). Each of the three rows are the three different adapter designs, while each of the three columns are a period of time, showing the material residing in the adapter in that time interval. The time intervals chosen are 0-30 minutes, 10-30 minutes, and 20-30 minutes.

Figure A1.34: Residence time study of a Newtonian fluid

Table A1.6 summarizes the results in Figure A1.15 by considering an average residence time as well as a maximum residence time within the adapter channel. The original design has the lowest average residence time at 0.36 min and the
lowest maximum residence time at 24.06 min. The longest residence time occurs in the first redesigned geometry.

Table A1.15: Residence time values for a constant viscosity Newtonian fluid

<table>
<thead>
<tr>
<th>Geometric Style</th>
<th>Average Residence Time (min)</th>
<th>Maximum Residence Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original Design</td>
<td>0.36</td>
<td>24.06</td>
</tr>
<tr>
<td>First Redesign</td>
<td>0.45</td>
<td>63.90</td>
</tr>
<tr>
<td>Second Redesign</td>
<td>0.39</td>
<td>31.0</td>
</tr>
</tbody>
</table>

The second part of Part II, we investigate the effects of shear-thinning behavior on residence time and compare this to a Newtonian fluid. As can be seen in Figure A1.16, the Cross model has areas of very high residence times and a larger region of material which stays in the adapter past 30 minutes.
Table A1.7 summarizes the results in Figure A1.16 by considering an average residence time as well as a maximum residence time. The average residence times are the highest with the shear-thinning Cross model compared to the Newtonian or PTT model. As the first redesign is studied, the average residence time increases from 1.19 minutes in the original adapter, to 1.47 in the redesign adapter. This is a very large increase from the Newtonian fluid and will be discussed in detail in the analysis section. The maximum residence times
increase drastically from the Newtonian and PTT cases to as high as 275.69 minutes.

Table A1.16: Residence time values for a shear-thinning Cross model

<table>
<thead>
<tr>
<th>Geometric Style</th>
<th>Average Residence Time (min)</th>
<th>Maximum Residence Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original Design</td>
<td>1.19</td>
<td>105.25</td>
</tr>
<tr>
<td>First Redesign</td>
<td>1.47</td>
<td>224.67</td>
</tr>
<tr>
<td>Second Redesign</td>
<td>1.53</td>
<td>275.69</td>
</tr>
</tbody>
</table>

A1.4 Analysis of Results

A1.4.1 R.T. Influence Part I Analysis

In Part I, the study was based around the geometry of the adapter and how influential the physical design was on residence time. In the initial or original geometry, material residing between four and six minutes was heaviest in near the plane of symmetry as well as the opposite side, or furthest point from the high pressure region as shown in Figure A1.1. There are small amounts of material with approximately 4.0 to 4.5 minutes around the perimeter of the low flow pressure regions. Moving to a time interval of six to eight minutes, the material around the perimeter has moved out of the system, leaving only the area near top and the area opposite of the high pressure region. The same is true for 8 to 23 minutes where the maximum residence time is shown. These two areas can
be assumed regions of flow hesitation resulting in material stagnation and consequently degradation. This degradation in the center is related to the long tail of colorant displayed previously in Figure A1.4. As the material sits stagnant, the cPVC turns to a char, resulting in a time-dependent flow behavior in physical processing, leading to process shut-down. This shut-down seen in manufacturing is costly, as the entire processing needs disassembled, cleaned, and reassembled. According to the simulations shown the process may only last for minutes before degradation occurs.

The primary goal in the first redesign was to remove the long tail and the region near the top of the adapter as previously discussed. By theoretically removing steel in this section, the flow is opened-up and is promoted to occur. In the results of the first redesign, the material does in fact leave this region much early, however, the results show an increase in residence time in the other high residence time region.

Building upon the results from the first redesign, we then theoretically removed steel from the portion away from the plane of symmetry, resulting in larger radii to encourage the flow of the cPVC. The final results show a much lower maximum residence of about 15 minutes. Relating this 15 minutes to the mixer curve displayed in Figure A1.7, the time to degradation in mixing is much lower compared to the residence times in simulation. While the simulations show a higher residence time, the shear rates in the adapter and coathanger are much lower than what is seen in the internal mixer. Though we can’t relate the two calculations easily, the process can be said to be much more stable and longer
production runs can be achieved by using the second redesigned adapter in manufacturing cases. Longer production runs result in product overall yield as well as an increased profitability to the manufacturing company.

A1.4.2 Residence Time Influence Part II Analysis

The second analysis is to investigate other material models. In Part I, we looked at a replicating a fully viscoelastic PTT model of the cPVC; in Part II, we studied a constant viscosity generalized Newtonian model and a shear-thinning Cross model. These models are chosen as a numerical exercise and should be studied as such. In the case of the Newtonian model, a constant viscosity and inelastic material showed higher residence times in general. The constant viscosity: maximum and average residence times were greatest in the first redesign, potentially magnifying the flow hesitation created when opening up the steel theoretical steel near the plane of symmetry. The lowest times were found to be in the original design, possibly hinting that the initial design from the manufacturer was based on Newtonian fluid calculations.

When considering a shear-thinning behavior using a Cross model in the adapter designs, the model showed the highest residence times. The areas of high shear rates displayed the lowest residence times and vice versa, the areas of very low shear rates showed very high residence times. In general, the average residence time using a Cross model, was much higher than both the Newtonian case and the PTT case. For these reasons, elasticity has shown to be a large factor in not only proper design, but reducing residence times in an adapter flow
channel which results in a manufacturing benefit. If the Cross model for example is chosen as a rheological input to design, the results are the poorest and the residence times are highest.

A1.5 Conclusion

In this work, a chlorinated, polyvinyl chloride (cPVC) was characterized and studied around residence time. This industrially-motivated project investigated how geometry of an adapter connecting a counter-rotating twin screw extruder to a wide coathanger die affects the residence time of the material. In Part I, we showed how a drastic improvement on residence time could be achieved by proper geometry design and displayed the need for simulation using CFD in industry related work. The reduction of residence time allows for longer production runs, lowered instabilities, and an overall yield in product, resulting in an increased profitability for a manufacturing company. In Part II, we showed how moving from the true differential viscoelastic model, the Phan-Thien Tanner model, to simplified cases such as a Newtonian and Cross model can be detrimental in design. In fact, by using the design cases from Part I, the Newtonian and Cross model, a constant viscosity and shear-thinning models, actually increases the theoretical residence time in the adapter channels.
A1.6 References


Ponting, Michael; et al., 49, 12111-12118 (2012)


Hatzikiriakos, Savvas G., Migler, Kalman B., Polymer Processing Instabilities: *Control and Understanding*, Marcel Dekker (2005)


S.G. Hatzikiriakos and K.B. Migler, Polymer processing instabilities: control and understanding, Marcel Dekker (2005).


O. Ishizuka and K. Koyama, Polymer, 21, 2 (1980).


