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ANALYSIS OF HYPERBRANCHED/LINEAR POLYMER EXTRUDATES

By

Joel Kellogg Sutton

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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ABSTRACT

ANALYSIS OF HYPERBRANCHED/LINEAR POLYMER EXTRUDATES

By

Joel Kellogg Sutton

In this study the effect of flow through a capillary die on the surface properties and morphology of a polymer blend was investigated. Previously, it was shown that mixing a "hyperbranched polymer", or HBP, with a linear polymer resulted in an increase in the apparent shear rate for a given shear stress, when compared to the virgin polymer. The postulate is that the HBP acts as a processing aid, whose viability may be influenced by the capillary length.

The hypothesis is that the two polymers form an immiscible mixture and a thin HBP layer near the fiber surface accounts for the increase in the apparent shear rate. Thus, it is important to examine phase separation as a function of capillary length to determine if a diffusive mechanism is present. Polymer samples were extruded through a 30 mm length capillary die and a zero-length capillary, or orifice plate; both the capillary and the orifice plate were 1.5 mm in diameter. A DSC study was performed to determine the effect of temperature and HBP concentration on phase separation. The extruded polymer samples were viewed in TEM to visualize the layers.

The results show that the shear rate increase does exist and that the HBPs and the virgin polymer do phase separate and that the HBP migrates to the surface as hypothesized. Further, capillary length influences the morphology, although the exact diffusive mechanism is unclear.

DEDICATION

I wish to dedicate this work to my parents, Bill and Sandra Sutton. All I have, I

owe to them.

.

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KEY TO ABBREVIATIONS AND SYMBOLS

Abbrev	viation	Meaning
LLDPE		Linear Low Density Polyethylene
LDPE		Low Density Polyethylene
PS		Polystyrene
HBP		Hyperbranched Polymer
PDMS		Polydimethylsiloxane
G(Number)		Generation (number) Dendrimer
H3200		Third Generation HBP, (10% -OH
		groups, 90% -C ₂₀ groups)
H40		Fourth Generation HBP, 100% -OH
		groups
H50		Fifth Generation HBP, 100% -OH
		groups
OP		Orifice Plate (zero-length capillary)
SAXS		Small Angle X-Ray Scattering
DCA		Dynamic Contact Angle Analysis
ATR-FTIR		Attenuated Total Reflection-Fourier
		Transform Infrared Spectroscopy
SANS		Small Angle Neutron Scattering
N/R		Not Recorded

.

	<u>Symbol</u>	Meaning
• m		Mass Flow Rate
Q		Volumetric Flow Rate
ρ		Polymer Melt Density (also Liquid Density); Definition depends on Chapter
$\dot{\gamma}_a$		Apparent Shear Rate
D		Capillary Diameter
L		Capillary Length
∆P		Capillary Pressure Drop
σ_{w}		Shear Stress
z		Depth of Immersion
а		Fiber Cross-sectional Area
d		Fiber Diameter
g		Gravitational Constant
k _B		Boltzmann's Constant
т		Absolute Temperature
r		Particle Radius

1. Introduction

In the field of polymer science, engineering, and chemistry, much work has been done on measuring the properties and behavior of linear polymers. A linear polymer is a macromolecule with a primary straight chain and identical repeating monomer units. Figures 1.1 and 1.2 depict two common linear polymers: Polystyrene (PS) and Polyethylene (PE).



Figure 1.1: Chemical Structure of a PS Monomer¹

 $-CH_2$ $-CH_2$

Figure 1.2: Chemical Structure of a PE Monomer¹

A simple literature search will reveal numerous papers and books on the properties of linear polymers. Obviously, linear polymers' properties may differ drastically from each other.

In order to capitalize on these different properties, copolymers were invented. A general definition of copolymers might be: a macromolecule comprised of two or more different monomer units.² Copolymers are subdivided into classes according to the various ways in which the different monomers may be organized in the molecule. Some examples of these classes are statistical, alternating, block, and graft copolymers.² Full definitions and descriptions of these classes may be found in any general polymer text. Copolymers should not be confused with polymer mixtures or polymer blends. A polymer blend is simply the mixture of two macromolecules, either in solution or mechanically, whereas a copolymer is a macromolecule constructed of two or more different monomers. Thus, it is possible to have a blend between two different copolymers. Polymer blends also generally involve two nonreactive and immiscible polymers, such as polystyrene and polyethylene.

Linear polymers differ radically from their cousins, the branched chain polymers since a branched chain polymer has either short chain or long chain branching emanating from the linear chain. A subgroup of the branched chain is the dendrimer. Dendrimers are interesting molecules in that they are well defined nanoparticles with a specific molecular weight and structure,³ with treelike branches emanating from a core.

The polymer chemistry used to create dendrimers can be quite involved. Suffice it to say that it involves reacting an AB_x structure repeatedly. Here, A and B represent two different types of functional groups and x≥2. The two primary methods proposed to date to create dendrimers are the "Divergent" and "Convergent" Growth Methods. "Divergent growth" was first proposed by Tomalia and coworkers.⁴ This method starts with a core and reacts the B_x groups outward, as shown in Figure 1.3.



Figure 1.3: Schematic of Divergent Growth⁴

The second method, first proposed by Hawker and Fréchet⁵ and used by Mourey,⁶ begins with the desired end groups (B_x) and reacts the A groups until they reach a common point. These are called "dendrons", which are then grafted onto a core. This method is referred to as "convergent growth". Figure 1.4, from Hawker and Fréchet,⁵ demonstrates this process.



Figure 1.4: Schematic of Convergent Growth⁵

If the dendrimer synthesis is not strictly controlled, then a Hyperbranched Polymer (HBP) is created. HBPs, therefore, exhibit similar properties to a dendrimer, including low viscosity, globular shape, and high functionality.⁷ The imperfect structure is the source of some differences. In summary, HBPs are essentially an intermediate between a dendrimer and a regular linear polymer.⁷ Some advantages of this imperfect structure are that HBPs are easier, cheaper, and faster to produce than a dendrimer. For an industrial process, this should be very attractive.

As a convention, both dendrimers and HBPs are given a generation number. This generation number represents the number of layers from the core. Each layer is a place where the B_x group has reacted. For example, a G3 dendrimer has three layers from the core. Figure 1.5 shows an example of a third generation HBP.



Figure 1.5: Schematic of a Boltorn H30 (G3) HBP Molecule

An interesting feature of both HBPs and dendrimers is the end group. This "end group" corresponds to the B_x mentioned earlier. In traditional wet chemistry, the outer groups of any molecule will dictate that molecule's behavior when it comes into contact with other molecules. The principle is the same for polymers, regardless of the size or structure. An important question, then, might be: what constitutes an outer group? In the case of dendrimers, the answer to this question is still under discussion. A brief overview of this debate is given by Fréchet.⁷ In the same paper, he concludes that in a dendritic polymer the end groups will concentrate at the surface due to a dislike of the framework. It may also be argued that due to their imperfect structure, HBPs are less constrained sterically than dendrimers and thus, the "outer groups" are the "end groups".

The HBPs used in this study were created using the divergent method. The HBPs used also exhibit similarities and differences in their respective generation numbers, end groups, and physical properties.

In this work, these HBPs were co-extruded with linear polymers and the blends were analyzed through a variety of techniques. All of the polymers used were commercial grade. Table 1.1 lists the basic information for all HBPs used, as well as the linear polymers with which they were blended.

HBP Name	Generation Number	End Group	Linear Polymer	System Name
Boltorn		10% -OH,		+
H3200	3	90 % C ₂₀	LLDPE	LLDPE/H3200
Boltorn H40	4	-OH	LLDPE	LLDPE/H40
Boltorn H50	5	-OH	PS	PS/H50

Table 1.1: HBP/Linear polymer systems studied

2. Extrusion Rheology for a 30 mm Die

2.1. Introduction

In order to properly understand the effect of the HBP on the extrusion process, it is first necessary to examine the rheology of the linear polymers. In Mackay and Henson,⁸ they concluded that in the flow of linear polymer melts that there are two competing effects: a deposited layer which slips along the capillary wall and a decrease in the flow area due to this deposited layer. In their work, they performed rheological tests on linear polystyrene, as well as LLDPE. Figure 2.1 shows a cartoon of this effect. The part labeled "Wall Layer" corresponds to this deposited layer.



Figure 2.1: Cartoon of Melt Flow

While Mackay and Henson performed their experiments with a rheometer, the polymer melt flow will be the same, regardless of flow geometry. There are two key phenomena that are observed in any flow system: shear stress and shear rate. Shear stress may be defined as the effect a force has on a fluid, while shear rate may be defined as the velocity gradient across a flow field. For a Newtonian fluid, the relationship between these two values should be linear. That is to say that the fluid viscosity is independent of either of these two values. Polymer melts, however, are Non-Newtonian fluids because their viscosities are dependent on the shear stress and shear rate. Equations [2.1] and [2.2] give the relations for the apparent shear rate and the shear stress in a capillary of finite length.

$$\dot{\gamma}_{a} = \frac{32 \, Q}{\pi D^{3}} = \frac{32 \, m}{\rho \pi D^{3}}$$

$$\sigma_{w} = \frac{D \Delta P}{4 \, L}$$
[2.1]
[2.2]

The Apparent Viscosity is a ratio of the Shear Stress to the Apparent Shear Rate.

The other important boundary is an understanding of the HBP's behavior. Hsieh, et al.⁹ performed a series of rheometric studies on two of the three HBPs used in this work: H40 and H50. Their main conclusion was that H40 and H50 behave as Newtonian fluids under both oscillatory and steady shear. Thus, the viscosity remains constant when the shear rate is constant.

In her thesis,¹⁰ Carmezini reported that adding a HBP in a quantity as low as 0.5 wt% to a linear polymer would result in a shift of the shear stress/shear rate master curve to a lower apparent viscosity. Carmezini performed an extensive study of the extrusion of several linear polymer/HBP mixtures and observed this decrease for at least one system studied per linear polymer. Thus, a necessary first step was independently corroborating this observation for three systems, denoted PS/H50, LLDPE/H3200, and LLDPE/H40.

2.2. Experimental Procedure

The following general procedure was followed for all three systems. Any deviations will be noted at each step.

The first step was to extrude the pure polymer and plot the apparent shear stress versus the apparent shear rate as a reference curve.

The next step was to extrude the 0.5 wt % polymer blends. In order to introduce the HBP into the system, it was dissolved in Tetrahydrofuran (THF). In order to aid its solubility, 500 mg HBP was heated to 100 °C and kept there for ten minutes. The HBP was then allowed to cool down to 60 °C. At this point, 50 mL THF was added and the solution was allowed to mix for a period of twenty-four hours. The dissolved HBP solution was then poured over the bulk polymer pellets, which were spread out on two trays, lined with aluminum foil.

In the case of PS, it is extremely important to note that the pellets must be spread out as much as possible, otherwise, due to the high solubility of PS in THF, the pellets could fuse together. After letting the pellets sit in the hood for a couple of days, the PS/H50 pellets had to be cut apart. LLDPE is insoluble in THF, and thus this cutting procedure is unnecessary.

Note that it is important to keep the PS/H50 and LLDPE/H40 out of the open air, as both H50 and H40 are highly hydroscopic, and any moisture or solvent in the system will cause foaming in the extrusion process. Finally, the pellets were allowed to sit under vacuum at room temperature for a week, after which extrusion was performed.

When performing the extrusion experiments, the pellets were fed into the hopper and the system was allowed to run until the system reached a pseudo-steady state. At this point the extrudate was cut off and a stopwatch was started simultaneously. After about 30 seconds, the stopwatch was stopped and the extrudate cut off at the same time. The time was recorded and the extrudate weighed and saved. Three runs were performed for each motor setting from 15 to 85 at increments of 10. These motor settings roughly correspond to 10 to 70 RPMs, respectively. Optical micrographs of the extrudates may be found in Section 3.5.

2.3. Materials and Equipment

The PS and LLDPE used were industrial grade Dow products. The PS was Dow Styron 678C-W, Lot #OH10017P08; the LLDPE was Dow Dowlex 2045A, Lot #NH1109Z1D. The HBPs were products of Perstorp, Inc. The THF was a product of Fischer Scientific. All products were used as delivered and without modification, except as noted above. The extruder used was a home built device and was the same extruder used in Carmezini's experiments.

2.4. Data Collection

The data collected for this section included the melt pressure, amperage used, motor RPMs, melt temperature, die temperature, barrel temperature, time of extrusion, and extrudate mass. This data was then used to generate the extrusion master curves. Equations 2.1 and 2.2 were used to calculate the apparent shear stress and shear rate.

2.5. Results/Discussion

Figures 2.5.1 through 2.5.3 are the master curves for shear stress/shear rate created following the procedure outlined above. While not identical to the previous work, they are extremely close. Thus, the observed behavior¹⁰ was independently corroborated, and it must be concluded that the phenomena exists.

In Figure 2.5.1, a comparison of the PS curve and the PS/H50 flow curve is made. These flow curves were conducted over a range of 178 °C to 227 °C for the apparent shear rate/shear stress as well as the apparent shear rate/apparent viscosity master curve. Adding H50 to PS resulted in a significant melt pressure drop for higher apparent shear rates. For example, a mixture of PS and H50 at an operating temperature of 227 °C and running at 43 RPMs has a melt pressure of 310 psi; PS, running at similar conditions, has a melt pressure of 460 psi. Thus, adding H50 to PS grants a 33% decrease in the melt pressure. In order to get PS to run at 340 psi, the extruder motor would have to be set at about 26 RPMs. In addition, adding H50 to PS yielded a substantial decrease in the apparent viscosity for higher apparent shear rates. The reason for this decrease is due to the reduction in melt pressure.



◆ PS Visc. ■ PSH50 Visc. ▲ PS Shear × PSH50 Shear

Figure 2.5.1: PS and PS/H50 Master Curves, Normalized to 227 °C

Figure 2.5.2 depicts the LLDPE/H3200 master curves in comparison to the LLDPE master curves, over a temperature range of 174 °C to 225 °C. In the higher apparent shear rate regimes, adding H3200 resulted in a melt pressure drop of about 19%. For example, at an operating temperature of 193 °C and about 44 RPMs, the melt pressure for LLDPE/H3200 is approximately 1640 psi, whereas at similar conditions, the melt pressure for plain LLDPE is approximately 2030 psi. In order to achieve a melt pressure of 1640 psi for the LLDPE system, the extruder motor would have to be slowed to 25 RPMs. Once again, adding H3200 resulted in a decrease in the apparent viscosity; this decrease also corresponds to a decrease in the melt pressure.



Figure 2.5.2: LLDPE and LLDPE/H3200 Master Curves, Normalized to 193 °C

Figure 2.5.3 illustrates the LLDPE and LLDPE/H40 master curves over a range of 171 °C to 227 °C. At higher apparent shear rates, adding H40 to LLDPE also resulted in a reduction in the melt pressure of about 44%. This value comes from comparing LLDPE/H40 operating at 193 °C and 44 RPMs, with a melt pressure of 1410 psi to LLDPE operating at similar conditions, with a melt pressure of 2030 psi. In order to extrude LLDPE at 1410 psi, the motor would need to run at about 20 RPMs. Here, again, the apparent viscosity is greatly reduced. Once again, this effect is due to the drop in the melt pressure.



◆ LLDPE Visc. ■ LLDPEH40 Visc. ▲ LLDPE Shear ● LLDPEH40 Shear

Figure 2.5.3: LLDPE and LLDPE/H40 Master Curves, Normalized to 193 °C

From the specific cases cited earlier, it is readily apparent that H50 and H40 increased the apparent shear rate for a given shear stress to a greater degree than H3200. The individual effects of H40 and H50 on the apparent shear rate are incomparable due the innate differences in the base polymers for these systems. However, H40 does affect a LLDPE blend master curve to a greater degree than does H3200 (44% vs. 19%). H50 also substantially affects the PS master curve (33%) quite a bit. These two large values (44% and 33%) suggest that the hydroxyl end groups are largely responsible for the shifts in the master curves. In support of this statement, all three HBPs studied have hydroxyl end groups, albeit varying amounts. H3200 has the least; it is a H30 HBP that has been altered such that 90% of its end groups are $-C_{20}$ groups,

instead of the usual –OH groups. H40 and H50 have 100% hydroxyl end groups, and they caused greater shifts in the master curves than did H3200.

Another obvious observation is that the increase in the apparent shear rate for both PS and LLDPE blends was greatest in the higher shear regions. Previous work by Hong^{11, 12} has shown that a HBP may be used as a processing aid.

This idea has recently been corroborated by Kil, et al.¹³ who extruded a reactive blend with a co-rotating twin-screw extruder. Their sample preparation differs from that stated in this work, but they observed the same decrease in viscosity as reported in this work.

Sendijarevic, et al.¹⁴ showed similar behavior for LLDPE/Alkyl terminated HBP systems. They showed, as was found here, that at higher operating temperatures that the benefit of the HBP is lost. One major difference between their work and this work is that they used a slit die for their extrusions, while a capillary die was used here.

Mulkern and Tan¹⁵ reported a decrease in the viscosity/shear rate curve for a PS/H40 system and also a PS/SMA copolymer blended with H40 (SMA stands for styrene maleic anhydride). This result concurs with these observations on a PS/H50 system, as well as Carmezini's results.¹⁰

All of this work was done with thermoplastics, i.e. LLDPE, PS, etc. Mezzenga, et al.¹⁶ showed that the phase separation and modified rheology was present in thermosets as well. In this work, they examined the effect of four

different HBPs, similar to those used in the present work, on DGEBA (Diglycidyl Ether Bisphenol A).

Thus, adding a HBP will affect the rheology of a wide range of base polymers, and it may be said that these HBPs are acting as processing aids. A processing aid is a component added to a polymer flow system to enhance system performance while reducing wear on a processing machine, such as an extruder, mixer, etc. Some examples of processing aids are fluoroelastomers, a second polymer, or some other compound.

One of the first recorded instances of "processing aid" being used was by Zelinger, et al. in 1976.¹⁷ In this work, they added methylmethacrylate, polystyrene, and polyvinylacetate to polyvinylchloride (PVC) in varying concentrations up to 5 wt%. They found that the addition of these compounds increased the polymer output without significantly affecting the overall physical properties of the bulk polymer.

Continuing with this work, Kanu and Shaw¹⁸ examined the effects of different capillary entrance geometries in an Ethylene-Propylene-Diene (EPDM)/Viton system. EPDM is a common copolymer; Viton is the trade name for a fluoroelastomer. They found that the Viton caused slip, but it did not form a true layer. Instead, they proposed that the Viton acted more like ball bearings, in which the bearings assisted the polymer melt flow through the capillary.

Building on this work, Akay¹⁹ investigated the rheology of a glass or calcium carbonate filled polypropylene and a glass or calcium carbonate filled Nylon 6,6 polymer system. In this work, Akay discovered that the glass and

calcium carbonate aligned in the polymer melt as it entered and passed through a capillary. In addition, he found that as the polymer melt exited the capillary that an aid-free region formed in the center of the polymer melt. He hypothesized that the reason for this separation was particle exclusion through vortex flow. He suggested that the aligned region is continuous throughout the entire length of the capillary.

In all of these cases, the processing aid phase separated from the bulk polymer to some extent.

3. Phase Separation

3.1. Introduction

In her thesis, Carmezini¹⁰ hypothesized that the decrease in the master curve was due to phase separation in the barrel, thus causing slippage on the screw. In order to test Carmezini's assertion of phase separation, two tests were performed on the extrudates. The first test was to create a phase diagram for the PS/H50 system in order to see if temperature or concentration played any role in the hypothesized phase separation. The second test involved using Transmission Electron Microscopy (TEM) to see the different phases. Thus, if Caremezini's assertion is correct, then there should be a larger fraction of HBP in the Wall Layer than the Bulk, as shown in Figure 2.1.

3.2. DSC Experimental Procedure

A Differential Scanning Calorimeter (DSC) is an instrument that is designed to measure the heat flow required to increase the temperature at a constant rate. At some point a phase transition will occur and the heat flow will change to maintain the constant rate. The heat flow versus temperature graph can be used to observe the phase transition.

The DSC experimental procedure was fairly straight forward. The DSC used in this study was a TA Instruments Q-1000. Part one entailed obtaining the glass transition temperature (T_g) for the HBPs. The sample preparation procedure followed was specified by the DSC documentation. Essentially, this involved weighing out 3-5 mg of sample into a special pan and placing the pan into the instrument. The first run was set up to heat the sample up to 100 °C and

keep it there for 10 minutes in order to drive off any bound water. Then, two isothermal modulated runs were performed on the sample, in 10 $^{\circ}$ C increments.²⁰ From the second run, the reversible heat flow curve was plotted and this plot was used to obtain the T_g for all of the HBPs tested.

Part two of this experiment was to create a phase diagram for the PS/H50 system. Because LLDPE is highly insoluble in any solvent, an attempt at such a phase diagram would be very difficult. PS, on the other hand, will easily dissolve in many solvents. Ideally, then, this phase diagram would demonstrate the concentration and temperature effects on the HBP phase separation.

The set-up was fairly simple. First, the HBP was dissolved in glass vials with THF as described in Section 2.2 in solutions of 5, 10, 15, 20, 30, and 50 weight percent. The vials were then sealed with polypropylene caps and allowed to mix overnight on a stir plate. The following day, the linear PS was measured into the vials in the appropriate concentrations and allowed to mix overnight. Finally, cyclohexane was used as a precipitating agent. This solution was allowed to sit in the hood for a week, after which it was placed into a vacuum oven for another week to remove any remaining solvent. The mixtures were then measured into the DSC pans as described above. Then, DSC runs were performed on the samples, starting at 100°C. The temperature was then increased by 10°C, and the test re-run. This process was repeated until phase separation was observed.

3.3. DSC Materials

Materials studied here include Boltorn H20, H30, H40, H50, as well as JE3 and JE4. All Boltorn HBPs have hydroxyl end groups; however, JE3 and JE4 are modified Boltorn H30 and H40.²¹ JE3 and JE4 differ from their base polymers in that per-fluorinated benzene groups have been substituted for the hydroxyl groups.²¹ PS and LLDPE are the same as that listed for the previous section. The solvents, THF and cyclohexane, were products of Fischer-Scientific.

3.4. DSC Results and Discussion

Table 3.4.1 shows the T_gs of all HBPs and linear polymers tested. H3200 is not listed because no T_g could be found; only a melt temperature transition was observed at 57 °C. The T_gs for H30 through H50 came from Malmström, et al.;²² these values were measured on a Perkin-Elmer DSC-7, also at 10 °C per minute. No value was reported in this paper for H20. Mulkern and Tan¹⁵ report a value of 32 °C for H40, which agrees very well with the value measured here. The T_gs for JE3 and JE4 come from Englund's thesis.²¹ In his work, he used both a Perkin-Elmer DSC as well as a Mettler DSC; the data reported here are for the Perkin-Elmer.

Generally, the rate of temperature increase for a DSC run is about 5 °C per minute. Runs were originally done at 5 °C per minute, but the results were inconclusive. Therefore, the heating rate was increased to 10 °C per minute since Kim and Beckerbauer²⁰ found that this higher rate gave better results for their substituted hyperbranched polyphenylenes by avoiding the crystallization

present at lower heating rates. This higher heating rate provided more accurate results for the HBPs studied.

	T _g (DSC)	T _g (Literature)	
Polymer	[°C]	[[•] C] ^{21, 22}	% Error
JE3	23.8	27.7	14.1
JE4	31.0	32.7	5.2
H20	2.9	N/A	N/A
H30	18.0	34.0	47.1
H40	· 30.7	37.0	17.0
H50	34.9	41.5	15.9
PS	99	~100	~1
LLDPE	N/A	~-20	N/A

Table 3.4.1: Polymer T_gs

The Q-1000 DSC data, on the whole, corresponded within reason for all but H30. Some possible reasons for these discrepancies in the data might be a difference in the instruments, sample size, difference in calibrations, or the type of sample pan used.

As was mentioned above, these T₉s would have been used to obtain the phase diagram for PS/H50. However, the precipitation step provided an unexpected result. Instead of forming a nice, even mixture, the HBP precipitated onto the sides of the vial as the cyclohexane/THF solution evaporated. This precipitation demonstrates that these linear and hyperbranched polymers are immiscible. This result agrees with the results that Massa, et al.²³ found for their linear polymer/HBP blends. Therefore, one of the driving forces in this system must be inherent immiscibility.

3.5. TEM Experimental Procedure

In performing these tests, it was desirable to determine whether the phase separation was a result of flow in the capillary. Therefore, two conditions were

set for each system. Condition one involved extrusion through the 30 mm capillary discussed earlier, while condition two involved extrusion through a zero length capillary, which is referred to as an orifice plate (OP).

Previous work¹¹ has shown that adding a HBP to a linear polymer will affect the surface appearance. As such, it was important to take optical micrographs of the surface in order to see how the surface was altered. In taking these pictures, a JAI, Inc. CV-S3200 digital camera was used with Visilog software. Because the fibers studied were cylindrical, it was impossible to get an image of the full surface. Therefore, only the highest point was focused on, as shown in Figure 3.5.1. The extrusion conditions for all optical micrographs are analogous to those shown in Tables 3.5.1 and 3.5.2.



Figure 3.5.1: 3D image showing area focused on

Figure 3.5.2 shows the virgin PS, while Figure 3.5.3 shows the effects of 0.5 and 5.0 wt% H50 on PS through the OP. Figures 3.5.4 and 3.5.5 show the same systems, except extruded through the 30 mm capillary. All images are at a lens magnification of 10X and a camera magnification of 26X. The addition of H50 to PS results in a smoother surface for both the OP and capillary.



Figure 3.5.2: PS extruded through the OP



Figure 3.5.3: PS/H50 extruded through the OP; (L) 0.5 wt%; (R) 5.0 wt%


Figure 3.5.4: PS extruded through the 30 mm Capillary



Figure 3.5.5: PS/H50 extruded through the 30 mm Capillary; (L) 0.5 wt%; (R) 5.0 wt%

Figure 3.5.6 shows a sample LLDPE extrudate through the OP. Figure 3.5.7 shows a sample LLDPE/H3200 extrudate of both 0.5 wt% and 5.0 wt%, also through the OP. Figure 3.5.8 shows the difference between 0.5 wt% and 5.0 wt% for the LLDPE/H40 system. Figures 3.5.8 through 3.5.11 show these same systems, except that they have been extruded through the 30 mm capillary, instead of the OP. These images differ from those shown for PS in that the surface now appears smoother for both the OP and the Capillary. This increased smoothness has been shown in previous work for a LLDPE/H3200 system.¹¹



Figure 3.5.6: LLDPE extruded through the OP



Figure 3.5.7: LLDPE/H3200 extruded through the OP; (L) 0.5 wt%; (R) 5.0 wt%



Figure 3.5.8: LLDPE/H40 extruded through the OP; (L) 0.5 wt%; (R) 5.0 wt%



Figure 3.5.9: LLDPE extruded through the 30 mm Capillary



Figure 3.5.10: LLDPE/H3200 extruded through the 30 mm Capillary; (L) 0.5 wt%; (R) 5.0 wt%



Figure 3.5.11: LLDPE/H40 extruded through the 30 mm Capillary; (L) 0.5 wt%; (R) 5.0 wt% Originally, it was intended to obtain TEM images of the 0.5 wt% blends extruded in the process of constructing the master flow curve, but this proved impractical due to the low HBP concentration. That is, even at high magnification, it was impossible to see the HBP. Thus, the HBP concentration was increased to a 5 wt% solution. According to previous work,¹⁰ a 5 wt% blend will also result in a master curve shift.

The pellets for the 5 wt% blends were created following the same procedure outlined in Section 2.2, with the obvious exception that more was HBP dissolved into solution.

After the pellets were created, they were extruded at operating temperatures of approximately 200 °C for PS/H50 and 190 °C for LLDPE/H3200 and LLDPE/H40. Additionally, all samples were extruded at a motor setting of 55, which equates approximately to 43 RPMs. These extrusion settings were selected on the basis of the master curves presented earlier (Figures 2.5.1 and 2.5.2); on these curves, the chosen temperatures and motor speed correspond to the reduced master curve regime. Thus, these two temperatures should yield TEM images analogous to ones expected for a lower weight percent. Tables 3.5.1 and 3.5.2 show the comparison of the flow rates at the selected motor settings and temperatures for both the OP and 30 mm capillary.

OP, 43	For LL	For LLDPE, T _{melt} =190 C; For PS, T _{melt} =200 C						
Material	mass (g)	time (s)	Mass Rate (g/s)	Amps (mA)	P _{melt} (psi)	Apparent Shear Rate (s ⁻¹)	Shear Stress (Pa)	Apparent Viscosity (Pa*s)
PS	1.2	35.53	0.0328	350	30	101	N/R	N/R
PS/H50 5.0 wt%	0.9	46.5	0.0086	240	40	60	N/R	N/R
LLDPE/ H3200 5.0 wt%	0.9	27.47	0.0335	270	130	104	N/R	N/R
LLDPE/ H40 5.0 wt%	0.9	37.43	0.0230	370	90	71	N/R	N/R

 Table 3.5.1: OP Flow Comparison

30 mm For LLDPE, T _{melt} =190 C; RPMs For PS, T _{melt} =200 C								
Material	mass (g)	time (s)	Mass Rate (g/s)	Amps (mA)	P _{melt} (psi)	Apparent Shear Rate (s ⁻¹)	Shear Stress (Pa)	Apparent Viscosity (Pa*s)
PS	1.1	31.69	0.0344	370	450	106	38000	360
PS/H50								
5.0 wt%	1.2	45	0.0267	360	260	82	22000	270
LLDPE	0.9	30.85	0.0299	650	2030	120	173000	1440
LLDPE/ H3200								
5.0 wt%	0.5	20.87	0.0255	320	620	102	53000	520
LLDPE/ H40								
5.0 wt%	0.7	37.06	0.0200	380	520	80	44000	550

 Table 3.5.2: 30 mm Capillary flow comparison

These tables show that the extrudates studied will fall within the desired apparent shear rate range, due to the increased mass flow rate and the decreased pressure.

It is very interesting to note the similarity in the values of the apparent shear rate for both the capillary and orifice plate. There are no reported values for the Shear Stress and Apparent Viscosity for the OP because the shear stress calculation requires dividing by finite length, and an OP has zero length (see Equation 2.2), and the apparent viscosity is dependent on the shear stress.

To facilitate TEM sample preparation, the fibers were pulled slightly as the polymer exited the extruder. These fibers were also handled with gloves in order to preserve the surface.

The extruded fibers were next carved into blocks, prior to sectioning. Figure 3.5.1 shows how the blocks were prepared from a cross-sectional perspective. It is important to note that the "Edge" region may also include a small section of "Bulk", but the goal was to get a section within the first few hundred nanometers from the edge. In this diagram, straight lines represent cutting lines and the grayed out areas are the places on the blocks that were sectioned. Sizes are exaggerated for illustration purposes.



Figure 3.5.12: Fiber sectioning diagram; from left to right: beginning cross-section, "Bulk" Section, and "Edge" Section. Grayed out areas are the areas that were sectioned.

After making the blocks, an Edgemaster II diamond knife in a RMC MT-7 ultramicrotome, with a cryo unit attachment, was used to section the 5 wt% extruded fibers into 80 nm sections. The cutting temperature used for all blends was -60 °C. This temperature was selected in order to ensure that the samples were below the T_g for both polymers in the system. The thin polymer sections were then placed onto 300 nm copper grids and vapor stained with OsO₄. In both previous works,^{11, 24} RuO₄ was used as the staining agent, but OsO₄ is very similar in most respects to RuO₄. From page 106 of Flegler, et al.,²⁵ "Its [RuO₄'s] fixative properties are closely related to those of OsO₄...but is a stronger oxidizing agent" (brackets and ellipses added).

These samples were then examined with a JEOL JEM-100CX II TEM using the 100 kV setting.

3.6. TEM Materials

The HBPs used were Boltorn H3200, H40, and H50 from Perstorp, Inc. The linear polymers were the same PS and LLDPE used in Section 2. OsO₄ was the staining agent and was obtained as a powder from Electron Microscopy Sciences and prepared by Dr. Alicia Pastor-Lecha in the Center for Advanced Microscopy at Michigan State University. The copper grids were from Ted Pella, Inc.

3.7. TEM Results and Discussion

The following pages show the TEM images recorded for the different systems. The systems will be presented in the following order: PS/H50,

LLDPE/H3200, and LLDPE/H40, with the 30 mm capillary images first, followed by the orifice plate images.

In Figures 3.7.1 through 3.7.4 the results of the PS/H50 system are compared. All images have a gray area, as well as darker spots. These darker spots represent the HBP, while the surrounding gray area represents the bulk polymer. These images correspond very well with the results observed by Kim and Webster.²⁴ Kim and Webster examined a 5 wt% PS/Hyperbranched Polyphenylene system.

It is interesting to note that in both the OP and capillary cases that there are more spots in the edge region than in the bulk region. The spots have been circled for easier identification.



Figure 3.7.1: PS/H50 30 mm Capillary, Bulk Region, at 27 kX



Figure 3.7.2: PS/H50 30 mm Capillary, Edge Region, at 14 kX



Figure 3.7.3: PS/H50 OP, Bulk Region, at 2.7 kX



Figure 3.7.4: PS/H50 OP, Edge Region, at 10 kX

In Figures 3.7.5 through 3.7.8 the results of the LLDPE/H3200 system are compared. Once again, it is obvious that there are some dark areas and some lighter areas. The darker areas again represent the HBP, while the lighter areas represent the bulk polymer. This interpretation is in disagreement with Hong et al.,¹¹ but the final results are the same in that they show a large amount of HBP in the edge region.

In the case of LLDPE/H3200, there is a higher concentration of the HBP in the edge region of the 30 mm capillary fibers than in the bulk region. In addition, the OP results also show a larger amount of HBP in the edge region than in the bulk region. The HBP has once again been circled for easier identification.



Figure 3.7.5: LLDPE/H3200 30 mm Capillary, Bulk Region, at 27 kX



Figure 3.7.6: LLDPE/H3200 30 mm Capillary, Edge Region, at 27 kX



Figure 3.7.7: LLDPE/H3200 OP, Bulk Region, at 14 kX



Figure 3.7.8: LLDPE/H3200 OP, Edge Region, at 10 kX

Figures 3.7.9 through 3.7.12 illustrate the LLDPE/H40 system. It is interesting to note the similarities between Figure 3.7.8 and Figure 3.7.12. This system shows the same phase separation as the other two. The large, white circles in Figure 3.7.12 are holes in the sample. These holes are probably the results of water vapor interacting with the H40 during the staining process. A similar phenomenon was observed in the PS/H50 system. As before, the darker areas generally represent the stained HBP. Some exceptions are grid bars, curled polymer parts, and shadowing.



Figure 3.7.9: LLDPE/H40 30 mm Capillary, Bulk region, at 14 kX



Figure 3.7.10: LLDPE/H40, 30 mm Capillary, Edge region, at 14 kX



Figure 3.7.11: LLDPE/H40 OP, Bulk Region, at 14 kX



Figure 3.7.12: LLDPE/H40 OP, Edge region, at 5 kX

The most important conclusion that may be drawn from these images is that the two polymers form two separate phases, even in the presence of mechanical mixing. In addition, the HBP migrates to the surface of the polymer melt regardless of whether or not the capillary die is present.

Other work^{26, 27} has shown strong microphase separation in HBP/linear polymer diblock copolymer systems. Mackay, et al.²⁶ attached a G6 polybenzyl ether to a linear polystyrene chain. They observed that dendron/linear copolymer system would phase separate. This separation moves from an ordered cylinder to an ordered lameller to a disordered lamellar as the linear mass fraction decreases. Roman, et al.²⁷ observed a similar phenomenon for chemically dissimilar hybrid block copolymer system. These phase separations were visualised by TEM and SAXS. Therefore, phase separation is a common occurrence between linear and hyperbranched polymers, even when they are physically attached to each other.

Lee and Archer²⁸ showed through Dynamic Contact Angle Analysis (DCA) and Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR) that for a PS/PDMS copolymer that the PDMS would concentrate at the surface of the blend, even when mixed in at a 2 wt% concentration. Despite the fact that the PDMS is linear, as was the PS, this work is valuable in that it shows that copolymer phase separation also exists for linear/linear systems as well as linear/branched systems.

Sendijarevic, et al.¹⁴ claimed that HBPs with C_{18} end groups are miscible, and that HBPs with smaller size end groups are immiscible. The TEM images presented here of the LLDPE/H3200 system, along with Hong's image of the same system,¹¹ show that this is not the case, and that a C_{20} terminated HBP phase separates. It is possible that the 10% -OH end groups are sufficient to cause the observed phase separation, but is unlikely due to steric hindrance.

Mulkern and Tan¹⁵ observed phase separation through Scanning Electron Microscopy (SEM) for a PS/H40 system. Ideally, they also would have used TEM, but it is important to note the complimentary result.

Bauer, et al.²⁹ showed that mechanical mixing of a fatty acid dendrimer and a polyolefin will result in an immiscible mixture through Small Angle Neutron Scattering (SANS). Their materials were analogous to the ones used here.

Therefore, a highly branched polymer and a linear polymer will refuse to blend together either when mixed in solution or mechanically dispersed in the extruder at any concentration, and that the HBP will migrate to the surface layers in both the capillary and the OP systems.

If this phase separation is independent of temperature, concentration, and capillary presence, why is the HBP to rapidly diffusing to the surface?

One possibility is Brownian diffusion. Brownian diffusion may be defined as the continuous fluctuation of a particle on a molecular scale. Equation [3.1] is the equation for the approximate diffusivity for Brownian motion.

$$D \approx \frac{k_B T}{6\pi r \eta_0}$$
[3.1]

Using the temperatures and the apparent shear rates from Table 3.5.2 for the capillary, along with the approximate diameters measured for HBP spots in Figures 3.7.2, 3.7.5, and 3.7.10, the approximate Brownian diffusivities may be obtained. In comparison, a molecule is generally on the order of 1 nm in diameter. Table 3.7.1 compares the Brownian diffusivities for both the 1 nm particle, as well as the HBP particles.

30 mm Cap., 43 RPMs	For LLDPE, T _{melt} =190 C; For PS, T _{melt} =200 C						
Material	Apparent Viscosity (Pa*s)	d (nm)	<i>D</i> (cm²/s) [d=previous column]	<i>D</i> (cm²/s) [<i>d</i> =1 nm]			
PS/H50 5.0 wt%	268	400	6.46E-14	2.58E-11			
LLDPE/H3200 5.0 wt%	516	170	7.91E-14	1.32E-11			
LLDPE/H40 5.0 wt%	550	200	6.30E-14	1.23E-11			

 Table 3.7.1: Comparison of Brownian Diffusivities for the Capillary

A quick examination of Table 3.7.1 shows the obvious fact that the diffusivity for a 1 nm particle is greater than the diffusivity for a particle greater than 100 nm. The self-diffusivity of PS is approximately between 10^{-8} and 10^{-12} cm²/s. Assuming that the self-diffusivity of LLDPE is of the same magnitude as the self-diffusivity of PS, it is obvious that the HBP diffusivity in the base polymer is at least two orders of magnitude smaller than this self-diffusivity. Thus, Brownian diffusion cannot explain the observed rapid diffusion, and the observed rapid diffusion must be flow induced.

4. Surface Analysis

4.1. Introduction

What effect, then, might a HBP have on a polymer surface?

One important way of determining the effects on surfaces is through advancing and receding contact angles. The advancing contact angle represents the dynamic change of a drop of liquid on a surface^{30, 31, 32} as the drop "advances" on the surface. In other words, it is a measure of a surface's amphophobicity. The receding contact angle represents the dynamic change as a droplet "recedes" on the surface. That is, the receding contact angle is a measure of a surface's amphophilicity.

Many different methods exist for finding these contact angles. Some of the most common methods are the Wilhelmy Plate, Capillary Rise, and the Sessile Drop.^{30, 31, 32} The Wilhelmy method consists of inserting a fiber into a liquid and measuring the angle that the liquid forms with the surface. The Capillary Rise method involves inserting a thin tube into a liquid and measuring the angle the meniscus form with the inside of the tube. The Sessile Drop method is simply the placement of a drop on a flat surface and measuring the angle that the edge of the drop makes with the surface. Figure 4.1.1 and Figure 4.1.2, from page 253 of Hiemenz and Rajagopalan,³⁰ show the Capillary Rise and the Wilhelmy Plate methods.



Figure 4.1.1: Diagram of the Wilhelmy Plate Technique³⁰



Figure 4.1.2: Diagram of the Capillary Rise Technique³⁰

In this study, the Wilhelmy Plate method will be used. Equation [4.1] shows the relationship between the surface tension of a liquid (γ), the fiber diameter (d), the contact angle (θ), and the wetting force for a Wilhelmy probe ($g\Delta m$).

$$g\Delta m = \pi d\gamma \cos\theta - \frac{\rho g d^2 z}{4}$$
^[4.1]

However, for a very thin fiber, the second term is approximately zero, since *d* is very small, and therefore the term is negligible. Thus, Equation [4.2] reduces to the simplified form of the Wilhelmy probe equation. Using a liquid with known properties, this equation may be used to compute the contact angle.

$$g\Delta m = \pi d \,\gamma \cos \,\theta \tag{4.2}$$

The advancing contact angle is further useful in that it provides a measure of the polymer surface properties. Over the last fifty years, Good³³ and Zisman³⁴ have both published excellent reviews tracing the history of contact angle usage from Aristotle and Archimedes to Young and Dupré to their respective present times (1992 and 1964). In addition, several good texts may be referenced on this subject, including Wu,³¹ Heimenz and Rajagopalan,³⁰ and Adamson and Gast.³² It is not the purpose of the present work to recount in detail the history or derivation before Young's Equation, shown as Equation [4.3], which relates the energy of the liquid, vapor, and solid interfaces.

$$\gamma_{LV} \cos \theta = \gamma_{SV} + \gamma_{SL}$$
 [4.3]

Here, L, S, and V represent the Liquid, Solid, and Vapor portions. Generally speaking, though, one may use L, S, and V to mean phases 1, 2, and 3.

The next step, proposed by Girifalco and Good, applied the Geometric Mean Equation to Young's Equation and yields the Girifalco-Good Equation, shown as Equation [4.4]. Alternatively, the Harmonic Mean Equation is sometimes applied to Young's Equation; the result is shown as Equation [4.5].

$$(1 + \cos\theta_{adv})\gamma_{liq} = 2\left[\left(\sqrt{\gamma_{liq}^d \gamma_{sol}^d}\right) + \left(\sqrt{\gamma_{liq}^p \gamma_{sol}^p}\right)\right]$$
^[4.4]

$$(1 + \cos\theta_{adv})\gamma_{liq} = 4\left[\left(\frac{\gamma_{liq}^{d}\gamma_{sol}^{d}}{\gamma_{liq}^{d} + \gamma_{sol}^{d}}\right) + \left(\frac{\gamma_{liq}^{p}\gamma_{sol}^{p}}{\gamma_{liq}^{p} + \gamma_{sol}^{p}}\right)\right]$$

$$(4.5)$$

Equation [4.4] will be used here as most of the advancing contact angles will be greater than 90° and the Harmonic Mean Equation fails in those cases.

The main discrepancy is in how to apply this equation. Van Oss, et al., cited in Adamson and Gast,³² page 376, suggested using a term that the overall surface tension was composed of three parts: the Liftshitz-Van der Waals (dispersion) forces, and the electron donor/electron acceptor interactions for the solid and liquid as well as the liquid and the solid. Equation [4.6] shows the commonly accepted form, from Van Oss, et al.³⁵

$$\gamma_L(1+\cos\theta) = 2\left(\sqrt{\gamma_s^{LW}\gamma_L^{LW}} + \sqrt{\gamma_s^+\gamma_L^-} + \sqrt{\gamma_s^-\gamma_L^+}\right)$$
 [4.6]

Another method was proposed by Fowkes.^{36, 37} Fowkes separated the overall surface tension into dispersive and polar parts, as shown in Equation [4.4]. Further, he proposed that for hydrocarbons only the dispersive form was crucial, thus leading to the following form, labeled Equation [4.7].

$$(1 + \cos\theta)\gamma_{liq} = 2\left[\sqrt{\gamma_{liq}^d \gamma_{sol}^d}\right]$$
^[4.7]

Both of these methods assume that the equilibrium spreading pressure is approximately zero for a hydrocarbon. Note, too, that Equation [4.7] and Equation [4.4] are identical if the solid acts as only a proton donor, and the liquid acts only as a proton acceptor, or vice versa. Good³⁸ stated that for most hydrocarbons that the overall equation (Equation [4.4]) would hold, except for a fluorinated hydrocarbon. As no fluorinated hydrocarbons were used in this study, Equation [4.4] will be sufficient to compute the values of the surface energy.

4.2. Materials

Polymer materials used are the same as those listed in previous sections. The methylene iodide was a product of Spectrum, Inc. The deionized (DI) water was purchased from Culligan by the Composite and Materials Center at Michigan State University. Table 4.2.1 shows the surface tension data for methylene iodide and DI water at 20 °C from page 179 of Wu³¹ for both the Geometric Mean and the Harmonic Mean Equations (Equations [4.4] and [4.5]).

Harmonic Equation Data						
Liquid	γi ^d (mN/m)	γi ^ρ (mN/m)	γi (mN/m)			
Methylene lodide DI Water	43.5	6.6 50.1	50.1 72.0			
Geon	Geometric Equation Data					
Liquid	γi ^d (mN/m)	າ) ^p (mN/m)	γi (mN/m)			
Methylene Iodide	47.7	2.3	50.0			
DI Water	21.6	50.4	72.0			

Hamman I. Paulatian Data

Figure 4.2.1: Liquid Properties for the Geometric and Harmonic Mean Equations³¹

There is a fair amount of discussion as to what the actual values are for methylene iodide;³¹ the ones used in these computations were measured using the interfacial tension between water and methylene iodide. These values were chosen in order to give allowance for any polarity in the systems studied.

4.3. Experimental Procedure

In their work, Sauer and DiPaolo³⁹ give a more extensive explanation of the experimental method followed here. However, the steps will be outlined here briefly. It is imperative to remember that this method is intended to obtain the parameters needed to solve either Equation [4.1] or Equation [4.2]. This same procedure was performed on both the virgin polymers as well as the polymer blends.

The first step, naturally, is to create the probe by stretching the polymer fiber as it is extruded. The fibers were extruded at the same conditions as the fibers created for the TEM analysis (see Tables 3.5.1 and 3.5.2). Fibers were extruded from the OP as well as the 30 mm capillary in order to be able to compare and contrast the surface energy of the melt inside the barrel with the melt exiting the capillary. The fibers were handled with gloves to prevent contaminants from adhering to the surface.

In order to attach this fiber to the Cahn 322 Microbalance at the High Sensitivity location, one end of the polymer fiber was bent into a "U" shape and held briefly against the extruder barrel in order to melt the fiber into a hook. The fiber was then trimmed with ceramic scissors as needed. All fibers were used within a day of extrusion.

The second step was to obtain the probe diameter. According to Sauer and DiPaolo,³⁹ the fiber should be 200-500 μ m. For large diameter fibers, a set

of microcalipers may be used to measure the diameter. Because these fibers were relatively large, the calipers were used to measure the diameter.

Sauer and DiPaolo³⁹ further state that even for fibers of 200-500 μ m that the buoyancy correction should be negligible and that Equation [4.2] may be used. However, as these fiber diameters seem rather large, the buoyancy will not be neglected, and Equation [4.1] will be used. Normally, measuring the buoyancy force is difficult due to the uncertainty of the parameters involved, primarily the depth of immersion. The microbalance used, though, allowed the operator to fix the approximate depth of immersion, and thus, this value may be reasonably evaluated.

Equation [4.1] was used, and through the computer's autoanalyze function together with the buoyancy correction option, the advancing and receding contact angles were determined. The Cahn 322 microbalance was programmed to lower the fiber into the liquid at a speed of 80 μ m/s. The fiber was inserted into the liquid to a maximum depth of 1 mm, and then permitted to equilibrate there for about 15 seconds. This maximum depth corresponds to *z*, the depth of immersion. The fiber was then pulled out of the liquid at a speed of 80 μ m/s. This same procedure was used throughout the experiment. Figure 4.3.1 shows a cartoon of the experimental set-up.



Figure 4.3.1: Microbalance Set-up

The computer was used to record and save the results. The fiber insertion yielded the advancing contact angle, while the fiber retraction yielded the receding contact angle. This experiment was repeated at least three times with both methylene iodide and DI water for all polymer systems. The resulting angles were then averaged. Figure 4.3.2 shows a sample plot generated from the data for PS/H50 and water.



Figure 4.3.2: Sample microbalance plot for PS/H50 and water

The advancing contact angle as well as the known surface tension data, found in Table 4.2.1, was inserted into Equation [4.4]. This yielded two equations with two unknowns, one equation for each liquid. These two equations were then solved simultaneously to get the two parts of the surface energy. The total surface energy was then simply the sum of these two parts.

4.4. Results

In addition to Sauer and DiPaolo,³⁹ several other studies^{31, 40, 41} have been devoted to using the polar-dispersive equation (Equation [4.4]) to compute the surface tension. Table 4.4.1 and Table 4.4.2 show the contact angles measured by the microbalance for the OP extrudates. The standard deviation was also computed.

OP	H₂O			
Material	θ _{adv} (deg)	θ _{rec} (deg)	Hysteresis (deg)	
PS	99 ± 3	85	14 ± 3	
PS/H50 5.0 wt%	95 ± 9	88	7 ± 9	
LLDPE	97 ± 5	83	14 ± 5	
LLDPE/H3200 5.0 wt%	91 ± 1	74	18 ± 1	
LLDPE/H40 5.0 wt%	95 ± 2	54	41 ± 2	

Table 4.4.1: H₂O Contact Angles for the OP

OP	CH ₂ I ₂			
Material	θ _{adv} (deg)	θ _{rec} (deg)	Hysteresis (deg)	
PS	50 ± 11	N/R	N/R	
PS/H50 5.0 wt%	47 ± 4	N/R	N/R	
LLDPE	61 ± 7	36	25 ± 7	
LLDPE/H3200 5.0 wt%	75 ± 3	48	27 ± 3	
LLDPE/H40 5.0 wt%	52 ± 8	28	24 ± 8	

Table 4.4.2: CH₂I₂ Contact Angles for the OP

The receding angles for PS and PS/H50 were not able to be measured.

The advancing angles were then inserted into Equation [4.4] and solved to

generate Table 4.4.3.

OP	Polymer					
Material	γ₅ ^d (mN/m)	γ _s ^ρ (mN/m)	γ₅ ^t (mN/m)			
PS	35.0 ± 5.3	3.9 ± 3.2	38.9 ± 3.8			
PS/H50						
5.0 wt%	36.5 ± 2.0	6.5 ± 6.4	42.9 ± 6.3			
LLDPE	28.6 ± 3.5	8.0 ± 3.8	36.6 ± 3.9			
LLDPE/H3200 5.0 wt%	20.5 ± 1.4	16.1 ± 1.1	36.6 ± 1.2			
LLDPE/H40 5.0 wt%	33.6 ± 4.1	7.1 ± 2.3	40.7 ± 2.8			

Table 4.4.3: Surface Energy Results for OP

Table 4.4.4 and Table 4.4.5 show the contact angles measured for the 30

mm capillary.

Capillary		н	₂ O
Material	θ _{adv} (deg)	θ _{rec} (deg)	Hysteresis (deg)
PS	95 ± 8	76	20 ± 8
PS/H50 5.0 wt%	99 ± 4	83	17 ± 4
LLDPE	92 ± 4	86	6 ± 4
LLDPE/H3200 5.0 wt%	94 ± 1	91	4 ± 1
LLDPE/H40 5.0 wt%	90 ± 3	31	59 ± 3

Table 4.4.4: H₂O Contact Angles for the 30 mm Capillary

Capillary		Cł	H ₂ I ₂
Material	θ _{adv} (deg)	θ _{rec} (deg)	Hysteresis (deg)
PS	54 ± 5	N/R	N/R
PS/H50 5.0 wt%	53 ± 4	10	42 ± 4
LLDPE	56 ± 5	21	35 ± 5
LLDPE/H3200 5.0 wt%	73 ± 3	59	14 ± 3
LLDPE/H40 5.0 wt%	59 ± 3	20	38 ± 3

 Table 4.4.5: CH₂I₂ Contact Angles for the 30 mm Capillary

No receding contact angle was able to be measured for PS. Table 4.4.6

shows the results of the surface energy calculations for the 30 mm capillary.

Capillary	Polymer				
Material	γs ^d (mN/m)	γ₅ ^ρ (mN/m)	γ₅ ^t (mN/m)		
PS	32.6 ± 2.4	7.7 ± 5.5	40.3 ± 5.4		
PS/H50 5.0 wt%	33.6 ± 1.8	4.0 ± 2.9	37.6 ± 2.9		
LLDPE	31.7 ± 2.5	10.9 ± 3.3	42.6 ± 3.4		
LLDPE/H3200 5.0 wt%	21.4 ± 1.6	13.2 ± 0.8	34.6 ± 1.0		
LLDPE/H40 5.0 wt%	29.9 ± 1.4	13.1 ± 2.1	42.9 ± 2.1		

Table 4.4.6: Surface Energy Results for the 30 mm Capillary

4.5. Contact Angle Discussion

Wu,³¹ as well as others,^{40, 41, 42, 43} have reported empirical literature values for both the contact angles and the surface energy values. There are two slight problems with this empirical work. First, in order to accurately measure the surface properties, one needs the advancing contact angles, not the equilibrium contact angles. Second, the empirical values apparently were measured using the Sessile Drop Method, whereas the work done here was with the Wilhelmy Method. Nevertheless, it is useful as a guide.

A brief attempt⁴⁴ has been made to provide theoretical correlation to these empirical values. Unfortunately, this attempt is highly idealized.

Volpe,⁴³ tested the advancing contact angle as a function of the speed of immersion of the Wilhelmy Plate. He found that the importance of the probe's insertion velocity depended greatly on the particular material being tested.

Table 4.5.1 shows a comparison between the equilibrium values used by Dalal,⁴⁰ the advancing angles also reported in Wu,³¹ the advancing angles reported by Owens and Wendt,⁴¹ the advancing angles by Volpe,⁴³ and the

theoretical values by El Ghzaoui.⁴⁴ The numbers across the top represent these reference numbers. Contact angles, if reported, are in degrees.

Cont. Ang.:	H ₂ O				
		Source (By Referer	nce Numbe	r)
Material	31	40	42	43	

91

102

Cont Ang · CHala

PS

LDPE

		Source (F	v Referei	nce Numbe	r)
Material	31	40 42		43	44
PS	N/A	35	35	N/A	35.9
LDPE	N/A	53	53	N/A	52.8

91

96

N/A

91

104

96

44

N/A

N/A

Table 4.5.1: Compiled Reference Data for Adv. Contact Angles

Once again, note that the values reported here, except for Reference 43, are for LDPE, not LLDPE, and were measured with the Sessile Drop Method under controlled conditions. In addition, the actual value of water on LDPE is still somewhat debatable. Fowkes³⁷ cites several authors, including Tardros, Adamson, et al.,⁴⁵ who reported a value of 88° for the system in question. According to Fowkes.³⁷ the polymer studied by Tardros, et al.⁴⁵ were not purified of all impurities, as was the case in other studies. The values measured in this work fitted within the boundaries cited.

As the fibers in this work were extruded and are industrial quality, it is possible that a small amount of contaminant is present in the system. Nevertheless, the contact angle values measured here for the base polymers are still very close to these literature values, with the exception of PS/methylene iodide (35° versus 54°), but this discrepancy could be explained by the presence of contaminants.

According to Mackay and Carmezini,⁴⁶ the advancing contact angle for both water and methylene iodide on the HBPs studied (H30 and H3200), was less than the angle measured for the two bulk polymers listed above. Thus, one might expect that blending the HBP with a linear polymer would reduce the advancing contact angle. This, however, is not the case. The value obtained here for the water advancing contact angle on LLDPE/H3200 agrees very well with previously published results.⁴³ The value measured in this study was 94 \pm 1° for the capillary and 91 \pm 1° for the OP. These values agree with Mackay and Carmezini,⁴⁶ who measured a value of 96° for a LLDPE/H3200 0.5 wt% film. However, there is a difference in the measured advancing contact angles for methylene iodide (OP: $75 \pm 3^{\circ}$ and Capillary: $73 \pm 3^{\circ}$ versus 57°, from Mackay and Carmezini).⁴⁶ The reason for this discrepancy is twofold. First, there is a difference in method; i.e., a fiber versus a film. Second, the fibers measured here have a slightly higher HBP weight percent. Shafrin and Zisman⁴² reported a maximum contact angle of 77° for a methylene rich, single crystal hydrocarbon. In this light, the values measured here make sense since LLDPE has a large number of methyl groups and H3200 has almost pure carbon (90% C₂₀ end groups). Thus, the measured value is believable. It is interesting to note that within the margin of error that there is no difference between the base polymer and the other polymer blends.

Sendijarevic, et al.¹⁴ measured contact angles on their LLDPE films and found that altering the end group changed the advancing contact angle. There are two problems with their results. First, they used a manual goniometer on a

polymer film. These instruments are difficult to use because the change from advancing contact angle to equilibrium contact angle is very fast, and no margin of error is reported in their work. Second, extruding a polymer film is not easy. Great care must be taken to keep the film flat and straight. In addition, surface defects are much more common with polymer films than with polymer fibers. Attempts were made to measure contact angles using tapes as was done by Sendijarevic, et al.,¹⁴ but were abandoned in favor of Sauer's and DiPaolo's method³⁹ that utilizes fibers and the Wilhelmy method due to the above stated problems.

4.6. Surface Energy Discussion

Despite any differences in the contact angle measurements, the surface energy values for the base polymers agree with each other within the stated margin of error. Table 4.6.1 lists literature values for the components of the surface energy from Dalal⁴⁰ for methylene iodide and water. Remember, these values were computed using equilibrium contact angles.

Material	γs ^d (mN/m)	γs ^p (mN/m)	γs ^t (mN/m)
PS	42.0	0.5	42.5
LDPE	33.7	0.0	33.7

Table 4.6.1: Literature Surface Data⁴⁰

Now, comparing those results with these from page 184 of Wu³¹ for LDPE, $\gamma_s^t = 35.7 \text{ mN/m}$, and for PS, $\gamma_s^t = 40.7 \text{ mN/m}$, it is obvious that the difference in angle is important, but not critical. It is also obvious that the experimental results for the base polymers easily fall between the two boundaries within their respective margins of error. Thus, these results are acceptable.

The next obvious question is: how good are the values for the blends? Mackay and Carmezini⁴⁶ have published some results for a 0.5 wt% LLDPE/H3200 blend using Fowkes' approximation (Equation [4.7]). Despite the fact that they concentrated only on the dispersive part, their results agree reasonably well with those reported in this work. Thus, the results for the blends are also reasonable.

The next question is: what trends exist in the data? Previously in this work, it was hypothesized that the capillary would affect the phase separation, and it does. The question then asked pertained to how the capillary affected the surface properties. The answer, of course, is that these two questions are one and the same. Looking at the data, it is readily apparent that there is no significant overall effect of the HBP on the surface energy of the blend within the margins of error. In addition, within the margins of error, there is no difference between the OP and the capillary results for any of the systems studied.

However, it is interesting to note that there are some changes in the makeup of the overall tension. Mackay and Carmezini⁴⁶ reached the same conclusion in their brief study. The main conclusion to be drawn from these results is that adding a HBP does not significantly alter the surface energy for either the OP or the capillary. This fits since similar results were observed in the TEM images.

5. Overall Conclusions

What, then, has been learned from this work? First, adding a HBP to a linear polymer does cause a reduction in the shear stress for a given shear rate. This reduction indicates that the HBP does act as a processing aid, provided it phase separates at the surface.

Second, TEM and DSC tests show that the polymers do phase separate. While the TEM images do not show any HBP directly on the surface of the OP or capillary fibers, they do show a higher concentration of the HBP in the edge layers than in the bulk region. Some possible reasons for the absence of the HBP directly at the interface are: 1. they were lost during the microtoming process, 2. the concentration in the edge region is sufficient to cause the observed flow increase, 3. the HBP layer was left attached to the interior of the capillary, as shown by Barone, et al.⁴⁷ for fluorinated LLDPE with Confocal Microscopy and Duschene, et al.,⁴⁸ for a fluoroelastomer/Polyethylene Glycol/LLDPE blend, 4. the HBP acts as a "ball-bearing",¹⁸ or 5. some combination of the above. Whatever the true reason, the phenomenon exists and it is general for an immiscible linear polymer/HBP system. An immiscible system will consist of two highly dissimilar molecules. This dissimilarity may arise from chemical constituents or structure. The phase separation is independent of temperature, concentration, and capillary use. The rapid diffusion of the HBP to the surface layers is driven by the flow.

Third, adding a HBP leaves the overall surface energy relatively unaltered, which may be an attractive feature. Optical microscopy shows that both LLDPE

blends and PS blends have smoother surfaces than the virgin polymers' surfaces.

Therefore, adding an HBP to a linear polymer is doubly useful in that it acts as a processing aid while leaving the overall surface energy unchanged and providing a potentially useful surface for a wide range of applications.

6. Suggested Future Work

Examine the surface effects of using a fluorinated polymer. Perform Scanning Electron Microscopy (SEM) or Atomic Force Microscopy (AFM) and measure the surface roughness. Dissolve the HBP out in solution and observe the effects. Test these blends in a twin screw extruder and observe the effects.
Works Cited

- 1. Kissin, Y.V. "Principles of Polymerizations with Ziegler-Nutta Catalysts". Handbook of Polymer Science: Vol. 1: Synthesis and Properties. Marcel Dekker: New York, 1989.
- 2. Brandrup, J.; Immergut, E.H., Eds. *Polymer Handbook: 3rd Ed.* John Wiley and Sons: New York, 1989.
- 3. Newkome, G.R.; Moorefield, C.N. *Dendritic Molecules : Concepts Synthesis Perspective*, 1st Ed. VCH Publishers, Inc. : New York, 1996.
- 4. Tomalia, D.A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. "Dendritic Molecules: Synthesis of Starburst Dendrimers". *Macromolecules* **1986**, *19*, 2466.
- 5. Hawker, C.J.; Fréchet, J.M.J. "Preparation of Polymers With Controlled Molecular Architecture. A New Convergent Approach to Dendritic Macromolecules". *Journal of the American Chemical Society* **1990**, *112*, 7638.
- Mourey, T.H.; Turner, S.R.; Rubinstein, M.; Fréchet, J.M.J.; Hawker, C.J.; Wooley, K.L. "Unique Behavior of Dendritic Molecules: Intrinsic Viscosity of Polyester Dendrimers". *Macromolecules* 1992, *25*, 2401.
- Fréchet, J.M.J.; Hawker, C.J.; Gitsov, I.; Leon, J.W. "Dendrimers and Hyperbranched Polymers: Two Families of Three-Dimensional Macromolecules With Similar But Clearly Distinct Properties". *Journal of Macromolecular Science* 1996, A33, 1399.
- 8. Mackay, M.E.; Henson, D.J. "The Effect of Molecular Mass and Temperature on the Slip of Polystyrene Melts at Low Stress Levels". *Journal of Rheology* **1998**, *42*, 1505.
- 9. Hsieh, T.-T.; Tiu, C.; Simon, G.P. "Melt Rheology of Aliphatic Hyperbranched Polyesters With Various Molecular Weights". *Polymer* **2001**, *42*, 1931.
- 10. Carmezini, G. (2001) MS Thesis. Stevens Institute of Technology.
- Hong, Y.; Cooper-White, J.J.; Mackay, M.E; Hawker, C.J.; Malmström, E.; Rehnberg, R. "A Novel Processing Aid for Polymer Extrusion: Rheology and Processing of Polyethylene and Polymer Blends". *Journal of Rheology* **1999**, *43(3)*, 781.

- Hong, Y.; Coombs, S.J.; Cooper-White, J.J.; Mackay, M.E.; Hawker, C.J.; Malmström, E.; Rehnberg, R. "Film Blowing of Linear Low Density Polyethylene Blended With a Novel Processing Aid". *Polymer* 2000, 41, 7705.
- 13. Kil, S.B.; Augros, Y.; Leterrier, Y.; Månson, J.A.E. "Rheological Properties of Hyperbranched Polymer/Poly(Ethylene Terphthalate) Reactive Blends". *Polymer Engineering and Science* **2003**, 329.
- 14. Sendijarevic, I.; McHugh, A.J. "The Influence of Alkyl End Groups on the Miscibility of Hyperbranched Polymers with Polyolefins". *Polymer Engineering and Science* **2002**, *42*, 2393.
- 15. Mulkern, T.J.; Tan, N.C.B. "Processing and Characterization of Reactive Polystyrene/Hyperbranched Polymer Blends". *Polymer* **2000**, *41*, 3193.
- 16. Mezzenga, R.; Luciani, A.; Månson, J.A.E. "Phase Separation and Gelation of Epoxy Resin/Hyperbranched Polymer Blends". *Polymer Engineering and Science* **2002**, *42*, 249.
- 17. Zelinger, J.; Volfová, E.; Zahradníková, H. "PVC Mixtures With Processing Aids". International Journal of Polyermic Materials **1976**, *5*, 99.
- Kanu, R.C.; Shaw, M.T. "Rheology of Polymer Blends: Simultaneous Slippage and Entrance Pressure Loss in the Ethylene-Propylene-Diene (EPDM)/Viton System". *Polymer Engineering and Science* 1982, 22, 507.
- 19. Akay, G. "Unstable Capillary Flow of Reinforced Polymer Melts". *Journal* of Non-Newtonian Fluid Mechanics **1983**, *13*, 309.
- 20. Kim, Y.H.; Beckerbauer, R. "Role of End Groups on the Glass Transition of Hyperbranched Polyphenylene and Triphenylene Derivatives". *Macromolecules* **1994**, *27*, 1968.
- 21. Englund, J.E. (2000) MS Thesis. Royal Institute of Technology.
- 22. Malström, E.; Johansson, M.; Hult, A. "Hyperbranched Aliphatic Polyesters". *Macromolecules* **1995**, *28*, 1698.
- 23. Massa, D.J.; Shriner, K.A.; Turner, S.R.; Voit, B.I. "Novel Blends of Hyperbranched Polyesters and Linear Polymers". *Macromolecules* **1995**, *28*, 3214.
- 24. Kim, Y.H., Webster, O.W. "Hyperbranched Polyphenylenes". *Macromolecules* **1992**, *25*, 5561.

- 25. Flegler, S.L.; Heckman, Jr.; J.W., Klomparens, K.L. *Scanning and Transmission Electron Microscopy: An Introduction*. Oxford University Press: New York, 1993.
- 26. Mackay, M.E.; Hong, Y.; Jeong, M.; Tande, B.M.; Wagner, N.J.; Hong, S.; Gido, S.P.; Vestberg, R.; Hawker, C.J. "Self Assembly of Hybrid Dendrimer-Linear Block Copolymers into Ordered Structures". *Macromolecules* **2002**, *35*, 8391.
- 27. Román, C.; Fischer, H.R.; Meijer, E.W. "Microphase Separation of Diblock Copolymers Consisting of Polystyrene and Acid-Functionalized Poly(propylene imine) Dendrimers". *Macromolecules* **1999**, *32*, 5525.
- Lee, H.; Archer, L.A. "Functionalizing Polymer Surfaces By Field Induced Migration of Copolymer Additives. 1. Role of Surface Energy Gradients." *Macromolecules* 2001, 34, 4572.
- 29. Bauer, B.J.; Ramzi, A.; Liu, D.W.; Scherrenberg, R.L.; Froehling, P.; Joosten, J. "Blends of Fatty-Acid-Modified Dendrimers with Polyolefins". *Journal of Polymer Science: Part B: Polymer Physics* **2000**, *38*, 95.
- 30. Hiemenz, P.C. ; Rajagopalan, R. *Principles of Colloid and Surface Chemistry*. Dekker: New York, 1997.
- 31. Wu, S. Polymer Interface and Adhesion. Dekker: New York, 1982.
- 32. Adamson, A.W.; Gast, A.P. *Physical Chemistry of Surfaces: 6th Ed.* John Wiley and Sons: New York, 1997.
- 33. Good, R.J. "Contact Angle, Wetting, and Adhesion: a Critical Review". Journal of Adhesion Science and Technology **1992**, *6*, 1269.
- 34. Zisman, W.A. "Relation of the Equilibrium Contact Angle to Liquid and Solid Constitution". *Advances in Chemistry Series* **1964**, *43*, 1.
- 35. Van Oss, C.J.; Giese, R.F.; Li, Z.; Murphy, K.; Norris, J.; Chaudhury, M.K.; Good, R.J. "Determination of Contact Angles and Pore Sizes of Porous Media by Column and Thin Layer Wicking". *Journal of Adhesion Science and Technology* **1992**, *6*, 413.
- 36. Fowkes, F.M.; McCarthy, D.C; Mostafa, M.A. "Contact Angles and the Equilibrium Spreading Pressures of Liquids on Amohophobic Solids". *Journal of Colloid and Interface Science* **1980**, *78*, 200.

- 37. Fowkes, F.M. "Dispersion Force Contributions to Surface and Interfacial Tensions, Contact Angles, and Heats of Immersion". *Advances in Chemistry Series* **1964**, *43*, 99.
- 38. Good, R.J. "Theory for the Estimation of Surface and Interfacial Energies". *Advances in Chemistry Series* **1964**, *43*, 74.
- 39. Sauer, B.B.; DiPaolo, N.V. "Surface Tension and Dynamic Wetting of Polymers Using the Wilhelmy Method: Applications to High Molecular Weights and Elevated Temperatures". *Journal of Colloid and Interface Science* **1991**, *144*, 527.
- 40. Dalal, E.N. "Calculation of Solid Surface Tensions". *Langmuir* **1987**, *3*, 1009.
- 41. Owens, D.K.; Wendt, R.C. "Estimation of the Surface Energy of Polymers". *Journal of Applied Polymer Science* **1969**, *13*, 1741.
- 42. Shafrin, E.G.; Zisman, W.A. "Upper Limits to Contact Angles on Solids". Advances in Chemistry Series **1964**, *43*, 145.
- 43. Volpe, C.D.; Cassinelli, C.; Morra, M. "Wihelmy Plate Measurements on Poly(N-isopropylacrylimide)-Grafted Surfaces". *Langmuir* **1998**, *14*, 4650.
- 44. El-Ghzaoui, A. "Determination of Contact Angles: Consistency Between Experiment and Theory". *Journal of Applied Physics* **1999**, *86*, 2920.
- 45. Tardros, M.E.; Hu, P.; Adamson, A.W. "Adsorption and Contact Angle Studies: I. Water on Smooth Carbon, Linear Polyethylene, and Stearic Acid-Coated Copper". *Journal of Colloid and Interface Science* **1974**, 49, 605.
- 46. Mackay, M.E.; Carmezini, G. "On the Surface Properties of Hyperbranched Polymers". *Langmuir* **2001**, *17*, 1708.
- 47. Barone, J.R.; Wang, S.Q.; Farinha, J.P.S; Winnik, M.A. "Polyethylene Melt Adsorption and Desorption During Flow on High-Energy Surfaces: Characterization of Post-Extrusion Die Wall by Laser Scanning Confocal Fluorescence Microscopy". *Langmuir* **2000**, *16*, 7038.
- 48. Duschene, D.; Blacklock, J.E.; Johnson, B.V.; Blong, T.J. "Improved Processability of Linear Low Density Polyethylenes Through the Use of Fluorocarbon Elastomers/Polyethylene Glycol Blends". In Society of Plastic Engineers (US) Technical Conference (47th ANTEC 89): Plastics Create a World of Difference. ANTEC: New York, 1989, pp. 1343-1347.

